THE GLOBAL ARSENIC PROBLEM: CHALLENGES FOR SAFE WATER PRODUCTION
Arsenic in the Environment

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The photograph shows an arsenic removal plant, designed by Layne Christensen, that was installed at El Mirage, Arizona in 2007. The system is designed to treat a water flow of up to 425 gallons (1610 liters) per minute and consists of two 7 foot (2.13 meter) diameter vessels in a lead-lag configuration, each containing 225 cubic feet (1870 liters) of ArsenX® adsorption media. The system typically treats between 300,000 and 400,000 gallons (1140–1510 m³) of water per day and lowers the arsenic content of the finished water to below the limit of 10 µg/L. The photo is courtesy of Dr. Paul Sylvester, Layne Christensen, Northborough, Massachusetts, USA.
The Global Arsenic Problem: Challenges for Safe Water Production

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About the book series

Although arsenic has been known as a ‘silent toxin’ since ancient times, and the contamination of drinking water resources by geogenic arsenic was described in different locations around the world long ago—e.g. in Argentina in 1917—it was only two decades ago that it received overwhelming worldwide public attention. As a consequence of the biggest arsenic calamity in the world, which was detected more than twenty years back in West Bengal, India and other parts of Southeast Asia, there has been an exponential rise in scientific interest that has triggered high quality research. Since then, arsenic contamination (predominantly of geogenic origin) of drinking water resources, soils, plants and air, the propagation of arsenic in the food chain, the chronic affects of arsenic ingestion by humans, and their toxicological and related public health consequences, have been described in many parts of the world, and every year, even more new countries or regions are discovered to have arsenic problems.

Arsenic is found as a drinking water contaminant, in many regions all around the world, in both developing as well as industrialized countries. However, addressing the problem requires different approaches which take into account, the differential economic and social conditions in both country groups. It has been estimated that 200 million people worldwide are at risk from drinking water containing high concentrations of arsenic, a number which is expected to further increase due to the recent lowering of the limits of arsenic concentration in drinking water to 10 μg L\(^{-1}\), which has already been adopted by many countries, and some authorities are even considering decreasing this value further.

The book series “Arsenic in the Environment” is an inter- and multidisciplinary source of information, making an effort to link the occurrence of geogenic arsenic in different environments and the potential contamination of ground- and surface water, soil and air and their effect on the human society. The series fulfills the growing interest in the worldwide arsenic issue, which is being accompanied by stronger regulations on the permissible Maximum Contaminant Levels (MCL) of arsenic in drinking water and food, which are being adopted not only by the industrialized countries, but increasingly by developing countries.

The book series covers all fields of research concerning arsenic in the environment and aims to present an integrated approach from its occurrence in rocks and mobilization into the ground- and surface water, soil and air, its transport therein, and the pathways of arsenic introduction into the food chain including uptake by humans. Human arsenic exposure, arsenic bioavailability, metabolism and toxicology are treated together with related public health effects and risk assessments in order to better manage the contaminated land and aquatic environments and to reduce human arsenic exposure. Arsenic removal technologies and other methodologies to mitigate the arsenic problem are addressed not only from the technological perspective, but also from an economic and social point of view. Only such inter- and multidisciplinary approaches, will allow case-specific selection of optimal mitigation measures for each specific arsenic problem and provide the local population with arsenic safe drinking water, food, and air.

We have an ambition to make this book series an international, multi- and interdisciplinary source of knowledge and a platform for arsenic research oriented to the direct solution of problems with considerable social impact and relevance rather than simply focusing on cutting edge and breakthrough research in physical, chemical, toxicological and medical sciences. The book series will also form a consolidated source of information on the worldwide occurrences of arsenic, which otherwise is dispersed and often hard to access. It will also have role in increasing
About the book series

the awareness and knowledge of the arsenic problem among administrators, policy makers and company executives and improving international and bilateral cooperation on arsenic contamination and its effects.

Consequently, we see this book series as a comprehensive information base, which includes authored or edited books from world-leading scientists on their specific field of arsenic research, but also contains volumes with selected papers from international or regional congresses or other scientific events. Further, the abstracts presented during the homonymous biannual international congress series, which we organize in different parts of the world is being compiled in a stand-alone book series “Arsenic in the Environment—Proceedings” that would give short and crisp state of the art periodic updates of the contemporary trends in arsenic-related research. Both the series will be open for any person, scientific association, society or scientific network, for the submission of new book projects. Supported by a strong multi-disciplinary editorial board, book proposals and manuscripts are peer reviewed and evaluated.

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Dedications

We dedicate this book to Ege University, the primier academic institutions in Izmir, Turkey upon the completion of 55th year in 2010. Ege University is committed to excellence in research and development as well as to teaching and education with its more than 3000 competent academic staff in order to contribute to the improvement of the quality of life at regional and national levels. The university has a pledge to produce new knowledge at global scale and to raise competent, capable and innovative students who are up-to-date in knowledge, well-equipped and also having an awareness of the national and global issues.

We also dedicate this book to the people of the beautiful ancient city of Izmir who have a great sensitivity for safe water production. The 8000-year old city of Izmir acquired its name from the Amazon Queen “Smyrna”, which has witnessed a history dated back neolithic age, and remained a host to many civilizations during history; owns historical traces of great civilizations and one of the seven wonders of the world (Artemision-Ephesus) and Agora from Roman times.
Table of contents

About the book series VII  
Editorial board IX  
Dedications XIII  
Foreword XVII  
Editors’ preface XIX  
List of contributors XXIII  
Acknowledgements XXVII

**Section I: Overview of global arsenic crisis and human toxicity**

1. The global arsenic crisis—a short introduction 3  
   *J. Bundschuh, M.I. Litter, P. Bhattacharya & J. Hoinkis*
2. Arsenic contamination in groundwaters in Bangladesh and options of sustainable drinking water supplies 21  
3. Toxic effects of arsenic on human erythrocytes 37  
   *M. Suwalsky, C. Rivera, F. Villena & C. P. Sotomayor*

**Section II: Arsenic removal: Mechanisms, current practices and experiences**

4. Mechanisms of arsenic removal from water 49  
   *W. Höll*
5. Granular iron hydroxide as an adsorbent for arsenic in water 59  
   *M. Streat & K. Hellgardt*
6. Arsenic removal from water using magnetites 81  
   *K. Ohe, T. Oshima & Y. Baba*
7. Study of the long term stability of ferric iron—arsenic precipitates 95  
   *N. Dimitrova & V. Nenov*
8. Arsenic and boron in geothermal water and their removal 103  
   *K. Yoshizuka, N. Kabay & M. Bryjak*
9. Arsenic removal from potable water: Point-of-use, point-of-entry and municipal experiences 121  
   *P. Sylvester, T. Möller & O. Boyd*
XVI Table of contents

Section III: Membrane processes and applications in arsenic removal

10 Review of membrane processes for arsenic removal from drinking water 131
   A. Figoli, A. Criscuoli & J. Hoinkis

11 Arsenic removal by small-scale reverse osmosis units 147
   J. Hoinkis, C. Pätzold & J. Bundschuh

12 Potential application to remove arsenic by functional polymers
   in conjunction with membranes and electrooxidation processes 157
   B.L. Rivas & J. Sánchez

Section IV: Innovations in arsenic removal techniques
   for safe water production

13 Testing of a new selective arsenic adsorbent and overview of field test data 175
   S. Neumann, R. Klipper, J. Stoll, M. Dahm, S. Breuer, B. Chudzik-Raeth,
   S. Trokowski & C. Wei Hsin

14 Chitosan dispersed with Fe(III) oxide particles: A sorbent used
   for selective removal of arsenic from contaminated waters 189
   L. Cumbal & M. Zuñiga

15 Field experiences with ArsenX®, a very effective and efficient
   hybrid media for arsenic removal 201
   E. Belsten, F. Boodoo, J. D’Alessandro, M. Garegnani & D. Larose

16 Low-cost solar technologies for arsenic removal in drinking water 209
   M.E. Morgada de Boggio, I.K. Levy, M. Mateu, J.M. Meichtry, S. Farias,
   G.D. López, D. Bahnemann, R. Dillert & M.I. Litter

Subject index 219

Locality index 239
Foreword

Water is a significant natural resource and a key component of our environment. The quality of water resources has deteriorated as a result of the rapid population growth, unplanned urbanization and environmental pollution that resulted from global industrialization. The increasing demands for irrigation and for domestic and industrial purposes, are negatively affecting the quality of water supplies and placing greater stress on water resources, the capacity of which is already limited. Nowadays, the decrease in availability of high quality water resources has already reached serious dimensions including major threats and impacts on sensitive ecosystems. Therefore, problems pertaining to water consumption and supply need to be solved on a global scale. In addition to these, global warming and climate change have begun to threaten the resources of water.

Considering the current development level, none of the available means are sufficient to combat the growing complexity of regional and global water problems. That is why there is a need for a visionary, predictive and proactive approach. The traditional approaches to managing water quality, supply and demand, including restrictive regulations, are no longer likely to be sufficient or satisfactory since changes in ecosystems are unpredictable and irreversible and most of them may occur after a long period of time. In some cases quality recommendations and standards may determine that previously acceptable water becomes unfit for particular uses due to only one or two low concentration problem substances being present in variable amounts in otherwise fresh water supplies. A significant example is arsenic (As) species in groundwater and other resources in many parts of the world and especially in developing regions.

In this context, an “International Congress on Production of Safe Water” was organized in Izmir city in Turkey from January 21 to 23, 2009 in cooperation with Izmir Metropolitan Municipality and Ege University in order to create an international platform where the most recent researches, experiences and applications on production of safe water were exchanged and presented, with particular emphasis on arsenic in the groundwater supplies to the city of Izmir.

I would like to congratulate the great efforts of the editorial team of this volume. I hope that this book will serve the people to acquire the scientific information and experiences required for safe water production.

Prof. Dr. Candeğer Yılmaz
Rector
Ege University
December, 2009
Editors’ preface

Water constitutes an important component of the environment and its availability is indispensable to the efficient functioning of the ecosystem. Water is an important element of the existence of humans, animals and plants. Water is also of vital importance to all socio-economic sectors—human, and economic development simply is not possible without a safe water supply. Total volume of water on the Earth is approximately $1.3 \times 10^9$ km$^3$, but only 4 million km$^3$, i.e., 0.3% of the total water volume is actually usable for humans. The sources of this portion are mainly rivers, lakes and groundwaters. The water resources are subject to increasing stress both in terms of quantity as well as quality. In recent decades, surface water resources have become highly contaminated with domestic and industrial wastes, as well as due to the human influence. Thus, safe water resources must be seen in the overall context of global sustainable development.

The water consumption was estimated as 86 cubic kilometers during the later half of the 17th century (1680), in 1900, this amount had risen to 522 km$^3$, but in 1980 to 2120 and in 2000 to 2700 km$^3$ per year. The forecast that human water consumption could triple once more in the next 30 years is alarming. At least 40% of the world’s population will live in countries that suffer from a chronic shortage of water. Today more than 50 countries suffer from a shortage of water but by 2025, the United Nations estimates that two-thirds of world population will not have enough drinking water.

Increased water demand from population and economic growth, environmental needs, changes in rainfall, flood, and contamination are the major factors that will continue to create water shortage problems. It was estimated that, about 70% of the water is used for agricultural activities. The problem with agricultural activities is not only consumption of large volume of water for irrigation but also the use of large amount of fertilizers, pesticides and other chemicals. Industry uses only 20% of water available for use. The remaining 10% is consumed for daily usage although this much depends on the regions of the world.

The existence of arsenic in water is of global concern because it is a serious threat to human health and many of its compounds are especially potential poisons. Elemental arsenic and arsenic compounds are classified as toxic and dangerous for the environment in the European Union directive (67/548/EEC). Arsenic concentration in ground- and surface waters in western US ranged from 80 µg/L to as high as 15 mg/L, because of the abundance of geothermal activities in this region. In some countries such as China, Tibet, Mongolia, India, Bangladesh, Vietnam, Cambodia, Thailand, Taiwan, Argentina, Chile and Mexico, a large portion of water is contaminated with arsenic at levels from 100 to over 2000 µg/L. It has been estimated that a population of more than 100 million are exposed to drinking groundwater with arsenic concentrations above the 50 µg/L limit, which is still the maximum permissible concentration in many countries of South Asia. The WHO revised its recommended guideline value for arsenic in drinking water to 10 µg/L in 1993, which was later adopted by the US in 2001. The United States Environmental Protection Agency (US EPA) drinking water standard for As was 50 µg/L set by US EPA in 1975, based on a Public Health Service standard originally established in 1942. The US Safe Drinking Water Act provided the stringent framework for protecting public health on the basis of which US EPA has established a health based non-enforceable Maximum Contaminant Level Goal (MCLG) for zero

XIX
As and an enforceable Maximum Contaminant Level (MCL) of 10 µg As/L in drinking water in January 2001, that applies to both non-transient, non-community water systems as well as to the community water systems.

In 2001, EPA adopted a new standard, and public water systems must comply with the 10 µg/L as permissible level in 2003. In some of the new member states from Eastern Europe, such as Hungary, Romania, and Slovakia who have joined the European Union recently, the levels of arsenic in drinking waters are higher than the guideline values proposed in the European Union Drinking Water Directive (Council Directive 98/83/EC). In these countries, there is a need to develop cost-effective and alternative treatment technologies for the removal of arsenic in order to comply with the drinking water standards of the European Union.

An International Congress on “Production of Safe Water” was organized in Izmir, Turkey from January 21 to January 23, 2009 with a theme on arsenic in the environment and its elimination by various methods for the production of safe water. Following the congress, *The Izmir Declaration 2009* for safe water production for sustainable human development in Turkey was chartered based on the realization of the fact that natural water resources are essential elements for human development. The presence of elevated concentrations of geogenic arsenic exceeding the Turkish and the World Health Organisation (WHO) guideline values of 10 µg/L in groundwater as the main resources for drinking and irrigation water poses the principal environmental health risk of the 21st century in affecting the urban as well as the rural water supplies in Turkey and globally, the organizers, international scientific committee members and participants of the International Congress for Production of Safe Water, 21–23 January 2009 in Izmir, Turkey unanimously resolved that:

- It is necessary to investigate the presence, origin and mobilization of arsenic in water resources.
- Arsenic should be listed as an obligatory parameter for analysis of water used for drinking and irrigation purposes.
- It is necessary to create awareness of the presence and adverse health effects of arsenic in the water resources for human consumption amongst the population, the water and public health and the food and agriculture authorities as well as in the scientific community.
- It is necessary to identify and promote appropriate techniques for treatment of water resources with high arsenic concentrations and/or alternative water resources for public water supply and to address also the safe disposal of the residues from such processes.
- It is recommended to initiate and promote international cooperation on research with an interdisciplinary and multidisciplinary approach on arsenic and related elements in the environment of Turkey. This should involve the fields such as geosciences, hydrogeology, hydrogeochemistry, chemical engineering, agriculture, food and nutrition, toxicology, epidemiology, public health and medical sciences.

This monograph entitled “Global Arsenic Problem and Challenges for Safe Water Production” is presented as the second volume of the inter- and multi-disciplinary book series “Arsenic in the Environment” which comprises contributions from distinguished scientists from both academia and industry who participated in the congress as invited lecturers from four continents and also a number of others who have been actively working in this area. The sixteen chapters in the volume are grouped under four thematic sections that cover the major aspects of the global arsenic problem, human health effects and technologies for safe water production.

The main goal of the book is to focus attention of all affected parties worldwide on global arsenic problems and to present some challenges for safe water production in order to invoke appropriate actions in efficient innovative directions. We hope that this book will be useful
Editors' preface

for environmental scientists and engineers in both academia and industries and for government and regulatory bodies dealing with water issues by providing an opportunity to acquire relevant scientific information and experiences in “Global Arsenic Problem and Challenges for Safe Water Production”.

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Section I

Overview of global arsenic crisis and human toxicity
CHAPTER 1

The global arsenic crisis—a short introduction

Jochen Bundschuh, Marta I. Litter, Prosun Bhattacharya & Jan Hoinkis

In order to understand the worldwide importance of the problem of high arsenic (As) concentrations in waters used for drinking water supplies, and the corresponding mitigation strategies, it is useful to analyze the history of the detection of As in water resources, starting at the end of the 19th century to the situation today. Characterizing the conditions under which As releasing aquifers occur or how As is released into surface water, is the starting point for the formulation of sustainable mitigation solutions, such as As removal from drinking water or zero-treatment options. This historical perspective can have relevance to emerging water resource issues related to As. As well as the biogeochemical factors that give rise to elevated As in water resources, political, social and economic reasons are also relevant. For example, in Bangladesh the acceptance of many remediation projects by the local population has not been sufficiently considered resulting in the failure of efforts to mitigate arsenic exposure.

1.1 GENERAL OVERVIEW OF THE ARSENIC PROBLEM

Inorganic As is a Class 1, non-threshold, carcinogen, and chronic exposure also causes a range of ailments such as skin lesions (hyperkeratosis, melanosis), nervous system impairment, irritation of respiratory organs and the gastrointestinal tract, anemia, liver disorders, vascular illnesses and even diabetes mellitus, skin, lung and bladder cancer (Del Razo et al. 2000, 2005, Albores et al. 2001, Endo et al. 2003, Kirk and Sarfaraz 2003, Rossman 2003). Chronic exposure to As can also affect the intellectual development of children (Borja et al. 2001, Wasserman et al. 2004).

Drinking and irrigation water abstracted from groundwater and surface water reserves where the water has elevated concentrations of inorganic As poses a direct threat to human health and environmental sustainability. Geogenic sources, such as rocks and minerals are the dominant origin of As in ground- and surface waters for most affected regions. When considering human exposure to inorganic As, besides direct ingestion from drinking water, other exposure pathways include water used in food preparation (such as rice cooking), direct contamination of food sources through the use of groundwater in agricultural irrigation or aquaculture, and the indirect contamination of food sources, such as feeding straw elevated in As to livestock.

At present, it is not possible to precisely assess the number of persons potentially exposed worldwide to elevated inorganic As from groundwater and surface water exposure routes at levels that constitute a health threat. However, some regional or countrywide estimates for drinking water exposure exist. In the Bengal delta, 31 million people are exposed to water with \( >50 \, \mu g \, L^{-1} \) and 50 million to \( >10 \, \mu g \, L^{-1} \) of As (Chakraborti et al. 2002), which is the WHO, EU and USA limit.

In Latin America, at least 4.5 million people are exposed to drinking water containing more than \( 50 \, \mu g \, L^{-1} \) of As (Castro de Esparza 2009), which is still the regulatory limit in some of the countries of that region. If the \( 10 \, \mu g \, L^{-1} \) limit is considered (see section 1.4), a value increasingly adopted by the countries of this region, then the number of exposed people increases to around 14 million.
1.2 GROUNDWATER ARSENIC: SOURCES, RELEASE AND MOBILITY

Elevated As in groundwater and to lesser extent in surface water is predominantly caused by the physical or chemical abiotic and biotic weathering of primary or secondary As-containing minerals. This allows aquifers with elevated As levels due to natural sources to be classified according to the origin of their As and the mechanism of mobilization into the groundwater and surface water:

- **Reduced alluvial aquifers where As is released from iron oxyhydroxide**: Major examples include the flood and delta plains of Himalayan rivers. Examples are: Ganges-Brahmaputra-Meghna plain/delta, India and Bangladesh (Bhattacharya et al. 2002a, b, 2007a, b); Indus plain, Pakistan (Nickson et al. 2005); Irrawady delta, Myanmar (WRUD 2001); Red River delta, Vietnam (Berg et al. 2001); and Mekong river delta Cambodia and Laos (Feldman and Rosenboom 2001).

- **Oxidized aquifers (normal pH range, 5 < pH < 10)**: In these mostly sedimentary aquifers, at high pH (8–9.5) desorption of As from Fe, Al, and Mn oxyhydroxides occurs. This is the principal mechanism that explains the high As concentration in the groundwater of extended areas of the Argentine Chaco-Pampean plain and its continuation into the neighboring countries of Uruguay, Paraguay and Bolivia (Smedley et al. 2005, 2009, Bundschuh et al. 2000, 2004, 2006, 2008a, 2009a, b, Bhattacharya et al. 2006); the Appalachian Highlands, NE Ohio (Matisoff et al. 1982); the Interior Plains, S. Dakota (Carter et al. 1998); the Carson Desert, Nevada (Welch and Lico 1998); the Pacific Mountain System, NW Washington (Goldstein 1988, Ficklin et al. 1989, Davies et al. 1991) and Arizona (Goldblatt et al. 1963, Nadakavukaren et al. 1984).

- **Oxidized environments at very low pH (pH < 4)**: In these environments, As is released by sulfide oxidation. This occurs in many areas with sulfide mineral deposits. Examples include the mineral deposits in the Andes and Andean Highlands, the Middle and North American cordillera, the Transmexican volcanic belt, the Appalachian belts from Massachusetts to Maine (Peters et al. 1999, Peters 2008, Zuen and Keane 1985, Boudette et al. 1985, Ayotte et al. 1998); the Interior Plains of E. Michigan, (Westjohn et al. 1998, Kolker et al. 1998); the Variscian mountains in Europe, the Central Balkan peninsula in Siberia (Dangic and Dangic 2007); Albania (Lazo et al. 2007); Ghana (Smedley 1996); Nigeria (Gbadebo 2005), and many mining sites all around the world.

As mobilization is further controlled by the geomorphological, geological and hydrogeological conditions as well as climate, land use patterns, and groundwater exploitation (Hasan et al. 2007, Mukherjee et al. 2007). Arid and semiarid climate can be a principal or an additional control and, due to evaporative concentration increases, contribute to the genesis of As-rich groundwater and surface water. Examples where climate contributes to the formation of aquifers with porewaters elevated in As and also surface waters include the Atacama desert in N Chile (Borgoño and Greiber 1971, Bundschuh 2008a, b, c, 2009a, b), aquifers in the Chaco-Pampean plain in Argentina (Bundschuh et al. 2000, 2004, 2008a, b, c, 2009b, c, Bhattacharya et al. 2006), shallow aquifers of the Carson Desert in Nevada (Fontaine 1994, Welch and Lico 1998) and shallow aquifers in the southern San Joaquin valley in California (Fujii and Swain 1995, Swartz 1995, Swartz et al. 1996).

1.3 THE HISTORY OF ARSENIC OCCURRENCE IN GROUNDWATER

1.3.1 From the 19th century to the 1960s

Early reports of geogenic As in groundwater came from the USA at the end of the 19th century. Hitchcock (1878) described the first cases of As poisoning in the northern Appalachian mountains. Further examples were reported in 1885 from Germany and in 1898 from Poland.
The global arsenic crisis—a short introduction

During the next one hundred years, the most widely characterized regions were Argentina, from the 1910s (predominantly aquifers), and Taiwan (predominantly aquifers), Chile (predominantly surface waters fed by groundwater) and Mexico (predominantly groundwater) from the 1960s. Other aquifers with high groundwater As concentrations found during this period include Canadian and New Zealand examples, discovered in the 1930s, which were of limited size and have received only marginal attention.

A scientific description of the health effects in humans from geogenically As-elevated drinking supplies, termed Belle Ville disease, was first reported from Bell Ville, Chaco-Pampean plain, Argentina in 1913 by the physician Dr. Mario Goyenechea (Goyenechea 1917). His pioneering work was followed by that of Dr. Abel Ayerza, who characterized the cardiovascular and cutaneous manifestations caused by elevated As in drinking water, terming it Chronic Endemic Regional Arsenicism (Ayerza, 1917a, b, 1918). Ayerza found that from a total population of 8534 inhabitants, 1300 (15%) suffered from arsenical disease (Ayerza 1917a, b). From 1921 other areas of the Chaco-Pampean plain were reported to have elevated As in drinking water, such as the Rio Tercero river basin, Cordoba province, and the north of the Santa Fe province (Reichert and Trelles 1921). Based on regional hospital statistics for Bell Ville, Trelles et al. (1970) found that in the period 1934–1944, 511 persons were registered as being affected by chronic arsenicism. In 1951, the physician Enrique E. Tello introduced a new term for the disease, Chronic Endemic Hydroarsenicism, because the As poisoning was drinking water derived (Tello 1951). Follow-up investigations by Tello registered 339 patients with arsenical disease originating from the provinces of Buenos Aires, Cordoba, Chaco, Santa Fe and Salta (Tello 1986, 1988). For the period 1972–1993, Biagini et al. (1995) found another 87 patients in the provinces of Santiago of the Esteoro, Chaco and Salta. Despite these investigations, arsenical disease caused by drinking groundwater did not achieve the necessary attention by the authorities, and still today remains unresolved in many rural and urban areas.

During the 1950s and 1960s ground- and surface waters with elevated As concentrations were described in Mexico, Chile and Taiwan. In Mexico, chronic exposure to As from groundwater was reported in 1958 in the Comarca Lagunera area, which spreads over extended parts of the states of Durango and Coahuila (Cebrian et al. 1994, Armienta and Segovia 2008). Later on, the problem was described in other Mexican states (e.g., Zacatecas, Morelos, Aguas Calientes, Chihuahua, Puebla, Nuevo Leon, Guanajuato, San Luis Potosi). It has been estimated that the number of Mexicans exposed to more than 50 µg L⁻¹ was ~450,000 (Castro de Esparza 2009, Armienta et al. 2008). No estimate exists of the number of people exposed to levels above the 2005 new drinking water regulatory maximum of 25 µg L⁻¹.

Chronic As-related health effects, such as skin lesions, were reported in Antofagasta, Chile in 1962, and later on in other areas of NW Chile. The As is predominantly released by the weathering/dissolution of volcanic rocks and sulfide ore deposits in the Andean volcanic chain, where As is mobilized following the snow melt and rain. This adds As to the overland flow and infiltrating water and transports it to the rivers, such as the Loa river, and springs which originate at the flanks of the Andean mountains and form the only freshwater resource in northern Chile. The contamination of the drinking water supply of Antofagasta was due to water abstraction from the Loa river and its tributaries, average As ~800 µg L⁻¹, from 1958 until 1970 when an As removal plant was installed (Bundschuh et al. 2009b). Around 130,000 people were exposed in Antofagasta to >50 µg As L⁻¹. In the NW Chile region, in total, ~500,000 people were exposed to >50 µg L⁻¹ (Castro de Esparza 2009). In 1978, in Kalama, the second largest city in the As affected area, a removal plant was installed. Both treatment plants resolved the As drinking water problem in these two cities, and in some larger urban areas (Rivara et al. 1997). Nevertheless, there are still smaller towns, villages, and isolated houses, where As contaminated water is the only source for drinking and irrigation purposes (e.g., Chiu Chiu; Smith et al. 2000). Because of the well-defined As exposure time, Chilean populations were extensively epidemiologically investigated during the following decades (Borgeño and Greiber 1971, Pizarro and Balabanoff 1973, Puga et al. 1973, Klohn 1974,

In Taiwan, the populations of several areas, in particular in the Chianan plain (SW Taiwan), were exposed to As from groundwater resources used for drinking water abstraction from the beginning of the 20th century. The disease (“spontaneous gangrene”) was first reported in the Journal of Formosan Medical Association in 1954 (Kao and Kao 1954). Awareness of the As problem started during the 1960s (Tseng et al. 1968) and the Taiwan As scenario became well known in the environmental health field due to the occurrence a unique As-related peripheral vascular illness, blackfoot disease (BFD), which was reported together with other As-related health effects. High As concentrations in groundwater (350–1100 µg L⁻¹) used for drinking purposes were reported (Chen and Wu 1962) and were suspected to be the most likely cause of the observed health problems (Chen et al. 1962). A dermatological survey performed during 1965 in 37 villages of the BFD area on the Chianan plain, found a close correlation between the occurrence of health effects, such as BFD, hyper-pigmentation, keratosis, and skin cancer, and drinking water As (Tseng et al. 1968).

1.3.2 From the 1970s to the end of the 20th century

From the 1970s on, the number of areas with aquifers elevated in groundwater As expanded. In Argentina, these new areas were predominantly in the Chaco-Pampean plain zone, but also in the Andean highlands (Astolfi et al. 1981, 1982, Nicolli et al. 1985, Smedley et al. 2005, Bundschuh et al. 2000, 2004, 2008a, b, c, 2009b). By the end of the 20th century, As-rich groundwater was confirmed in the provinces of Córdoba, Rio Negro, Tucumán, Santa Fe, La Pampa, Santiago del Estero, Salta and Chaco (Ministerio de Salud 2001). Severe health effects due to As uptake through groundwater used for drinking purposes and food preparation have been identified not only in Chaco and Córdoba province (Hopenhayn-Rich et al. 1996, 1998; Concha et al. 1998a, b), but also in the Andean highlands, e.g. in San Antonio de los Cobres, Salta province (Concha et al. 1998a, b). The As problem was also described in the Ilo valley, Peru, at the beginning of the 1990s (Castro de Esparza 2009, Bundschuh et al. 2008c, 2009b).

Arsenic in groundwater rose to prominence during the 1990s due to the discovery that large tracts of the Bengal delta, amongst the most densely populated parts of the planet, were afflicted with this natural toxin. The disaster due to elevated As in groundwater in the Bengal delta was initiated in the 1970s when WHO UNICEF launched, in good faith, a campaign to provide the rural population of Bangladesh with drinking water free of microbial pathogens. This program attempted to switch the drinking water supply coming from surface and rainwater sources to groundwater via hand-pumped tubewells. Unfortunately, the groundwater had not been tested for As before the tubewell program was instigated. Although the first cases of As intoxication were reported in 1983 by Krishna Chandra Saha in the Indian part of the Bengal delta, and for Bangladesh in 1987 (Saha 1995, Mandal et al. 1996), the problem was not considered serious and did not receive much attention until 1995 when Dapankar Chakraborti, a West Bengali chemist, reported surveys of As in Bengal Delta groundwater, and started to widely publicize his findings (Mandal et al. 1996). Since 1998, an international aid effort has been deployed in the region to attempt to mitigate the As elevated groundwater. Many treatment methods have been developed and tested. However, the social acceptance aspect was often neglected, resulting in mitigation failure. Also, the problems of distributing and maintaining mitigation technologies in such a poor, rural-based economy, has not been addressed. Over 10 million tubewells have been sunk in Bangladesh, around half of which are As contaminated, creating a massive health problem.

In many countries, especially in the developing world, As was not included as a parameter in standard drinking water analysis. As a consequence, aquifers containing As-rich
groundwater were often detected by accident, e.g. during scientific investigations performed originally for other purposes.

Over the last two decades of the 20th century, several sites with high As concentrations in groundwater were described in northern China: Xinjiang Uyghur Autonomous Region (NW China; Wang 1984) and later in the Mongol Autonomous Region (Inner Mongolia) and in the province of Shanxi (Wang 1984, Wang and Huang 1994, Niu et al. 1997, Smedley et al. 2001, Mukherjee et al. 2009). In the 1990s, As concentrations above 50 µg L⁻¹ have been detected in the southern Pannonian basin, Hungary (Varsányi et al. 1991), aquifers of Cenozoic sedimentary basins in Spain (Duero, Ebro, and the Madrid Tertiary detrital aquifer), (Cama et al. 2008) and at different sites in the USA (Welch et al. 1988, 2000).

From 1970–1990, several sites were described where aquifers had elevated porewater As due to sulfidic ore deposits and/or mining activities. An especially severe case is that of southern Thailand, where in 1987 As poisoning related to mining activity was detected in the Ron Phibun district (Nakhon Si Thammarat province). There, about 1000 people were affected by skin disorders due to As exposure (Williams 1996, Choprapatwon and Rodeline 1997). Other areas with elevated As in groundwaters and surface waters related to sulfidic ore bodies and/or mining activities were described in Mexico (Armienta et al. 2008), the Iberian peninsula (Cama et al. 2008), Ghana (Smedley 1996), Burkina Faso (De Jong and Kikietta 1980), and elsewhere (Ravenscroft 2007).

Elevated As in groundwater due to geothermal activities resulting in a high As discharge into freshwater aquifers or surface water bodies, is also potentially an important source of human exposure.

1.3.3 The 21st century

Half of the 70 countries with As contaminated aquifers, and to a lesser extent surface water, were only identified within the last 10 years (Ravenscroft 2007). The new discoveries are predominantly geogenic in origin, covering >200 locations, distributed over all the inhabited continents (Ravenscroft 2007, Nriagu et al. 2007) (Fig. 1.1). Thus, many future discoveries of aquifers with high As concentrations in groundwater and surface water may be expected. These geographically widespread recent discoveries have finally changed the outdated notion of the limited occurrence of aquifers elevated in porewater As. Some recent examples in Latin America include Nicaragua, Bolivia, El Salvador, Ecuador, Honduras, Baja California State (Mexico), Uruguay, Colombia, Guatemala, Costa Rica, Cuba, and Venezuela (Bundschiuh et al. 2008a, 2009a). In 2008, groundwater with high As concentrations that was used for drinking water was reported in Turkey (Izmir). In Asia, from 2000–2002, high As concentrations have been detected in the groundwater of 6 new nations: Cambodia and Laos (Feldman and Rosenboom 2001), Pakistan (Nickson et al. 2005), Myanmar (WRUD 2001), Vietnam (Berg et al. 2001) and Nepal (Tandukar et al. 2001, 2005, 2006, Shrestha et al. 2003). In India, new As-affected areas were discovered: Bihar (Chakraborti et al. 2003), Uttar Pradesh (Ahamed et al. 2006), Jharkhand (Bhattacharjee et al. 2005), and Assam (Chakraborti et al. 2004).

1.4 PRESENT DAY AWARENESS, REGULATORY LIMITS, AND REMEDIATION MEASURES

This exponential growth in the number of sites where groundwater and surface water resources are contaminated by As, mostly of geogenic origin, highlights the global importance of elevated As in water supplies. New studies on the toxicological effects of chronic human exposure to As, together with the wider availability of sophisticated analytical instrumentation, which allow the detection of less than 1 µg As L⁻¹, caused the World Health
Figure 1.1. Countries with aquifers and surface water bodies with high concentrations of dissolved As as known today. Where space permitted individual arsenic-affected areas are shown within the individual countries. Adapted from Bundschuh and Litter (2010) based on compilations from: Welch et al. 2000, Smedley 2006, Ravenscroft 2007, Bundschuh et al. 2008a, 2009a, and from unpublished information of the authors. The digital elevation model PIA3395 (http://photojournal.jpl.nasa.gov) is courtesy of NASA/JPL-Caltech.
Organization (WHO) to reduce the provisional As guideline value for drinking water from 50 to 10 µg L\(^{-1}\) in 1993 (WHO 1993), which was made the Maximum Contaminant Level (MCL) in 2001 (WHO 2001). This further raised global awareness of As affected groundwater and, in some cases, of surface water. This new As limit became law in Jordan (1991), Japan (1993), Namibia, (1994), Syria (1994), Nicaragua (1994), Honduras (1995), Costa Rica (1997), El Salvador (1997), European Union (1998), Mongolia (1998), Colombia (1998), Guatemala (1998), Panama (1999), Peru (1999), Taiwan (2000), USA (2001), Argentina (2007), Chile (2008), Vietnam (2008), and other countries will follow. Most other countries have a 50 µg L\(^{-1}\) limit and some others have regulatory limits in between the 10 and 50 µg L\(^{-1}\) e.g. Canada 0.025 µg L\(^{-1}\) (1999) or Mexico 0.025 µg L\(^{-1}\) (2005). Only Australia has a limit lower than 10 µg L\(^{-1}\); 7 µg L\(^{-1}\) from 1996 onwards.

However, in many countries, As is still not included as a parameter for standard drinking water quality analysis. A consequence of such neglect becomes evident from a Nicaraguan example where in 1994 the national water company drilled a well in El Zapote to supply the population with clean drinking water. The water resource was not analyzed for As, resulting in the poisoning of the population for 2 years by As at a concentration of 1320 µg L\(^{-1}\) in the drinking water (Barragne 2004, Bundschuh et al. 2007a, Altamirano Espinoza and Bundschuh 2009). Similar situations may be occurring in other countries.

There are plenty of options to remediate As-contaminated drinking water supplies/sources (for overviews see Newcombe and Möller 2006, Pirnie 2000, Bianchelli 2004, Mohana and Pittman 2007, Jekel and Amy 2006). The individual advantages and disadvantages of a particular technology depend on complex and interacting factors, such as size of treatment device, chemical composition of the water to be treated, As concentration and distribution of species in the raw water, required As concentration of the purified water, economic constraints, social acceptance by the population, maintenance, routine performance testing, etc.

In-situ methods, where As is immobilized directly in the aquifer, consist of permeable reactive barriers (PRB), colloidal reactive barriers (CRB), and mobile reactive barriers (MRB) whose usefulness depends on the local hydrogeological conditions and the remediation end-points.

Ex-situ methods include:

- membrane technologies (micro-, nano-, ultrafiltration and reverse osmosis),
- adsorption methods which use natural adsorbents (e.g., limestone, clays, zeolites, biomass) or treated natural adsorbents (e.g., clay or sand particles coated by Fe or Mn oxides or hydroxides) or artificial adsorbents (e.g., activated alumina, ferric oxyhydroxides),
- coagulation/flocculation techniques: Adsorption/coprecipitation using ferric oxhydroxides e.g., by adding a ferric salt (typically sulfate or chloride), chemical or photochemical or photocatalytic oxidation of As(III) to As(V),
- anion exchange.

Since several of these methods for As removal often comprise advanced technologies, they are used at an industrial scale, providing solutions for urban areas which count on a centralized water supply. The situation in rural areas is quite different, especially in countries in transition and in developing countries. Smaller cities, towns, villages and dispersed settlements still, generally, depend on untreated drinking water containing As at toxic levels. There are different reasons for this. Primarily, many technologies for As removal from water are not suitable for small communities, particularly dispersed rural settlements, which require simple and low-cost equipment that they can manage themselves. However, there exist methods that meet these requirements and simplified equipment based on adsorption and membrane technologies. Most of these methods have only been developed at the laboratory scale. Only in a very limited number of cases have these techniques been tested and proven in the field, and in even fewer cases have they been deployed on a large scale to solve the As problems of the rural population. Authorities and industry generally ignore mitigation for the rural population, slowing down the commercial development of low-cost remediation methods.
suitable for these communities, despite the potential of developed sustainable solutions. Key to this problem is convincing the responsible authorities of the importance of elevated As in the drinking water supply. The Chaco-Pampean plain in Argentina (Bundschuh et al. 2008a, c, 2009c) is an example of the difficulties in deploying mitigation in rural communities, where about 12% of the population live in dispersed settlements of less than 50 inhabitants. Here, despite the possible solutions provided by numerous national and international scientists (Luján and Graieb 1994, 1995, Luján 2001, Claesson and Fagerberg 2003, Mellano and Ramirez 2004, Storniolo et al. 2005, Lindbäck and Sjölin 2006, Morgada et al. 2008, 2009, Morgada de Boggio et al. 2006, 2009, Bundschuh et al. 2007b, 2009c, Jakariya 2007, Jakariya et al. 2005, 2007), local, provincial and national governments have never seriously tried to solve the problem, with the exception of some non-sustainable actions, to provide a long-lasting solution to the rural population.

1.5 PROVIDING ARSENIC-SAFE DRINKING WATER TO ALL PEOPLE

As stated above, until the 21st century, the problem of As in drinking water was not recognized as a global problem. Reasons for this were poor international cooperation, limited information exchange and ignorance. Consequently, in many countries As is not a standard obligatory parameter for drinking water analysis. To change this, a key demand is to recognize problems at an early stage. Acting on this knowledge can be done either using alternative water resources or by installing adequate water treatment devices. Although many treatment technologies exist, their further development is required in order that they can be adapted to provide optimal solutions for individual cases. Additionally, lessons can be learned from the many cases where unsuitable remediation methods were provided to the population. For example, in Argentina reverse osmosis plants were installed at localities where a lack of electricity supply, limited local maintenance, or missing funds for changing the membranes hindered the running of the plants for many years or, in some cases, forever. Another example is Bangladesh, where provided household filters were only used for a short time because practical acceptance of the method by the population was not obtained. Water taken directly from the well was much cooler than that sitting about produced by above ground treatment technologies. Furthermore, rural areas are often neglected by state agencies and authorities, which hinders their development. This barrier must be overcome if progress is to be made.

The selection of adequate remediation measures requires detailed knowledge about the individual aquifer or surface water body, or about regions with aquifers or surface water bodies that have the same geochemical or other similar characteristics, which control As mobilization. In the case of aquifers, this must be accompanied by a conceptual flow and solute transport model of the aquifer system to better understand the occurrence of As in the well water in the frame of the general water chemistry, which allows forecasting future changes in water chemistry. Since the occurrences of the principal types of As-contaminated groundwater and surface water bodies can be attributed to particular geological settings and climate conditions (see section 1.2), it is possible to take advantage of this relationship. Thus, if an affected aquifer (or surface water) is detected in a specific environment, it is also possible to expect to find similar aquifers (surface water) in other regions with similar geological and climatic conditions. Ravenscroft (2007) applied the likelihood of such an approach of finding or not-finding As-elevated aquifers on a worldwide scale to calculate probability distributions of As occurrence. Three examples of the usefulness of such approach are given below:

- Considering the alluvial aquifer of Bengal delta, the similar geological and geochemical conditions of other flood and delta plains of other Himalayan rivers such as the Indus, Irrawady, Red and Mekong rivers would have suggested the probable occurrence of As in these regions many years ago. Instead, the discoveries in these areas were not made until the first decade of the 21st century, exposing many people unnecessarily to As.
Another example is that of western Nicaragua, where a few small spots with high As concentrations in groundwater in shallow aquifers, composed of weathering products from Cenozoic volcanic rocks, were found. Again, the similar geological conditions found in large parts of Nicaragua and in the neighboring countries would allow the discovery of other impacted aquifers in this region.

The same assumption is valid if the Argentine Chaco-Pampean plain and its extension into the neighboring countries of Bolivia, Paraguay and Uruguay is considered. In the entire region, sediments of Andean origin are found. In Argentina, until now, affected aquifers were found at many sites in 16 provinces (Bundschiuh et al. 2008c). The similar geological condition makes probable the discovery at other sites, such as in the Argentine provinces of Formosa, Entre Rios and Misiones, as well as in the adjacent plains in Bolivia, Paraguay and Uruguay. Therefore, it is not surprising that in 2006, nearly 100 years after the detection of the problem in the same regional sediment basin, As was found in the groundwater of the aquifers of SW Uruguay (Guéréquiz et al. 2006, Bundschuh et al. 2008c).

International interdisciplinary cooperation must be strengthened to build-up a robust global, on-line database, periodically updated, containing information regarding related As topics. This would allow easy access to information, which otherwise would not be readily accessible. A dynamic global network for As research is required which allows problem-oriented discussions to find direct solutions to geological, physical, chemical, toxicological, medical and other specific issues. It is not sufficient that these activities and efforts remain in the hands of a few, normally poorly resourced, scientists, working overtime. The research base needs to be adequately financed to facilitate the development of technologies and approaches to combat the global As problem. Only this will allow an integrated approach from the occurrence of As in rocks and mobilization into the groundwater and surface water, soil and air, and into the food-chain. Human As exposure, bioavailability, metabolism and toxicology need to be considered together with related public health effects and risk assessment in order to reduce human As exposure. Arsenic removal technologies and other mitigation methods must be addressed, not solely from the technological perspective, but also, from economic and social points of view, considering legislative and political issues. Adequate resources are essential, along with increasing awareness and knowledge dissemination among administrators, policy makers and company executives. Additionally, international and bilateral cooperation on the geogenic As hazard and its global effects needs to be strengthened.

REFERENCES


The global arsenic crisis—a short introduction


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CHAPTER 2

Arsenic contamination in groundwaters in Bangladesh and options of sustainable drinking water supplies

Prosun Bhattacharya, Jochen Bundschuh, Mattias von Brömssen, Mohammad Hossain, Kazi Matin Ahmed, Jan Hoinkis & Marta Litter

2.1 INTRODUCTION

Groundwater sources used for drinking in many parts of the world contain geogenic arsenic (As) with levels of concentrations above the drinking water guideline value of the World Health Organisation (WHO, 10 µg L⁻¹). Occurrence of arsenic in groundwater has been known a century ago from Argentina, where the toxic effects on public health were described already in the year 1917. However, it was not before half a century later, that the As problem achieved world interest. This was the consequence of a UNICEF program to provide the rural population of Bangladesh with microbe-free drinking water by changing the drinking water resource from surface- and rainwater to groundwater exploited from shallow aquifers. However, the quality of the groundwater was not tested for As and caused, after 10 years of exposure of large parts of the population, toxicological effects. This became the beginning of extended international aid efforts to mitigate the As problem in Bangladesh and adjacent West-Bengal, India, where many treatment methods have been developed and tested, and brought the groundwater As topic to wide scientific and public interest.

Since several decades, the contamination of groundwater and to less extent of surface water by geogenic As is well known from countries such as Mexico, Chile, Peru, Taiwan and some small regions in European countries such as Hungary. Until recently, it was thought that the problem is limited to these countries. However, there were many new discoveries all over the world such as in several regions of the People’s Republic of China (1993–1996), Nicaragua (1996), Chhattisgarh, India (1999), Nepal (2000), Bolivia (2001), Thailand (2001), Vietnam (2001), Australia (2001); Bihar, India (2002), Uttar Pradesh, India (2003), Jharkhand, India (2004), Assam, India (2004), Myanmar (2004), Cambodia (2004), Pakistan (2005), El Salvador (2005), Ecuador (2005), Honduras (2006), Baja California State, Mexico (2006), Lao People’s Democratic Republic (2006), Cambodia (2007), Manipur, India (2007), and more recently in Sumatra, Indonesia (2009) and Izmir province, Turkey (2009) (Fig. 1.1 in chapter 1 of this book).

2.2 ARSENIC CRISIS IN SOUTH EAST ASIA

The magnitude of the arsenic crisis has increased greatly in recent years in several countries of Southeast Asia including Bangladesh and West Bengal, and a population of up to 125 million are estimated to be exposed to the potential risk of As toxicity in South Asia. Since the discovery of the chronic As related health disorders in the state of West Bengal, India in 1984 (Guha Mazumder et al. 1988, Das et al. 1996, Bhattacharya et al. 1997, Mukherjee et al. 2006), the crisis deepened following the discoveries in the adjoining country of Bangladesh (Dhar et al. 1997, Ahmed 2001, Bhattacharya et al. 2002a, b, Ahmed et al. 2004) and more states of India namely Bihar, Uttar Pradesh, Jharkhand, Assam, Chhattisgarh, Manipur (Chakraborti et al. 2004, Mukherjee et al. 2006, Hasan et al. 2007). Although the adverse impact of groundwater As contamination on human health are reported worldwide, the
health impacts are severe in the south Asian countries of India and Bangladesh, where nearly 50–70% of South-Asian population are exposed to high levels of As from ground-water sources and contaminated agricultural products.

2.3 REAPPRAISAL OF THE GENESIS OF HIGH CONCENTRATIONS OF GEOGENIC ARSENIC IN GROUNDWATER

Based on the detailed studies of prevailing aquifer conditions, the scientific community has been able to delineate the principal mechanisms of the genesis and mobilization of As in many aquifers (BGS and DPHE 2001, Bhattacharya et al. 1997, 2002a, b, 2006, Smedley and Kinniburgh 2002, van Geen et al. 2003, Ahmed et al. 2004, Bundschuh et al. 2004, Hoque et al. 2004, McArthur et al. 2004, Nickson et al. 1998, Smedley et al. 2005). However, in many of the regions, the concentration of As in groundwater is extremely heterogeneous, both laterally and vertically. The safe and unsafe tubewells in many cases, installed in the same aquifer, are often found <25 m from each other. On the basis of the hydrogeological settings, the prevailing aquifer conditions and the theories of mobilization, many of the arsenic-safe tubewells should in fact have high concentrations of As. Consequently, the “patchy distribution” has often been explained in terms of “local variations in sedimentary characteristics, hydrogeological and hydrogeochemical conditions” both in the case of Bangladesh and other areas such as in the Rio Dulce alluvial cone in Argentina (BGS and DPHE 2001, Bhattacharya et al. 2002a, b, McArthur et al. 2004, Smedley et al. 2002, 2005, Bundschuh et al. 2004, Bhattacharya et al. 2006) and hence no, or at the best a poor, explanation has been given for the As-safe tubewells. However, recent studies in Bangladesh and West Bengal, India (Harvey et al. 2002, Jonsson and Lundell 2004, McArthur et al. 2004, van Geen et al. 2004, von Brömssen et al. 2007) of the aquifer and groundwater characteristics have been refined.
or specified in such way that they can be used to distinguish As-safe or unsafe aquifers for the installations of tubewells.

The spatial and depth-wise distribution of As in Bangladesh is illustrated in Figure 2.2. The mechanism of enhanced mobilization of As triggered by reductive dissolution of Fe-oxyhydroxides in the Holocene aquifers is a plausible explanation for the set of groundwater samples in area marked A, while within area B the geological model with older and oxidized Pleistocene aquifers with low inherent As concentrations seems applicable. However, for the As-safe tubewells within area C (corresponding to about 50% of all tubewells), a reappraisal of the geological and hydrogeological model and/or mobilization theory needs to be readdressed. In recent studies in Bangladesh (Harvey et al. 2002, McArthur et al. 2004, van Geen et al. 2004), detailed aquifer and groundwater characteristics have been refined in such way that they have produced feasible hypotheses for explaining the great spatial distribution. In these studies, the groundwater chemical composition has been correlated to specific aquifer sand characteristics.

2.4 OPTIONS FOR SAFE DRINKING WATER AND THE RATIONALE FOR SEARCHING SAFE AQUIFERS

2.4.1 Various arsenic mitigation options and the lessons learnt

In order to provide safe drinking water, the Bangladesh Rural Advancement Committee (BRAC) provided alternative safe water options to those households exposed to arsenic from tubewell water first in two focus upazilas Sonargaon and Jhikargachha between 1999 and 2001. During the period of this project, safe water options were provided to approximately 10,905 households (Table 2.1) with an overall cost of more than 0.5 million US$ (BRAC 2000). Safe-drinking water options comprised different filters for As removal, rain water harvesting, and groundwater based options, such as dugwells, re-installed tubewells (<150 m) and deep tubewells (>150 m) (Jakariya et al. 2007). Before the implementation of the project, various motivational and training programs including focus group meetings, popular theatres,
presentation of video films on arsenic and health impacts and mitigation were initiated to increase community awareness and acceptance. Subsequently, a detailed evaluation of the implemented options was carried out during 2004–2005, and assessed on different criteria, such as community acceptability as well as technical and economic viability. Unfortunately, acceptability of many of them has not been encouraging (Fig. 2.3) as most of the distributed filters were discarded and abandoned by the community, since they did not find them as convenient as tubewells (Hoque et al. 2004, Jakariya et al. 2007). This resulted in a sharp decline of safe water coverage from 38 to about 14% and increased the total population exposed to contaminated sources from 45 to about 65% (Fig. 2.3). Among the safe water options, the so called “deep hand tubewells” (<150 m) (DTW) have become an accepted option as they extract groundwater from pre-Holocene and As-safe aquifers. However, drilling to depths more than 150 m is related to higher costs and thus is not affordable to the poor communities. The reasons of the ineffectiveness of the mitigation options are summarized in Table 2.1.

It has been realized that the magnitude of the human tragedy will depend on the rate at which As-mitigation programs can be implemented in Bangladesh and elsewhere (Ravenscroft et al. 2005). Considering the number of exposed population of approximately 30–60 million (only in Bangladesh) and the low rate of outcomes from mitigation programs driven by the government and donor organization (APSU 2005), it is obvious that there is an urgent need for the communities themselves to find practical mitigation options. For this reason and due to the facts stated above, we argue that a concept, to be used by the affected people themselves, for targeting As-safe aquifers for siting wells is the best opportunity to meet the Millennium Development Goals (MDGs) for ensuring safe drinking water.

### 2.4.2 Community based approach of targeting safe aquifers for drinking water supplies

Since the concept of the supply of drinking water from tubewells is deeply rooted in the daily life of the Bangladeshi people and is therefore difficult to change, there have been emerging initiatives from the local drillers to explore aquifers that offer a possible alternative source

<table>
<thead>
<tr>
<th>Option</th>
<th>Source water</th>
<th>Major concerns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pond sand filter (PSF)</td>
<td>Surface</td>
<td>Several ponds used for pisciculture</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bacteriogenic contamination in pond waters</td>
</tr>
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<td></td>
<td></td>
<td>Acceptability not universal</td>
</tr>
<tr>
<td>Rainwater harvester (RWH)</td>
<td>Rainwater</td>
<td>Rainfall not uniform through out the year and in all areas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Prohibitive costs for poor households</td>
</tr>
<tr>
<td>Arsenic removal filters</td>
<td>Arsenic-contaminated groundwater</td>
<td>Effectiveness in removing arsenic questionable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sludge disposal is a concern</td>
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<td></td>
<td></td>
<td>Difficulties in maintenance on a long-term basis, particularly, for poorer households</td>
</tr>
<tr>
<td>Dugwell</td>
<td>Shallow groundwater</td>
<td>Susceptible to microbial contamination</td>
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<td></td>
<td></td>
<td>Non availability of water during dry seasons</td>
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<tr>
<td></td>
<td></td>
<td>Presence of manganese, iron, and arsenic in some wells</td>
</tr>
<tr>
<td>Deep well</td>
<td>Deep aquifer (&gt;150 m below the surface)</td>
<td>More expensive than tubewells</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Some uncertainties as a long-term source for arsenic-free water</td>
</tr>
<tr>
<td>Piped water</td>
<td>Deep aquifer or treated surface water</td>
<td>Lack of treatment facilities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expensive for country-wide implementation</td>
</tr>
</tbody>
</table>
of As-safe drinking water (Fig. 2.4). However, drilling to depths more than 150 m is costly and may not always be possible with the local drilling techniques. Two new approaches have thus emerged in recent years, from local people’s own initiatives: i) switching to low-As shallow tubewells and; ii) installation of shallow tubewells to tap a presumed safe aquifer (van Geen et al. 2002, 2003, Jakariya 2003, Jakariya et al. 2007, von Brömssen et al. 2007). The last initiative is based on the sediment color as an indicator for safe aquifers and could provide a viable option for As mitigation in the BDP. The initial studies by Jonsson and Lundell (2004) and von Brömssen et al. (2007) examined and validated the possible relationship between the color of the aquifer sediments, the groundwater chemical characteristics and As

![Figure 2.3. Status of the various arsenic mitigation options in two high risk areas in Sonargaon and Jhikorgachha upazilas, Bangladesh (modified from Jakariya et al. 2007).](image1)

![Figure 2.4. Arsenic mitigation options for providing safe drinking water in rural Bangladesh.](image2)
consideration. This is in contrast to the wells installed previously at shallow depths (<100 m) using this sediment color indicator.

2.5 COMMUNITY BASED INDIGENOUS DRILLING FOR TARGETING SAFE AQUIFERS IN BANGLADESH

2.5.1 The study area in Matlab upazila, Bangladesh

The study area, Matlab upazila of Chandpur district, is located approximately 60 km southeast of Dhaka, near the confluence of the Ganges (Padma) and Meghna rivers (Fig. 2.2), about 3 km east of the Meghna river. Each year the area is inundated by flood water following the monsoon rains. The sediments are represented by Holocene alluvial silt deposited by the rivers Meghna and its tributary Gumti. The Holocene sediments are expected to be relatively thick here as the Meghna river dissected the delta plain during the latest glacial maximum (Umitsu 1987, 1993, Goodbred et al. 2003).

Studies within an ongoing Arsenic Mitigation Project in Matlab (AsMat) by the International Centre for Diarrhoeal Disease Research, Bangladesh (ICDDR,B) and Bangladesh Rural Advancement Committee (BRAC) revealed that approximately 80% of the domestic tubewells (n = 13,000) have As levels above the Bangladesh drinking water standard. The distribution of high As tubewells were found to vary significantly in the different villages of Matlab upazila (Wahed et al. 2006, Jakariya et al. 2007).

Reductive dissolution of Fe(III)-oxyhydroxides under strongly reducing conditions of the Holocene black to grey sediments is the cause for mobilization of As in Matlab upazila (BGS and DPHE 2001, Bhattacharya et al. 1997, McArthur et al. 2004, Nickson et al. 1998, Stüben et al. 2003, van Geen et al. 2004). The spatial distribution of aqueous As can be explained by the sediment characteristics in the study area. From a practical point of view, if local drillers could target safe aquifers, it would be a very viable option for As mitigation at the Bengal delta plain as the practice of using tubewells is well rooted in the minds of the local community (Hoque et al. 2004, Jakariya et al. 2007).

2.5.2 Indigenous drilling for tubewell installation

The installation of domestic tubewells in Matlab upazila is carried out by hand-percussion drilling (Fig. 2.5), which is a simple and low-cost method used in Bangladesh and many other parts of southeast Asia. Using the hand drilling, it is possible to install tubewells to depths of more than 100 m, especially if the sedimentary characteristics are favorable (Horneman et al. 2004, Rahman and Ravenscroft 2003, von Brömssen et al. 2007). The strainer of the tubewell is installed in sands with high hydraulic conductivity and where the water has no smell, color or taste.

The depth for installation of domestic tubewells in the study area varied between 20 and 80 m and the driller’s characterization of the sediments was based on straightforward description of texture and color of the sediments as well as the content of dissolved iron in the groundwater (semi-quantitatively or qualitatively using the smell of the water as indicator for low or high Fe concentrations) (Jonsson and Lundell 2004). The sediment colors used by the drillers working in the area were black, white, off-white, yellow and red. The colors blue and green were also used but to a lesser extent. Based on their experience, the drillers had a consistent and definite understanding of the local lithology and, according to them, a thick (30–40 m) layer of black sediments overlies whitish and reddish sediments to depths of at least 80 m where most drillers stop (Jonsson and Lundell 2004). The drillers prefer to install tubewells to a greater depth than earlier (approximately 60 m instead of 30 m), primarily because of low concentrations of dissolved iron in the groundwater derived from the reddish aquifer sands. The fact that these sediments contain low-As water is an additional consideration. This is in contrast to the wells installed previously at shallow depths in the
black sediments, where rapid oxidation of iron in pumped water produced a reddish precipitate. The drillers are well aware of the health impacts of elevated As in groundwater and are actively working to alleviate the As problem in Matlab upazila together with NGO-Forum for Drinking Water Supply and Sanitation, Bangladesh.

2.5.3 Groundwater- and sediment sampling and analyses

Groundwater sampling was carried out together with one of the experienced local drillers from 38 old and 2 newly installed tubewells with known depth and color of the sediments (as described by the driller) at the tubewell-screen in two villages, Dighaldi and Mubarakdi, within the Matlab upazila. The tubewell waters were sampled during May 2004 (n = 40) from strainers placed at depths varying from 17–82 m. The field parameters pH, redox potential (Eh), temperature, and electrical conductivity (EC) were measured in-situ using a flow-through cell. The detailed water chemistry analysis was carried out on: (i) filtered samples (using Sartorius 0.20 μm online filters) for determination of major anions and (ii) filtered samples (acidified with suprapure 14 M HNO₃) for determination of cations and other trace element including As (Bhattacharya et al. 2002a). Arsenic speciation analysis was carried out using Disposable Cartridges® (MetalSoft Center, PA) in the field. Major anions, F⁻, Cl⁻, and SO₄²⁻ were analyzed in filtered unacidified water samples, using a Dionex DX-120 ion chromatograph with an IonPac As 14 column. NO₃⁻, PO₄³⁻ and NH₄⁺ were analyzed with a Tecator Aquatec 5400 spectrophotometer. The major cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) and minor and trace elements including Fe, Mn and As were analyzed by inductively coupled plasma with optical emission spectrometry (ICP-OES) (Varian Vista-PRO Simultaneous ICP-OES) at Stockholm University. Dissolved organic carbon (DOC) in the water samples was determined on a Shimadzu 5000 TOC analyzer (0.5 mg L⁻¹ detection limit with a precision of ±10% at the detection limit).
In addition, three boreholes were drilled at different sites within the study area to confirm the driller’s perception of the sediment color and the lithology of the aquifer sediments. Disturbed sediment samples were collected for every 3.0 m, or more often if the characteristics of the sediment changed (Fig. 2.5b). Only washed and disturbed sediments could be sampled as a result of the hand-percussion technique (Rahman and Ravenscroft 2003). Washed sediments were collected in a bucket and allowed to settle before being transferred on a bamboo carpet (see Fig. 2.5). Later, the sediment samples were allowed to drain before putting them into plastic bags; however, draining of excess water did not change the color of the sediments and the sediment oxidation status. Each of the sediment samples were described on the basis of texture and color by the local driller in the field, and later visual inspection of the sediments was carried out and compared with the Munsell standard soil color chart for color classification.

2.5.3 Groundwater- and sediment characteristics

2.5.3.1 Sediment characteristics
The three boreholes that were drilled confirmed the driller’s perception of two separate lithological sequences (Fig. 2.6). The sediments within these units could be distinguished by the driller’s color description as well as by visual inspection and the Munsell color classification. A layer of black to grey sediments overlies a unit with yellowish-grey to reddish-brown sediment. Quartz and feldspars with a substantial content of micas dominated these sediments. The relatively high content of biotite and other dark colored ferromagnesian and opaque minerals are responsible for the dark black and grayish color of these sediments. The black to grey unit extended from the surface down to a depth of 37–56 m and indicates a general fining upward cycle that presumably represents fluvial sediments of Holocene age (Goodbred et al. 2003). The boundary between the both units could be identified by the change in sediment color as well as by the presence of a 2–6 m thick clayey layer. This clay was collected as hard cylindrical clay lumps. This clay has been exposed to drained and oxidized conditions and perhaps acts as a hydraulic impervious barrier in the system. Below the clay, a yellowish-grey to reddish-brown sandy unit was encountered. The sediment of this unit had relatively lower abundance of biotite with Fe(III)-oxyhydroxides as coatings on quartz, feldspars and other mineral grains, which gave the sediments its color. This lower unit was more heterogeneous in texture and color. Visual inspection of the yellowish-grey to reddish-brown aquifer indicated that these sediments were exposed to sub-aerial weathering and oxidation, while the sea level in the BDP was significantly lower (McArthur et al. 2004, Umitsu 1987, 1993, van Geen et al. 2004).

The driller’s colors were used for simplified classification of the sampled wells into four groups, namely black, white, off-white and red. A typical perception of the sediment color by the local drillers and their Munsell color characteristics is presented in Figure 2.7.

2.5.3.2 General hydrogeochemical characteristics in relation to the color of aquifer sediments
In general, the groundwater reflected a circumneutral character with pH ranging between 6 and 7. The redox potential (Eh) corrected for the standard hydrogen electrode (SHE) varied between +0.105 and +0.387 V. The Eh measurements, although not completely stabilized in field, indicated a trend of increasing Eh in the groundwaters abstracted from the black, through the white, off-white and the reddish group of sediments. The groundwater had high HCO₃⁻ concentrations (up to 500 mg L⁻¹).

The major ion chemistry of the samples indicate a predominant Ca-Mg-HCO₃⁻ or Na-Cl-HCO₃⁻ type groundwater (or a mix of them), with HCO₃⁻ as the predominant anion (Fig. 2.8). Groundwater abstracted from the black sediments are mostly of Ca-Mg-HCO₃⁻ type, while the wells placed at the white, off-white and red sediments also exploit groundwater of Na-Cl-HCO₃⁻ type. The concentrations of Cl⁻ varied from 12 to 648 mg L⁻¹, which suggests
mixing of fresh groundwater with relict sea water trapped in the underground. The presence of relict seawater and the mixing between fresh and brackish groundwater suggest that the flushing rate of the aquifers is slow and/or that high Cl$^-$ water trapped in clay-rich layers is gradually diffusing into the aquifer.

The groundwaters are characterized by low concentrations of SO$_4^{2-}$ and NO$_3^-$ (median values of 0.25 and 0.63 mg L$^{-1}$, respectively) and high concentrations of Fe and Mn (median
values of 3.1 and 1.7 mg L⁻¹, respectively, as discussed in detail in von Brömssen et al. (2007). The total As concentrations varied between <5.2 and 355 µg L⁻¹ and in about 98% of the samples As(III) species dominated over As(V) species. This dominance of As(III) was observed in all the groups of sediment color. These four different groups reflected distinct groundwater composition (Fig. 2.9a–b). DOC concentrations were considerably higher in the samples abstracted from the black sediments as compared to the sediments from the oxidized unit (Fig. 2.9) where the sedimentary organic matter might have been oxidized during the period of its sub-aerial exposure. There is also a trend of higher HCO₃⁻ concentrations in the water samples from the black sediments, presumably due to its generation in redox reactions (Bhattacharya et al. 2002a, Nickson et al. 2005).

The groundwater abstracted from the black sediment had relatively high concentrations of dissolved NH₄⁺, DOC, Fe, P, As and relatively low Mn and SO₄²⁻ concentrations, which indicates

<table>
<thead>
<tr>
<th>Drillers description and color class</th>
<th>Black</th>
<th>White</th>
<th>Off-white</th>
<th>Red/Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Munsell description</td>
<td>Olive black</td>
<td>Grey</td>
<td>Dark greyish yellow</td>
<td>Yellowish brown</td>
</tr>
<tr>
<td></td>
<td>Dark greyish yellow</td>
<td>Yellowish grey</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Munsell code</td>
<td>2.5Y 3/1</td>
<td>2.5Y 4/1</td>
<td>2.5Y 4/2</td>
<td>2.5Y 5/4</td>
</tr>
</tbody>
</table>

Figure 2.7. Simplified color description of sediments according to the drillers’ perception and Munsell color characteristics.

Figure 2.8. Piper diagram showing the major ion composition of Matlab upzila groundwater samples.
Figure 2.9. Box plots showing the variability in the concentrations of the redox sensitive aqueous species: (a) HCO$_3^-$; (b) DOC; (c) SO$_4^{2-}$; (d) NH$_4^+$; (e) Mn; (f) Fe; (g) PO$_4^{3-}$; and (h) total As in the analyzed groundwaters from four different sediment color groups.
the strongly reducing character of these sediments. Elevated (>10 µg L⁻¹) concentrations of As were, with few exceptions, found in the samples from the black sediments. In contrast, groundwater abstracted from the off-white and reddish sediments had relatively high dissolved Mn and low Fe concentrations. This suggests that the aquifers have a redox status where Mn(IV) in the solid phases is reduced, but the redox status is not sufficiently low for the reduction of Fe(III) species in the sediments. The cause for low As groundwater from the oxidized unit is either that the redox status of these sediments is higher, hence reductive dissolution of Fe(III)-oxyhydroxides has not yet resulted in supersaturation of adsorption sites for As, or simply that the As content in the reducible fraction is low. In the oxidized sediments, the concentration of dissolved Mn is high: 75% of the groundwater samples have concentrations of Mn greater than the WHO guideline value of 0.5 mg L⁻¹.

2.6 CONCLUSION

The Bangladesh study showed that the alternative safe water options provided by international organizations were not well accepted by the villagers. In fact, the concept of drinking tubewell water is so deeply rooted in the mind of the people of Bangladesh that it seems difficult to change the current practice of drinking water collection to other sources not as convenient and cheap as fetching water from hand-pumped tubewells. In most of the cases, owners of safe tubewells were willing to share water with neighbors and poor people with no other safe drinking water source. However, there were a few cases where owners were reluctant to share water with non-relatives or distant neighbors. Given the present crisis of lack of safe water sources, the intensity of such type of conflict might increase in the near future. Therefore, further studies are required to develop coherent strategies that will motivate owners to share their safe water.

The option of targeting safe water is promoted by the people themselves, socially accepted by women and men, affordable by most people and provides water in excess that can be used for sanitation purposes and shared with others lacking safe drinking water sources. The concept presented in this chapter is based on the idea that the identification of safe aquifers can be done on the basis of visible geological features, their relationship to groundwater chemical composition and relative risk for high As occurrences. If the mitigation approach can be validated as sustainable in Matlab upazila and other areas of Bangladesh and the world, it would represent an extraordinary approach to facilitate solutions for the As problem. On the other hand, if the sustainability cannot be proved, the local initiative needs to be stopped immediately.

The results from this study give a clear indication that the groundwater composition is linked to the color characteristics of the sediments. The driller’s awareness of high concentrations of As in groundwater and frequent problems with high concentrations of dissolved Fe has resulted in a change in well depths. Their perception of the subsurface lithology is based on straightforward descriptions of the sediments texture, color characteristics and content of dissolved Fe in the groundwater. Presently, most tubewells are installed to a depth of about 60 m (instead of 30 m earlier). The drillers described this aquifer as free of dissolved Fe and the sediments as whitish or reddish in color instead of black of the overlying black sediments. The drillings that were carried out in the study area verified the driller’s perception of the subsurface lithological conditions that includes a black to grey unit, down to approximately 45 m, that overlies a yellowish-grey to reddish-brown unit. The deeper unit has previously been exposed to oxidation and weathering. There were minor discrepancies between the driller’s color classification of the sediments and the Munsell description presented in this study, but even in these cases the sediments could broadly be classified into four distinct color groups. The chemical characteristics of the groundwater correlates well with the color of the aquifer sands. The redox conditions follow a trend from very reducing conditions for black (as described by the drillers) sediments with increasing redox-potential in sequence through
white, off-white to red sediments. This study shows the potential for educating local drillers to target safe aquifers on the basis of the color characteristics of the sediments. Through the use of the technical knowledge of local drillers, it may be possible to obtain safe water in many parts of Bangladesh where high-As water is being ingested.

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REFERENCES


CHAPTER 3

Toxic effects of arsenic on human erythrocytes

Mario Suwalsky, Cecilia Rivera, Fernando Villena & Carlos P. Sotomayor

3.1 INTRODUCTION

Arsenic (As) can exist in four oxidation states: −3, 0, +3, +5. Under reducing conditions, arsenite [As(III)] is the dominant form; arsenate [As(V)] is a generally stable form in oxygenated environments. As can be inhaled, absorbed through the skin or even ingested. It exerts its toxic effect through several mechanisms as reviewed by Hughes (2002), the most significant of which is a reversible combination with sulfhydryl groups. It binds to the pyruvate dehydrogenase complex, blocks the Krebs cycle and interrupts oxidative phosphorylation, resulting in a marked depletion of cellular ATP and eventually the death of the metabolizing cell. Through sulfhydryl group binding, As also interferes with the transformation of thiamine and inhibits numerous cellular enzymes involved in glucose uptake, gluconeogenesis, fatty acid oxidation and the glutathione production. However, binding of arsenate at nonessential sites in proteins may be a detoxication mechanism (Aposhian et al. 2000). A second major form of toxicity is termed arsenolysis. As a phosphate analogue, arsenate is known to affect oxidative phosphorylation by competition with phosphate. As a consequence, arsenate diminishes the formation of ATP and uncouples many reactions, which results in energy loss for the cell. Phosphate in the sodium pump can also be replaced by arsenate anions, as well as the anion exchange transport system of the human red blood cell (Kenney and Kaplan 1988). Arsenic metabolism plays an important role in its toxic effects. Many mammalian species methylate inorganic As (i-As). Although there is variation between different species in the rate and the extent of methylation, i-As is metabolized by a sequential process involving a two-electron reduction of pentavalent As to trivalent As, followed by oxidative methylation to monomethylarsonic acid and dimethylarsinic acid (reviewed by Thomas et al. 2001), which are excreted, along with residual i-As, in the urine. However, if the dose of As is very high, the elimination half-life becomes prolonged.

Both aquatic and terrestrial biota show a wide range of sensitivity to different As species (see Meharg and Hartley-Whitaker 2002 for a review on As toxicity in terrestrial plants). Soluble i-As is acutely toxic and the ingestion of large doses leads to gastrointestinal symptoms, disturbances in the cardiovascular and nervous system functions and eventually death. In survivors, bone marrow depression, hemolysis, hematemesis, melanosis, and encephalopathy might be observed. Long-term exposure to As in drinking water is causally related to an increased risk of skin, lung, bladder and kidney cancer (Kitchin 2001, Vähter 2002, Rossman 2003, Smith and Smith 2004) as well as other skin changes such as hyperkeratosis and pigmentation changes (Smith et al. 1998, Thomas et al. 2001). Mechanism or mode of action by which i-As causes toxicity, including cancer, has not been well elucidated. Arsenic exposure may cause DNA hypomethylation due to continuous methyl depletion, facilitating an aberrant gene expression that results in carcinogenesis. Further, though As is nonmutagenic, it interacts synergistically with genotoxic agents in the production of mutations and also induces chromosome abnormalities and cell proliferation (Roy and Saha 2002). Non-cancer effects are thought to be related to the inhibitory effects on cellular respiration at the mitochondrial level. Oxidative stress might also have an important role in both cancer and non-cancer effects.

Despite the well documented information, there are insufficient reports concerning the effects of As compounds on both structure and functions of cell membranes, particularly...
those of human erythrocytes (Winski et al. 1997, Winski and Carter 1998, Zhang et al. 2000). Cell membrane is a diffusion barrier which protects the cell interior. Therefore, its structure and functions are susceptible to alterations as a consequence of interactions with chemical species. In the course of in vitro systems search for the toxicity screening of chemicals of biological relevance, different cellular models have been applied in order to examine their adverse effects. Erythrocytes were chosen because although less specialized than many other cell membranes they carry on enough functions in common with them such as active and passive transport and the production of ionic and electric gradients, to be considered representative of the plasma membrane in general. The capacity of four different As compounds, two inorganic and two methylated, to interact with human erythrocytes was studied by scanning electron microscopy (SEM) on intact red blood cells and by fluorescence spectroscopy on isolated unsealed human erythrocyte membranes (IUM). These systems and techniques have been used in our laboratories to determine the interaction with and the membrane-perturbing effects of other inorganic compounds (Suwalsky et al. 2008, 2009). Compounds under study were sodium arsenite (NaAsO$_2$), sodium arsenate (Na$_2$HAsO$_4$), disodium monomethylarsonate [MMA(V), Na$_2$CH$_3$AsO$_3$] and sodium dimethylarsinate [DMA(V), sodium cacodylate, Na(CH$_3$)$_2$AsO$_2$].

3.2 MATERIALS AND METHODS

3.2.1 Scanning electron microscopic (SEM) studies of human erythrocytes

Blood was obtained from healthy human male donors not receiving any pharmacological treatment. Blood samples (0.1 mL) were obtained by puncture in the ear lobe and collected in Eppendorff tubes containing 10 µL of heparin (5000 UI mL$^{-1}$) in 0.9 mL of phosphate buffered saline (PBS) at pH 7.4. Samples were then centrifuged (1000 rpm × 10 min) and the supernatant was discarded and replaced by the same volume of PBS; the whole process was repeated three times. Sedimented red blood cells were suspended in 0.9 mL of PBS and fractions of this stock of red blood cells suspension (RBCS) were placed in Eppendorff tubes in order to prepare (1) the control, by mixing 100 µL of PBS solution plus 100 µL RBCS, and (2) a range of concentrations of each of the As compounds (0.1–20 mM) by mixing 100 µL of RBCS with 100 µL of adequate As stock solution in PBS. All samples were then incubated for one hour at 37°C, period aligned with the larger effects of studied compounds on red cell shape (Zimmermann and Sounpasis 1985, Malheiros et al. 2000). After the incubation, the samples were centrifuged (1000 rpm × 10 min), the supernatant discarded, and then were fixed overnight at 4°C by adding 1 mL of 2.5% glutaraldehyde to each one. Fixed samples were washed with distilled water, placed over Al glass cover stubs, air dried at 37°C for 30 min to 1 h, and gold-coated for 3 min at 10$^{-1}$ Torr in a sputter device (Edwards S150, Sussex, England). Resulting specimens were examined in a Jeol SEM (JSM 6380, Japan).

3.2.2 Fluorescence measurements of isolated unsealed human erythrocyte membranes (IUM)

The influence of the As compounds on the physical properties of IUM was examined by fluorescence spectroscopy using DPH and laurdan (Molecular Probe, Eugene, OR, USA) fluorescent probes. DPH is widely used as a probe for the hydrophobic regions of the membrane phospholipid bilayer because of its favorable spectral properties. Their steady-state fluorescence anisotropy measurements were used to investigate the structural properties of IUM as it provides a measure of the rotational diffusion of the fluorophor, restricted within a certain region such as a cone due to the lipid acyl chain packing order. Laurdan, an amphiphilic probe, has high sensitivity of its excitation and emission spectra to the physical state of membranes. With the fluorescent moiety within a shallow position in the
bilayer, laurdan provides information about the polarity and/or molecular dynamics at the phospholipid glycerol backbone level. Quantification of the laurdan fluorescence spectral shift was effected by means of the generalized polarization (GP) concept (Parasassi and Gratton 1995). Erythrocytes were separated from heparinized venous blood samples obtained from normal casual donors by centrifugation and washing procedures. IUM were prepared by lysis, according to Dodge et al. (1963). DPH and laurdan were incorporated into IUM by addition of 2 µL mL⁻¹ aliquots of 0.5 mM solutions of the probe in dimethylformamide and ethanol, respectively, in order to obtain final analytical concentrations of 1 µM, and incubated them at 37°C for 45 min. Fluorescence spectra and anisotropy measurements were performed in a phase shift and modulation K2 steady-state and time resolved spectrofluorometer (ISS Inc., Champaign, IL, USA) interfaced to computer. Software from ISS was used for both data collection and analysis. IUM measurements were made at 37°C using 10 mm path-length square quartz cuvettes. Sample temperature was controlled by an external bath circulator (Cole-Parmer, Chicago, IL, USA) and monitored before and after each measurement by means of an Omega digital thermometer (Omega Engineering Inc., Stanford, CT, USA). Anisotropy measurements were made in the L configuration using Glan Thompson prism polarizers (I.S.S.) in both exciting and emitting beams. Emission was measured through a WG-420 Schott high-pass filter (Schott WG-420, Mainz, Germany) with negligible fluorescence. DPH fluorescence anisotropy (r) was calculated according to the definition: $r = \frac{I_\| - I_\perp}{I_\| + 2I_\perp}$, where $I_\|$ and $I_\perp$ are the corresponding parallel and perpendicular emission fluorescence intensities with respect to the vertically polarized excitation light (Lakowicz 1999). Laurdan fluorescence spectral shifts were quantitatively evaluated using the GP concept (see above) which is defined by the expression $GP = \left(\frac{I_b - I_r}{I_b + I_r}\right)$, where $I_b$ and $I_r$ are the emission intensities at the blue and red edges of the emission spectrum, respectively. These intensities have been measured at the emission wavelengths of 440 and 490 nm, which correspond to the emission maxima of laurdan in both gel and liquid crystalline phases, respectively (Parasassi et al. 1990). Each one of the As compounds was incorporated in IUM suspensions by addition of adequate (10 mM) aliquots of the corresponding solution in order to obtain the different concentrations used in this work. Samples thus prepared were then incubated at 37°C, for ca. 15 min and measured at 37°C because that is the normal temperature at which erythrocytes circulate in humans. Blank subtraction was performed in all measurements using unlabeled samples without probes. Data presented in the corresponding figures represent mean values and standard error of ten measurements in two independent samples. Unpaired Student’s t-test was used for statistical calculations.

3.3 RESULTS

3.3.1 Scanning electron microscopic (SEM) studies of human erythrocytes

SEM examinations of human erythrocytes incubated with the four different As compounds indicated that all of them induced echinocytosis. In that altered condition, the red blood cells lost their normal biconcave profile and changed it to a spiny configuration with blebs in their surfaces. The extent of these shape changes was dependent on the concentrations, as it can be observed in Figs. 3.1a–d. Figure 3.2 shows a comparison of the percentage of morphological changes induced by each of the As compound as a function of their concentrations. NaAsO₂ increased the number of echinocytes in the 0.01–15 mM concentration range from about 4 to 100%, while Na₂HAsO₄ increased from 14 to 83% in the same concentration range. When the red cells were incubated with MMA and DMA no significant changes were observed with the lowest assayed concentration (0.01 and 0.1 mM). However, in the range 1–15 mM MMA induced echinocytosis from 6 to 95%; 100% was attained with 20 mM MMA, whereas for DMA echinocytosis ranged from 15 to 35% in the range 1–15 mM, increasing to 86% with 20 mM DMA. From these results it can be concluded that at low concentrations
Figure 3.1. Scanning electron microscopy (SEM) images on the effects of (a) sodium arsenite, (b) sodium arsenate, (c) disodium monomethylarsionate (MMA), and (d) sodium dimethylarsinate (DMA) on the morphology of human erythrocytes.

(0.01 to 1 mM) the maximum effects were induced by the inorganic compounds (arsenite and arsenate), being DMA the As compound that produced the minimum effects on the human erythrocyte morphology in practically all the range of assayed concentrations. It should also be mentioned that low concentrations of the arsenicals, with the exception of DMA, induced a few cells to change their normal shape into stomatocytes (a cup-shaped form with evagination of one surface and a deep invagination of the opposite face).
3.3.2 *Fluorescence measurements of isolated unsealed human erythrocyte membranes (IUM)*

Structural effects of the four As compounds on IUM were determined at 37°C at the hydrophilic/hydrophobic interface and at the acyl chain hydrophobic core of the erythrocyte membrane bilayer by evaluation of both laurdan GP and DPH steady-state fluorescence anisotropy ($r$), respectively. Figure 3.3 shows that the incorporation of arsenite, arsenate and MMA at very low concentrations produced a considerable increase of the GP values, which practically level off with higher concentrations. These results differ from
those observed with DMA, which showed a biphasic pattern. As shown in Figure 3.3, an initial sharp decrease of GP occurred with low concentrations of this compound, followed by a gradual increase of this parameter at higher concentrations. On the other hand, as shown in Figure 3.4, the four As compounds did not induce any significant change to the
3.4 DISCUSSION

Erythrocytes are the first target site of As compounds when they attack the body after systemic absorption, and the cell membrane is the frontier facing the attack (Zhang et al. 2000). However, there is a lack of reports concerning the effects of As compounds on the structure of cell membranes, particularly those of human erythrocytes. In order to contribute to understand the nature of these interactions scanning electron microscopy (SEM) observations on intact human erythrocytes and fluorescence determinations on human erythrocyte membranes (IUM) were performed.

SEM of specimens showed that in fact the four As compounds induced a change of shape of the normal biconcave erythrocytes. Although some echinocytes were observed with concentrations as low as 0.01 mM (for the i-As) the number of echinocytes considerably increased with higher concentrations, reaching a 100% of the cells with 15 mM NaAsO₂, while these percentages at this concentration were lower for the rest of the As compounds. On the other hand, only scanty stomatocytes were observed. According to
the bilayer-couple hypothesis (Sheetz and Singer 1974, Lim et al. 2002), shape changes are induced in red blood cells due to the insertion of foreign species in either the outer or the inner monolayer of the erythrocyte membrane. Thus, spiculated shapes (echinocytes) are observed in the first case while cup shapes (stomatocytes) are produced in the second due to the differential expansion of the corresponding monolayer. Given the extent of the echinocyte formation, it can be concluded that the four As compounds were inserted into the outer monolayer of the erythrocyte membrane. These results were confirmed by the fluorescence experiments performed in IUM. In fact, they allow to hypothesize that the As compounds at low concentrations induced structural perturbations in the phospholipid polar group packing arrangement of the erythrocyte membrane lipid bilayer: arsenite, arsenate and MMA decreasing, and DMA increasing water content and/or molecular dynamics, presumably due to ordering and disordering effects, respectively. On the basis of these results it might be confirmed that cell membranes lipid bilayers are in general potential targets for As compounds. These experimental findings are of interest as they indicate that As compounds alter the normal biconcave shape of red blood cells. It must be considered that these alterations into echinocytes might increase their resistance to entry into capillaries, which could contribute to decreased blood flow, loss of oxygen, and tissue damage through microvascular occlusion (Winski and Carter 1998, Svetina et al. 2004). It should be taken into account that these studies were performed in vitro, in which used concentrations were higher than those found in As-contaminated drinking water. Similar concentrations have also been used in other in vitro studies performed in erythrocytes (Delnomdedieu et al. 1995, Winski and Carter 1998, Zhang et al. 2000). However, it cannot be disregarded that after chronic exposure arsenicals can accumulate in red blood cell membranes inducing the reported morphological effects.

Historically, methylation of i-As has been regarded as a detoxification mechanism (Gebel 2002). In recent years, however, this interpretation has been questioned (Sakurai et al. 2005). It has been previously shown that in forming toxic and carcinogenic As species, reduction from the pentavalent state to the trivalent state is of major importance. However, as suggested by Kitchin (2001) for i-As, oxidative methylation followed by reduction to trivalence may be activation rather than a detoxification pathway, which would be particularly true for arsenate. Of the four assayed As compounds the arsenite proved to be the one that exerted the maximum effect on the erythrocyte change of shape, whereas DMA induced the least effect. Arsenite is present as As(OH)\(_3\) at the almost neutral pH in which the experiments were carried out (Kumaresan and Riyazuddin 2001). Due to the non-bonded electron pair localized on the As atom, it is likely to present a polar pyramidal conformation. Therefore, it is hardly plausible that it can penetrate deeply into the hydrophobic core of the erythrocyte membrane lipid bilayer. Most likely, the arsenite molecules interact with the positively charged terminal amino groups of lipids located in the outer monolayer of the erythrocyte membrane disrupting their packing arrangement (Suwalsky et al. 2007). However, there are also evidences of the interaction of arsenite with sulfhydryl groups of the membrane proteins (Zhang et al. 2000). A comparison of the results obtained from the two assayed i-As compounds indicates that their effects on human erythrocytes are in the order: arsenite > arsenate. These results differ from those reported by Winski and Carter (1998), who found that red blood cells were as much as 1000 times more susceptible to arsenate than arsenite. However, Delnomdedieu et al. (1995) found that the toxic effects induced to rabbit erythrocytes were arsenite > arsenate > MMA > DMA, which are more similar to our own results. This decreasing capacity of altering red cells might be related, among other factors, to the molecular size of these compounds: thus their insertion in the erythrocyte membrane outer monolayer should be more difficult to achieve for the bulkier dimethylarsinate (DMA) than for the smaller arsenite. Thus, judging from our experimental results and their sole effects on human erythrocytes, methylation might constitute a detoxification pathway.
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Section II
Arsenic removal: Mechanisms, current practices and experiences
CHAPTER 4
Mechanisms of arsenic removal from water

Wolfgang Höll

4.1 INTRODUCTION

Arsenic (As) occurs in the natural environment in the oxidation states –3, 0, +3 and +5 and is found in about 200 different minerals including elemental As, arsenides, sulfides, oxides, arsenates and arsenites (EPA 2000, Riedel 1994). The most abundant mineral is arsenopyrite, FeAsS, which is often the host for gold. Arsenic is a well-known poison and not an element essential for the human body. In water, As is found in the two oxidation states +3 and +5. The trivalent form, As(III), is hydrolyzed as arsenic acid $H\text{AsO}_3$ and is present as the free acid or as one of the species resulting from its dissociation. The pentavalent form, As(V), is also hydrolyzed as As-acid $H\text{AsO}_4$ and occurs as the non-dissociated acid or as their dissociated species. The two acids, however, show completely different patterns of dissociation as shown in Figure 4.1 for a total As concentration of 100 $\mu$g L$^{-1}$. Arsenic acid is almost completely dissociated at pH values $>$ 4, while arsenous acid shows substantial dissociation only at pH values above 8 (Fig. 4.1).

As-concentrations in bodies of waters may range from $<$ 1 $\mu$g L$^{-1}$ in uninfluenced surface waters to $>$ 400 $\mu$g L$^{-1}$ in rivers and lakes affected by geothermal or industrial waste waters. Aquifer concentrations vary from very low to several mg L$^{-1}$ stemming from both, natural and industrial sources (EPA 2000, Ahmed 2009).

The different methods of As-species elimination are based on the chemical and physical properties of the two sets of As-species and their reactions with other dissolved species or with solid surfaces.

4.2 ARSENIC REMOVAL BY PRECIPITATION METHODS

The insolubility of certain inorganic As(V) compounds is the basis of many hydrometallurgical As-removal processes. The most common methods for removing As from process streams are by precipitation as As(III) sulfide, calcium arsenate or ferric arsenate. Unfortunately, all of these materials are unstable under certain conditions and, therefore, not suitable for direct

![Figure 4.1. Speciation of As(III), (left), and As(V), (right). Total As concentration: 100 $\mu$g L$^{-1}$.](image-url)
disposal to uncontained sites as they will produce As-bearing leachates (Bothe and Brown 1999, Nishimura et al. 1993, Robins 2006, Robins et al. 2001, Twidwell et al. 1999).

As-sulfide, As$_2$S$_3$, can be generated by adding ferrous sulfate solutions and by means of sulfate-reducing bacteria (Tenny 2001):

$$8\text{Fe}^{2+} + \text{SO}_4^{2-} + 20\text{H}_2\text{O} \rightleftharpoons 8\text{Fe(OH)}_2^- + 14\text{H}^+ + \text{H}_2\text{S}$$

Arsenic is then precipitated by sulfide according to:

$$2\text{H}_3\text{AsO}_4^- + 5\text{HS}^- \rightleftharpoons \text{As}_2\text{S}_3 + 3\text{H}_2\text{O} + 5\text{OH}^-$$

As-sulfide has its lowest solubility below pH = 4 but the solubility is significantly higher than accepted by standards. Precipitation by direct application of hydrogen sulfide gas is not as effective and requires pH ranges of 2.5–3.0.

Calcium arsenate compounds are generated by adding CaO or Ca(OH)$_2$ to As contaminated waters. Different precipitates can be generated (Table 4.1). When operated at pH values > 10.5, a high As-percentage can be precipitated from solutions bearing >50 mg As L$^{-1}$. However, it is difficult to achieve final concentrations below 1 mg L$^{-1}$, although concentrations of about 10 µg L$^{-1}$ have been reported (Robins 2006, Robins et al. 2001). Solid calcium arsenate reacts with carbon dioxide to form CaCO$_3$, while As is remobilized. Addition of magnesium salts leads to the formation of Mg$_4$(AsO$_4$)$_2$. To a certain small extent, this method is applied to achieve arsenate fixation in soils, sediments and wastes (Magalhães 2002).

As(V) can be removed through precipitation of ferric arsenate. One possibility is the addition of ferric salts to As-bearing water (Nishimura et al. 1993):

$$\text{Fe}^{3+} + \text{AsO}_4^{3-} \rightleftharpoons \text{FeAsO}_4(s)$$

Precipitation is possible at pH values below about 2 and leads to an amorphous material with particle sizes of about 100 nm. Conversion to crystalline material (scorodite) requires temperatures >90°C (Robins et al. 2001).

Another approach uses ferrous salts (e.g., ferrous sulfate) and subsequent oxidation by means of ferrate ions (Vogels and Johnson 1998):

$$\text{Fe}^{2+} + 4\text{AsO}_4^{3-} \rightleftharpoons \text{FeAsO}_4^- + \text{FeO(OH)}(s)$$

$$\text{FeAsO}_4^- + 4\text{FeO}^{2+} \rightleftharpoons \text{FeAsO}_4(s) + \text{FeO(OH)}(s)$$

Table 4.1. Total concentration of As in aqueous solutions in equilibrium with calcium, magnesium and iron arsenates (Magalhães 2002).

<table>
<thead>
<tr>
<th>Solid phase</th>
<th>Temp. (K)</th>
<th>pH</th>
<th>As$_{\text{total}}$ (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaHAsO$_4$ · H$_2$O</td>
<td>308</td>
<td>acid</td>
<td>0.12–1.2</td>
</tr>
<tr>
<td>Ca$_2$(AsO$_4$)$_5$</td>
<td>293</td>
<td>6.90–8.35</td>
<td>1.5 × 10$^{-3}$–3.5 × 10$^{-3}$</td>
</tr>
<tr>
<td>Ca$_3$(AsO$_4$)$_2$ · 4.25 H$_2$O</td>
<td>296</td>
<td>7.32–7.35</td>
<td>1.1 × 10$^{-3}$–6.5 × 10$^{-3}$</td>
</tr>
<tr>
<td>Ca$_6$(AsO$_4$)$_3$·(OH)$_2$</td>
<td>310</td>
<td>5.56–7.16</td>
<td>7.5 × 10$^{-4}$–4.4 × 10$^{-4}$</td>
</tr>
<tr>
<td>Ca$_6$(AsO$_4$)$_3$Cl$_2$</td>
<td>310</td>
<td>4.67–7.42</td>
<td>1.9 × 10$^{-4}$–3.7 × 10$^{-5}$</td>
</tr>
<tr>
<td>Mg$_4$(AsO$_4$)$_2$</td>
<td>293</td>
<td>6.50–7.40</td>
<td>1.5 × 10$^{-3}$–4.6 × 10$^{-3}$</td>
</tr>
<tr>
<td>FeAsO$_4$</td>
<td>293</td>
<td>1.90–2.95</td>
<td>3.7 × 10$^{-4}$–8.5 × 10$^{-5}$</td>
</tr>
<tr>
<td>FeAsO$_4$ · 2H$_2$O</td>
<td>293</td>
<td>5.53–6.35</td>
<td>1.4 × 10$^{-4}$–2.5 × 10$^{-3}$</td>
</tr>
</tbody>
</table>
The solubility decreases with increasing dosage of Fe\(^{3+}\) (West General 2006). Ferric arsenate in either form is thermodynamically not stable in the neutral to higher pH range. The materials are also not stable in alkaline cement cast admixes (Magalhães 2002). The solubility of different precipitates is summarized in Table 4.1.

4.3 ARSENIC REMOVAL THROUGH SORPTION METHODS

4.3.1 General
Dissociation of both arsenous and arsenic acid leads to anionic As-species which can be sorbed onto surfaces of solids which bear a positive charge. Such solids may be synthetic polymeric ion exchangers or inorganic materials, predominantly hydrous metal oxides. The latter ones can be applied as granular packed beds or as freshly precipitated hydroxides. A comprehensive review of the majority of sorption processes and proposals for As removal has been presented in literature (Mohan and Pittman Jr. 2007).

4.3.2 Arsenic removal using synthetic ion exchangers
One possibility for As removal is the application of synthetic ion exchange resins. These resins are usually based on a cross-linked polymer matrix (polystyrene) to which charged functional groups (various amine or quaternary ammonium) have been attached. For As-species removal commercially available strongly basic ion exchange resins in the chloride form have been proposed (EPA 2000):

\[
R-[\text{N(CH}_3\text{)}_3]^+\text{Cl}^-+\text{H}_2\text{AsO}_4^- \rightleftharpoons R-[\text{N(CH}_3\text{)}_3]^+\text{H}_2\text{AsO}_4^-+\text{Cl}^-
\]

where R = matrix and overbarred symbols refer to the exchanger phase. Regeneration of the resins is achieved by means of NaCl solutions. The effective exchange capacity of these exchange resins strongly depends on the composition of the raw water and the influence of competitive sorption of other anions from the background composition. The relative sorption follows the so-called series of selectivity. For strongly basic resins of type 1 and common anions the following series has been found (Clifford 1999):

\[
\text{SO}_4^{2-} \gg \text{NO}_3^- > \text{HAsO}_4^{2-} > \text{Cl}^-
\]

As a consequence, arsenate species will be eliminated. Unfortunately, there is a strong interference by sulfate and possibly also by nitrate anions. Efficient arsenate species elimination becomes possible only for sulfate concentrations below 50 mg L\(^{-1}\) where filter throughputs of \(\approx 750\) bed volumes between two regenerations can be achieved. At higher sulfate concentrations the service cycles become too short for an economic elimination. An oxidation is required prior to the ion exchange step with As(III) species in the raw water. Some studies report on the application of iron oxide-loaded or MnO\(_2\)-loaded anion exchangers (Lenoble et al. 2004).

4.3.3 Arsenic removal using hydrous metal oxides/hydroxides
4.3.3.1 General principle
The second possibility of As-species sorption consists of the application of hydrous metal oxides among which activated alumina and ferric oxides/hydroxides have obtained importance. In contact with water these surfaces possess hydroxyl groups which are subject to protolytic reactions. The degree of protonation or deprotonation depends on the surface
properties and is characterized by the so-called point of zero charge pH value, $pH_{PZC}$. At pH values below $pH_{PZC}$, the surface is predominantly protonated and bears a net positive charge. For $pH > pH_{PZC}$, however, the surface is predominantly deprotonated and bears a negative charge which has to be balanced by cations. Using Me as the symbol for a trivalent metal atom at the surface, the respective reactions can be written as (Horst and Höll 1997):

$$>\text{Me} - \text{OH} + \text{H}^+ \rightleftharpoons >\text{Me} - \text{OH}_2^+ >\text{Me} - \text{OH}^- + \text{An}^- \rightleftharpoons >\text{Me} - \text{OH}_2\text{An}$$

$$>\text{Me} - \text{OH} - \text{H}^+ \rightleftharpoons >\text{Me} - \text{O}^- >\text{Me} - \text{O}^- + \text{Cat}^+ \rightleftharpoons >\text{Me} - \text{OCat}$$

The compounds generated at the surface are designated as surface complexes. Depending on the liquid phase pH value, As-species can be attached to one or two surface groups (monodentate and bidentate surface complexes; Fig. 4.2) similar to the mechanism on a weakly basic anion exchanger (Stumm 1992).

### 4.3.3.2 Activated alumina

Activated alumina, $\text{Al}_2\text{O}_3/\text{Al(OH)}_3$, is one of the inorganic amphoteric exchange materials applied for As-removal. It has a large internal surface in the range of 200–300 m$^2$ g$^{-1}$. Its $pH_{PZC}$ is approximately 8.2. As a consequence, it exhibits an increasing As-removal capacity with decreasing pH value. At $pH = 6$ As removal capacities of about 1.6 g L$^{-1}$ of packed bed have been reported (Frank and Clifford 1990). Like polymeric anion exchange resins, activated alumina exhibits a preference of ions according to a series of selectivity (Clifford 1999):

$$\text{OH} >> \text{HPO}_4^{2-} > \text{HAsO}_4^{2-} > \text{F}^- > \text{SO}_4^{2-} >> \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-$$

As a consequence, arsenate species are highly preferred and major decreases of the sorption capacity are only due to phosphate while the competitive sorption of sulfate ions is less efficient. Regeneration can be carried out by NaOH solutions followed by rinsing with acid to re-establish the positive surface charge. Regeneration is more difficult and less effective compared to ion exchange resins and leads to the displacement of only 50–80% of As species (Clifford and Lin 1986, Driehaus 1999, Wang et al. 2000). Furthermore, there is some loss of material due to the dissolution of activated alumina in high-alkaline media. Advantages of the application of activated alumina are the simple technology in which service cycles extend to the treatment of several thousand bed volumes of raw water before regeneration is required. Disadvantages include the relatively narrow pH range and the difficulties of regeneration. Compared to polymeric ion exchangers, the rate of sorption is considerably smaller and significantly longer contact times/smaller rates of filtration are required (EPA 2000).

### 4.3.3.3 Iron oxides/hydroxides

Much better As removal has been found for iron oxide/hydroxide-based materials. Several products have been developed among which Granular Ferric Hydroxide, GFH® revealed a superior performance. It is a synthetic akaganeite material with a point of zero charge at $pH = 7.9$. This material has been tested in many laboratory, bench and pilot scale experiments and is

![Figure 4.2](image-url)  
Postulated monodentate (left) and bidentate (right) surface complexes at hydrous oxides. “Me” symbolizes the metal (e.g., Al, Fe, and similarly Mn, Ti).
Manufactured and applied on a large scale. Its advantage is that arsenate anions are strongly retained and, therefore, immobilized while small product water concentrations are achieved. The total AsO$_4^{3-}$ capacity amounts to 28 g l$^{-1}$. At feed water concentrations of 10–50 µg L$^{-1}$, 50,000 to 300,000 bed volumes of raw water can be treated, depending on pH and phosphate concentration (Driehaus 2002, Pal 2001).

A similar material which also has successfully been applied for As removal is Granular Ferric Oxide (Bayoxide®, GFO), which is a material with <70% Fe$_2$O$_3$ and a specific surface of 120–200 m$^2$ g$^{-1}$. GFO has also been applied in numerous As removal plants. At raw water concentrations of 10–50 µg L$^{-1}$ of As, product water concentrations of around 4 µg L$^{-1}$ of As can be achieved while the length of the service cycle amounts to 80,000–125,000 bed volumes (Severn Trent Services). Further iron oxide-based materials have been developed (Mohan and Pittman Jr. 2007).

Unlike activated alumina, these metal oxides are not regenerated but discharged to landfill deposits and replaced by fresh material. Because of the strong immobilization, As-species are not re-mobilized under aerobic conditions (Badruzzaman 2001).

4.3.3.4 Oxides/hydroxides of other metals
Among various novel inorganic adsorbents granular titanium dioxide presents favorable properties. The commercially available sorbent (Adsorbia®) has a specific surface area of 200–300 m$^2$ g$^{-1}$. Depending on the raw water composition service cycles of 50,000 to 150,000 bed volumes can be achieved. Some full-scale plants for drinking water supply are already in service (DOW 2005, Wrigley and Vance 2009).

From further metal oxides cerium oxide powder in a polymeric matrix provides a high selectivity toward As species. This has been the basic idea for the development of a cerium oxide-based sorbent which can be applied for sorption of As species, but also of phosphate, fluoride and borate. Arsenic removal from both, drinking water and industrial wastewater has been realized in full scale using this material (Shimoto 2006, Amimono 2006).

A third inorganic material that has successfully been studied for As-species removal is manganese dioxide, MnO$_2$ (Driehaus et al. 1995, Dlugosch 2001). Similar to iron oxide materials, As-species are effectively eliminated and relatively large solid-phase concentrations can be achieved. Similar to GFH®, As(III) species are oxidized at the surface and then sorbed as As(V) species (Prasad 1994).

4.3.3.5 Other materials
The specific sorption of As onto iron oxides is also used by iron-coated sand. The material has frequently been described as a cheap sorbent for As in both household devices and small technical plants. The material can be regenerated and re-used (Joshi 1996, Ahmed 2001, Thirunavukkarasu et al. 2004). Manganese dioxide can also be applied to coat sand (Bajpai and Chaudhury 1999).

A new approach consists in iron oxide-coated limestone particles. Experiments in the pilot scale revealed that this material can sorb As(III) and As(V) species besides other ions such as heavy metals and phosphate. It is typically applied in cartridges for home treatment systems. After exhaustion the material can easily be recycled into concrete (Banavali et al. 2008).

During the last 20 years several further iron/manganese oxide-based materials have been investigated, partly in the framework of field tests (Deschamps et al. 2005, EPA 2000, Prasad 1994, Shevade and Ford 2004, Zeng 2003). Among these are greensand and other natural materials as well as iron-coated sand. The mechanisms of sorption are more or less identical to those described above. Some of them have to be regenerated.

4.3.4 Hybrid sorbents
One of the disadvantages of the granular hydrous metal oxides/hydroxides it the slow rate of sorption which can be overcome only by increasing the specific outer surface which means...
by smaller particles. Because micro-particles do not allow a conventional filter operation, micro-particles with magnetic properties are being developed, together with the respective technology of application (Dahlie et al. 2003). Another development is based on a polymeric network comparable to that of ion exchange resins, in which nano-particles of iron oxide/hydroxide are introduced. These sorbents combine the efficient sorption onto ferric oxide/hydroxide material with the fast sorption onto nano-particles and the application of conventional packed beds (DeMarco and Sengupta 2003, SOLMETEX 2004). The respective materials (ArsenX® and LEWATIT® FO 36) have been applied in demonstration and technical installations, especially in Bangladesh and India (DeMarco et al. 2003, SOLMETEX 2004, LANXESS 2008, Sengupta 2009). These materials can easily be regenerated and re-used. The eluted As species are concentrated in a small volume of regenerant that can easily be post-treated.

### 4.4 ARSENIC ELIMINATION THROUGH COAGULATION AND FILTRATION

Coagulation and filtration is one of the classical possibilities to remove As-species from water that has been studied in a large number of investigations. It has been applied to the treatment of drinking water in a manifold of cases. Coagulants can be alum [Al(SO₄)₃], ferric chloride (FeCl₃), or ferrous sulfate (FeSO₄) (Baldauf 1995, Jekel and Van Dyck-Jekel 1989, Seith and Jekel 1999). The mechanism of As-elimination is that of a sorption onto the freshly precipitated Al(OH)₃ and Fe(OH)₃ particles or flocs. The results clearly indicate that the application of iron salts provides generally better elimination than aluminum salts. Elimination was effective, when As was present as As(V). At dosages of >5 mg L⁻¹ FeCl₃, almost complete As-elimination has been observed. At concentrations of 10–50 µg L⁻¹ in the raw water, a dosage of 1–2 mg L⁻¹ Fe₃⁺ leads to a satisfactory As-elimination below the standard for drinking water of 10 µg L⁻¹. Opposite to that, elimination of As(III) species was rather unsatisfactory. However, oxidation by means of H₂O₂, NaOCl, or Cl₂ quickly converts As(III) to As(V) and leads to an efficient elimination also of As(III). Application of FeCl₃ generates relatively big flocs, while finer flocs are formed from FeSO₄ (Baldauf 1995, Jekel and Van Dyck-Jekel 1989, Seith and Jekel 1999). The advantages of the process are the simple technology, the application of usual chemicals and small specific cost of the installation. Furthermore coagulation/filtration can be applied for large throughputs of raw water. The disadvantage of the process lies in a relatively large volume of As-bearing sludge that needs to be discharged.

Arsenic can also be eliminated by adsorption onto Fe(OH)₃ flocs which result from corrosion in steel tubes (Karschunke 2005, Manning et al. 2002).

### 4.5 UNDERGROUND ARSENIC REMOVAL

A similar mechanism of reaction of As-species with freshly precipitated hydrous oxides/hydroxides occurs during oxidation of Fe and Mn from reduced groundwater by aeration. As-elimination is fairly efficient during Fe-precipitation whereas it is less efficient during Mn-precipitation (Baldauf 1995). This kind of As-elimination is common practice in many drinking water works using reduced groundwater as raw water. The same kind of As-elimination has been proposed and studied in field experiments for an underground As-elimination. In this case, reduced groundwater is pumped out, saturated with oxygen and re-infiltrated into the underground. Because of the oxygen, Fe and Mn are oxidized and generate oxide and hydroxide flocs onto which As(V) species are sorbed and, thus, immobilized (Rott and Friedle 2000). The process has been realized in large scale in West Bengal, India (de Goot et al. 2007).

Among the most recent investigations is the use of zerovalent iron particles for As sorption and removal (Manning et al. 2002). Results from basic investigations, application with
Mechanisms of arsenic removal from water

sand-filled cartridges and reactive barrier systems are reported (Su and Puls 2001, Smyth et al. 2001, EPA 2005, Leupin et al. 2005). The method has also been applied in large scale (Leupin et al. 2005).

4.6 ARSENIC ELIMINATION BY MEMBRANE PROCESSES

Membrane processes offer additional possibilities for As-removal. Elimination can be achieved by i) filtration of As-bearing particles, ii) exclusion because of size of hydrated ions, or iii) electric repulsion by the membrane (see references in EPA 2000).

Microfiltration and ultrafiltration do not allow any direct elimination because As-species are by far too small and can pass the membrane. With these processes, elimination is due to a physical sieving of As-bearing particles. Microfiltration per se cannot remove any As. However, it can well be combined with coagulation by means of ferric chloride or alum and can, therefore, be applied (EPA 2000).

Ultrafiltration can remove colloidal constituents and can therefore be applied if the raw water contains As or As-bearing species attached to such particles. Elimination can be enhanced using electrically charged UF membranes. Comparison of some neutral and negatively charged membranes yielded unsatisfactory elimination rates of up to 63%. The results were confirmed during pilot scale experiments with the most promising UF membranes (EPA 2000).

Nanofiltration, which usually shows a predominant removal of divalent species, can eliminate As(III) and As(V) species predominantly through size exclusion. Therefore, it presents a reliable method for As-elimination. As-removal rates in bench and pilot scale experiments amounted to 60 to >95%. Again the results were less satisfactory for As(III) which may pass the membrane as a non-charged species. Because of the small pore size, however, nanofiltration membranes are subject to fouling at high DOC levels. This may cause reducing conditions at the membrane which leads to a change in speciation from As(V) to As(III) and to a substantial drop of the elimination performance (EPA 2000).

Reverse osmosis has been shown to be another reliable method for As-elimination. Both, bench and pilot-scale experiments demonstrated As(V) elimination rates >95% and As(III) elimination rates of about 74%. A slight increase of performance was observed for high DOC raw waters (EPA 2000).

Electrodialysis is a membrane process which removes ionic species by rejection at the membrane with the same charge sign as the ion. Electrodialysis with reversal of the polarity of the electrodes (EDR) has been investigated for As removal and has been studied in pilot scale experiments. Because the separation effect is based on the presence of charged species, elimination of As(III) is generally poor. In pilot tests with a raw water predominantly containing As(III), the As-concentration was reduced from 188 to 136 µg L⁻¹ (only 30%). The efficiency was better and amounted to 73% with a mixed As(III)/As(V) composition (EPA 2000).

4.7 CONCLUSIONS

A variety of methods has been developed to remove As species from water including precipitation, sorption processes of different kind and membrane separations. According to their individual properties these methods have different areas of application:

- Precipitation processes can be applied for treatment of industrial wastewaters. Relatively high raw water As concentrations can considerably be decreased while solid products are generated. The limited chemical stability of the precipitates, however, requires a safe final deposition to avoid As to re-enter into the water cycle. Application to drinking water treatment seems to be excluded.
• Sorption processes are by far more selective and allow an As removal which is safe with respect to drinking water requirements. Dosage of ferric chloride leads to As removal that can be combined with classical coagulation/flocculation of organic matter. Novel sorbents based on oxides/hydroxides of different metals allow a very selective sorption of As species, usually in a one-time application. Recently developed hybrid sorbents show a similar efficiency but have the advantage that they can be regenerated and re-used. Exhausted sorbents and solids from treatment of spent regenerant solutions have to be carefully disposed on safe landfill deposits. Sorption onto iron oxides/hydroxides is also possible in the underground after aeration or addition of zerovalent iron. However, control of this kind of processes seems to be less safe than elimination in a reactor or filter column.

• Among membrane processes reverse osmosis and nanofiltration are applicable. However, their general disadvantage is that elimination is not selective and that a demineralization is achieved which is not needed in most of the cases. Other membrane processes do not allow a satisfactory direct elimination.

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CHAPTER 5
Granular iron hydroxide as an adsorbent for arsenic in water

Michael Streat & Klaus Hellgardt

5.1 INTRODUCTION

5.1.1 Arsenic and trace elements in the environment

Water is essential for sustaining human, animal and plant life. Drinking water contains many trace contaminants, both cationic and anionic. The sources of contamination of the aqueous environment can arise directly from geological sources, factory effluent and waste treatment plants or indirectly from the soil by agricultural or industrial runoff. There are several European Union standards for drinking water that cover thousands of pollutants, e.g. inorganic and organic materials (75/440/EC 1975, 80/778/EC 1980, 98/83/EC 1998). A list of some typical maximum permitted levels of contaminants is given in Table 5.1.

There are well known toxicological effects associated with several drinking water contaminants. For example, chlorination by-products can cause bladder and colon cancer (Cantor 1997). An elevated quantity of nitrate in potable water can cause a blood disorder commonly referred to as the “blue baby” syndrome (methaemoglobinaemia) (Sorg 1978a). Studies in Spain and the UK have also shown a link between high nitrate levels in water and stomach cancer (Barzilay et al. 1999). Teeth can become mottled above an optimum fluoride concentration, particularly amongst small children. Exposure to high levels of arsenic in drinking water results in hyper-pigmentation, gangrene and gastrointestinal cancer (Sorg 1978b). Selenium is an element essential to humans and animals; however chronic exposure results in dermatitis and problems with the central nervous system (Sorg 1978b).

Adsorption/ion exchange is a proven technology for the removal of trace contaminants from water. The most effective method of removing nitrate and chromate is by using a specific ion exchange resin (Ghurye et al. 1999, Clifford 1990). Fluoride can also be removed by ion exchange or by activated alumina (Sorg 1978a, Fleming 1986). Conventional iron or aluminum

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Maximum permitted value (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>200</td>
</tr>
<tr>
<td>Arsenic</td>
<td>10</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5</td>
</tr>
<tr>
<td>Chloride</td>
<td>250000</td>
</tr>
<tr>
<td>Chromium</td>
<td>50</td>
</tr>
<tr>
<td>Fluoride</td>
<td>1500</td>
</tr>
<tr>
<td>Iron</td>
<td>200</td>
</tr>
<tr>
<td>Lead</td>
<td>25</td>
</tr>
<tr>
<td>Mercury</td>
<td>1</td>
</tr>
<tr>
<td>Nitrate</td>
<td>50000</td>
</tr>
<tr>
<td>Phosphorus (as P₂O₅)</td>
<td>5000</td>
</tr>
<tr>
<td>Selenium</td>
<td>10</td>
</tr>
<tr>
<td>Sulfate</td>
<td>250000</td>
</tr>
</tbody>
</table>

Table 5.1. EU standards (98/83/EC 1998) for drinking water levels of selected inorganic contaminants.
sulfate (alum) precipitation can remove more than 90% As(V) at pH < 7 and lime softening removes all As(V) present at pH > 10.6. Arsenate can also be removed by either activated alumina or bone char (Sorg 1978b). Selenium is effectively removed (>90%) by reverse osmosis, ion exchange (Sorg 1978b) and activated alumina (Ghosh and Cox 1994). More recently, chitosan has been used to reduce the concentration of both cations and anions from solution. For example, copper, chromium (Schmuhl et al. 2001), platinum (Guibal et al. 1999) and vanadium (Guzman et al. 2002), have successfully been removed. Arsenate sorption has also been achieved with molybdate impregnated chitosan beads (Schwertmann and Cornell 1991).

Arsenic (As) removal from water can be accomplished using a variety of adsorbents, e.g. activated alumina (Bellack 1971), activated carbon (Gupta and Chen 1978), activated bauxite (Gupta and Chen 1978), granular ferric hydroxide (Driehaus et al. 1998, Streat et al. 2008), and several composite materials.

5.1.2 Preparation and properties of granular ferric hydroxide

Driehaus et al. 1998 have developed a granular form of hydrous ferric hydroxide that is similar in structure to akaganeite and that possesses a much greater affinity for As than activated alumina. Pierce and Moore 1982 found that amorphous ferric hydroxide possesses 5–10 times greater capacity for As than activated alumina. They have reported column studies that indicated an effluent concentration of 10 μg L⁻¹ reached after passing 30,000–40,000 BV of solution containing an influent As concentration of 21 μg L⁻¹. The use of granular ferric hydroxide in water treatment is distinctly advantageous since the process involves little maintenance or manpower and there is no pre-treatment required other than chlorination and prefiltration. The spent As-loaded ferric hydroxide can be sent to landfill or alternatively eluted with a strong base, e.g. sodium hydroxide, and reused if required.

Hydrous ferric oxide occurs naturally in mineral forms such as goethite, hematite and ferrihydrite. Akaganeite is found in marine, chloride-containing environments as a corrosion product of iron (Refait and Génin 1997).

Iron oxides are produced by the precipitation of ferric salts but the products vary in chemical structure, composition, and physical characteristics. Preparative techniques alter the surface area, morphology and color of the final product. A diagram illustrating the complexities of iron chemistry is given in Figure 5.1 and Table 5.2 lists the oxides with their respective formulae.

The basic structure of all iron oxides is octahedral with a central Fe ion surrounded by O or OH ions. The α-phase of a mineral is more stable than the γ-phase and has hexagonally close packed layers of O and OH ions; the latter type has cubic close-packed layers. The Fe octahedra can be linked by edge-sharing or corner-sharing which results in the many types of iron oxide. The FeOOH oxides all possess double band edge-sharing FeO₆(OH)₂ octahedra. Only half of the octahedral interstices are filled with Fe³⁺ (Schwertmann and Cornell 1991).

<table>
<thead>
<tr>
<th>Formula</th>
<th>Mineral</th>
<th>Morphology</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FeOOH</td>
<td>Goethite</td>
<td>Needles</td>
<td>Yellow</td>
</tr>
<tr>
<td>β-FeOOH</td>
<td>Akaganeite</td>
<td>Rods</td>
<td>Brown</td>
</tr>
<tr>
<td>γ-FeOOH</td>
<td>Lepidocrocite</td>
<td>Plates, fibrous</td>
<td>Orange</td>
</tr>
<tr>
<td>δ-FeOOH</td>
<td>Feroxyhyte</td>
<td>Non-crystalline</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe₃O₄·4H₂O</td>
<td>Ferrihydrite</td>
<td>Spherical</td>
<td>Red</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>Hematite</td>
<td>Cubic, ellipsoidal</td>
<td>Bright red</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>Maghemite</td>
<td>Acicular</td>
<td>Reddish brown</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Magnetite</td>
<td>Needles, octahedra</td>
<td>Black</td>
</tr>
</tbody>
</table>
Goethite forms tunnels through octahedra sharing vertices, akaganeite consists of double chains of multiple octahedra joined lengthwise by sharing corners to make channels, and lepidocrocite forms corrugated layers of distorted edge-sharing octahedra (Wells 1950, Parfitt 1978).

Akaganeite has been identified as the most effective As adsorbent and can be produced by the hydrolysis of ferric chloride or fluoride at 60–100°C for approximately 6 hours. The slow hydrolysis of ferric chloride always produces akaganeite (Weiser and Milligan 1935). It can also be precipitated from 0.5 M ferric chloride at 75°C by adding 3.5 M K₂CO₃ (Paterson and Rahman 1983). Ammonium carbonate has also been used as a precipitating agent (Deliyanni et al. 2001). The dry oxidation of Fe₅(OH)₆·FeCl₂ with an intermediate product of Fe₅(OH)₆·Cl transforms to akaganeite (Mackay 1960). Akaganeite can also be formed by the damp oxidation of FeCl₃·H₂O (Refait and Génin 1997).

Akaganeite is formed in ferric chloride solutions due to the interaction of chloride ions with the surface of the hydrous ion (Mackay 1960, Paterson and Rahman 1983, Mackay 1962). Murphy et al. 1976 have shown that there was little effect on the final product if chloride ions were added after a certain period of ageing. Anions were possibly acting as bridging
ligands, similar to olation and intermediate polynuclear chains were produced (Dousma et al. 1978).

In a freshly prepared akaganeite sample, chloride was present up to a ratio of 1:5 Cl:Fe (Weiser and Milligan 1935). The chloride trapped in the sample pores can be partially removed by prolonged washing with distilled water (Mackay 1960), ammonia (Weiser and Milligan 1935), displacing the chloride ions with either nitrate or fluoride ions (Ellis et al. 1976), and by dialysis (Deliyanni et al. 2001). However approximately 2% of the chloride remains (Ellis et al. 1976, Mackay 1960). Extensive washing with a base leads to transformation to goethite (Refait and Génin 1997, Paterson and Rahman 1984).

The presence of chloride therefore affects the stability of the compound. The chloride (or fluoride) ions are sufficiently small to diffuse into the elongated pores and stabilize the structure (Flynn 1984). Perchlorate, iodide and bromide were not able to displace the chloride, indicating that there is an ion exclusion due to the size restriction of the pores (Deliyanni et al. 2001, Paterson and Rahman 1984).

The beta form on prolonged ageing oxidizes to hematite (Dasgupta and Mackay 1959, Butler and Ison 1965). This transformation is an example of the Stranski rule, where the least stable form (i.e. akaganeite) will nucleate first, as interfacial requirements are more easily met (Matijevic and Scheiner 1978). At pH > 5, akaganeite is not formed, as OH− competes with chloride ions, hence hematite is formed even if chloride salts are used (Cai et al. 2001). Similarly, akaganeite oxidizes to hematite when suspended in water and heated (Butler and Ison 1965). Transformation to hematite occurs at around 200°C when heated in air, although this figure was lower with lower amounts of chloride present in the compound.

After the material has been aged to increase the particle size, the precipitate is washed and dried at room temperature to increase the solids content. The iron oxide material produced cannot be heated to reduce the moisture content, as akaganeite is transformed to hematite (Mackay 1960). Conventional freeze-drying results in a powdery material, unsuitable for a column application. However the material can be dewatered further using freeze/thaw technology. The degree to which it is dried before freezing alters the effectiveness of this process.

5.2 EXPERIMENTAL

Three samples of synthetic granular ferric hydroxide were prepared in the laboratory:

- Akaganeite prepared by partial neutralization of ferric chloride;
- Granular ferric hydroxide dewatered by freeze/thaw technique (designated NN);
- Granular ferric hydroxide dewatered at ambient temperature (designated VL).

These three samples were compared physically by scanning electron microscopy and X-ray diffraction. We also examined and compared a commercially available granular ferric hydroxide product (designated COM).

5.2.1 Akaganeite preparation

A pure sample of the mineral akaganeite was produced using the partial neutralization of ferric chloride, outlined by Schwertmann and Cornell (1991). 26.9 g FeCl₃ · 6H₂O was dissolved in 100 mL deionized water, i.e. a 1 molar solution was prepared. 75 mL 1 M NaOH was added to partially neutralize the solution. A temporary brown precipitate formed which redissolved on shaking to give a dark brown solution. The vessel was left for two days, after which 20 mL 10 M NaOH was added to the vessel and the mixture heated at 70°C in an oven for one week. The resulting precipitate was washed with deionized distilled water and filtered using a Buchner funnel. The filter cake was frozen at −20.5°C and then placed in a freeze-drier for 17 hours.
5.2.2 Sample NN preparation

The following experimental procedure was used for the production of ferric chloride. Dilute solutions of 0.1 M ferric chloride and 0.3 M sodium hydroxide were prepared with deionized distilled water according to stoichiometric quantities shown in the reactions below:

\[
3\text{NaOH} + \text{FeCl}_3 \rightleftharpoons \text{Fe(OH)}_3 + 3\text{NaCl} \\
\text{Fe(OH)}_3 \rightleftharpoons \text{FeOOH} + \text{H}_2\text{O}
\]

1 liter each of 0.1 M ferric chloride and 0.3 M sodium hydroxide were added simultaneously to a plastic beaker, using a double-headed positive displacement pump. The contents of the beaker were held at 40°C using a water bath. The flowrate of both the reagents was approximately 30 mL min\(^{-1}\). The pH of the reaction was maintained at 4.2 ± 0.1, by slight adjustment to the flow of sodium hydroxide.

Throughout the reaction the material was vigorously stirred and the temperature was maintained at 40°C. The contents of the beaker were stirred further for one hour to allow the reaction to reach equilibrium, i.e. there was no change noted in the pH. The vessel was removed from the water bath, covered and left for four days at room temperature (approximately 18°C). From previous experimental work this has been shown to be the optimum ageing time for the material. The final pH of the material was approximately 4 ± 0.05.

After the ageing period, the supernatant was removed and the remaining material was washed by decantation with 16 bed volumes of water. Decantation was carried out four times, i.e. four bed volumes of water were used each time to wash the sample. After washing, the sample was allowed to settle, the excess water removed by decantation and the precipitate immediately filtered using a Buchner funnel and a Whatman 3 filter. The filter cake was removed and left on a warm surface (approximately 25°C) until the solids content was in the range 25–30% (see Table 5.3).

5.2.3 Sample VL production

A separate iron oxide sample (VL) was prepared on a larger scale. 25 L 0.9 M NaOH was added at 150–270 mL min\(^{-1}\) to 25 L 0.3 M FeCl\(_3\) held in a glass reactor at 40–50°C by a steam heat exchanger. Continuous mixing of reagents was maintained by a stainless steel stirrer. The reaction was terminated when pH 5.5 was reached (after 1.5–3 h), but stirring continued for another hour. After 30 L of wash water was added, the settled volume of the precipitate was 19 L.

The slurry was initially dewatered by a ceramic cross-flow microfilter (0.14 μm cut-off), reducing the precipitate volume to 10–12 L. Subsequently, the material was left as a thick cake to air dry for 3–5 days on perforated sheets, rather than employing a freeze-thaw method. Moisture content of the final material (described previously) was 20%. Hence the total amount of material produced was over 3 kg. The resulting dry material formed large chunks, which were washed, crushed and sieved before being used for adsorption experiments.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent used</td>
<td>Hydrated ferric chloride</td>
</tr>
<tr>
<td>Flowrate of reagents</td>
<td>30 mL min(^{-1})</td>
</tr>
<tr>
<td>Washing method</td>
<td>Decantation</td>
</tr>
<tr>
<td>Solids content</td>
<td>25–30%</td>
</tr>
<tr>
<td>Freezing method</td>
<td>Controlled freezing at 1 K h(^{-1})</td>
</tr>
<tr>
<td>Thawing method</td>
<td>Left overnight in the fridge at 7°C</td>
</tr>
</tbody>
</table>
5.2.4 COM production

For the purposes of comparison, we have included a commercially available granular ferric hydroxide adsorbent. The exact production method for this material is unknown but a limited amount of information has been provided by the manufacturer. We know that sodium hydroxide and ferric chloride are contacted at 40°C and the resulting precipitate is washed, passed through a membrane then stored in plastic tubs. The tubs are conditioned in situ with a solids content as low as 15%, then left to naturally dewater, until the volume is reduced by 75%. The equilibrium pH of the product is stated to be 7.

5.3 RESULTS AND DISCUSSION

5.3.1 Scanning electron micrographs

Akaganeite was produced using the partial neutralization of ferric chloride, as described by Schwertmann and Cornell (1991). The product appears to be granular with an average particle size of 500–650 µm (see Fig. 5.2). The crystal structure is also longer and thinner, unlike the other samples, which are more spherical. There appear to be impurities on the surface, which could be sodium chloride, a by-product of the reaction procedure. The surface is smooth, with no aggregate material.

Sample NN was produced in our laboratory using a freeze/thaw methodology. An SEM (Fig. 5.3) shows a robust structure without aggregated material. There is some fine material on the surface. There is no visual evidence of any pore structure at the resolution used.

Similar images were obtained for sample VL and commercially available COM that showed little if any variation from the images above.

Figure 5.2. SEM images of synthetic akaganeite, (a) magnification × 50, (b) magnification × 2000.

Figure 5.3. SEM images of sample NN, (a) magnification × 135, (b) magnification × 2000.
5.3.2 X-ray diffraction studies

The X-ray powder diffraction pattern (XRD) for sample NN (Fig. 5.4) shows that it is amorphous, i.e. that there is no evidence of strong distinct peaks, which would be expected from a more crystalline material. Conversely both the commercial sample COM and the other laboratory produced sample, VL, exhibit a higher degree of crystallinity, comparable to that of synthetic akaganeite. Both the latter samples are not pure, as there is a peak associated with hematite (33°), VL showing a stronger intensity implying a greater quantity of the impurity is present.

Cai et al. 2001 found that reaction pH affected the crystallinity of the final iron oxide product. Nucleation and growth occurred most rapidly at pH < 1.5 (Fig. 5.5). At low pH the peaks are narrow and distinct, at higher pH there are two wide peaks for the diffraction pattern at

![Figure 5.4. XRD data for all samples compared to synthetic akaganeite.](image1)

![Figure 5.5. XRD patterns of granular ferric hydroxide prepared at different pH values (Cai et al. 2001; A = akaganeite; G = goethite; H = hematite).](image2)
pH 4 (the production pH for sample NN), similar to Figure 5.5. At pH > 6, the iron oxide produced was a mixture of goethite (G) or hematite (H).

Therefore, the reaction pH does affect the final nature of the iron oxide material. Sample VL was not prepared at a constant pH, but NaOH was added to ferric chloride until the pH was 5.5. Hence akaganeite may have formed initially whilst the pH < 5, after which hematite began to form, as hydroxide is more competitive for structural sites than chloride (Driehaus et al. 1998). Chloride (or fluoride) is essential for the formation of akaganeite as it brings stability to the tunnel structure (Matijevic and Scheiner 1978).

The time of ageing the precipitate can also be a contributing factor to increased crystallinity. The longer a material is left the more crystalline it becomes. Further details regarding the time of ageing or reaction pH are not supplied for sample COM, but the XRD outputs are very similar. It may be assumed that these variables are comparable to those used for VL.

Ellis et al. 1976 state that the quantity of chloride present in the final product affects the XRD output, a lower chloride content causes peak broadening. Sample VL possesses the highest quantity of chloride, followed by COM and NN chloride content is significantly lower than the former samples. Chloride content of the samples would be affected by the degree of washing. This trend is reflected in the degree of crystallinity.

A final factor that could affect the nature of the product formed is the temperature of reaction. However all samples were prepared at 40°C, therefore it is not a contributing parameter.

5.3.3 Specific surface area and pore size distribution

The BET surface area and average pore size values of two samples prepared in our laboratory (NN and VL) were measured by nitrogen adsorption and compared with values obtained for the commercial product COM. The derived data are given in Table 5.4. All the granular ferric hydroxide samples have a specific surface area in the range 200–300 m² g⁻¹ and the measured average pore size implies that these materials are predominantly mesoporous.

All three samples show Type IV adsorption isotherms with a hysteresis loop in the adsorption isotherm. This characteristic of mesoporous substances indicates capillary condensation due to the bottleneck effect between micro and mesopores. The shape of the hysteresis loop differs for each sample. The adsorption isotherm for sample NN does not have a well-defined loop (Fig. 5.6a), indicating a small amount of mesoporosity and the presence of slit-shaped pores (Petro et al. 1987). COM and sample VL on the other hand have distinct desorption loops and therefore show greater mesoporosity. The desorption branch closure is not very steep which indicates that the diameters of the pores are not particularly uniform (Brinker and Scherer 1990).

The initial steep gradient to the ‘knee’ of the isotherm reveals that there are some micropores present in all iron oxide samples. The shape of isotherm in Figure 5.6b indicates that COM has the largest proportion of micropores, sample NN has a comparable number of micropores (Fig. 5.6a) whereas sample VL possesses a smaller proportion (Fig 5.6c). This trend is mirrored in the order of specific surface area given in Table 5.4.

The proportion of micropores may be related to the precision of pH control during preparation. The pH of sample NN, and we believe COM, were kept constant throughout the reaction procedure, whereas sample VL was prepared by the addition of NaOH to ferric chloride.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Average pore size BET (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN</td>
<td>240</td>
<td>40</td>
</tr>
<tr>
<td>COM</td>
<td>310</td>
<td>29</td>
</tr>
<tr>
<td>VL</td>
<td>204</td>
<td>53</td>
</tr>
</tbody>
</table>
Granular iron hydroxide as an adsorbent for arsenic in water

67

until the pH > 5.5. This lack of pH control could be the reason for the production of a more heterogeneous material with fewer micropores.

The pore size distributions of samples COM and VL are similar in shape and magnitude in the low pore size range (see Fig. 5.7). Sample NN appears to have fewer mesopores which correlates with the slight hysteresis seen in Figure 5.8a. This agrees with the shape of the adsorption isotherm, i.e. a rapid increase in nitrogen adsorption at very high relative pressures (Figs. 5.6a–c). It is expected that an amorphous material (NN) has a high degree of macroporosity, moreover the presence of larger pores in sample VL is probably due to poor pH control.

5.3.4 Batch adsorption

Samples of COM, NN and VL were studied in the pH range 4–9. Two 5 L volumetric flasks of 100 µg L⁻¹ As(V) were prepared by dissolving Na₂HAsO₄ ⋅ 7H₂O (sodium arsenate), in

Figure 5.6. Nitrogen adsorption isotherm of (a) sample NN, (b) sample COM, and (c) sample VL.
18 MΩ deionized distilled water. The first flask was used to prepare all of the NN samples in the range pH 4–9, i.e. six samples in all and COM in the range pH 4–7. The second flask was used to prepare the remaining COM samples, i.e. at pH 8 and 9 and VL across the pH range 4–9.

In each case, 490 mL of solution were decanted into 500 mL Nalgene® bottles and adjusted to the desired pH value by the addition of a known volume of 0.1 M HCl or NaOH prior to the addition of 5 mg of adsorbent. The adsorbent was weighed on a Sartorius BP210D balance, accuracy ±0.0005 g. The particle size of the material used was 150–300 µm.

The sample bottles were agitated at 25 ± 1°C in an orbital shaker and the pH maintained at its initial value by addition of acid or alkali twice a day. Any addition to the solution volume was noted and was <0.5% of the total batch volume. It was assumed that the solutions had reached equilibrium when there was no change in the pH. The As loading of the material was calculated as:

\[
q = \frac{C_0 V_0 - C_{eq} V_{eq}}{m}
\]  

(5.1)

where:  
- \( q \) = adsorption loading (mmol g⁻¹)  
- \( C_0 \) = initial concentration (mmol L⁻¹)  
- \( V_0 \) = initial volume of solution (L)  
- \( C_{eq} \) = equilibrium concentration (mmol L⁻¹)  
- \( V_{eq} \) = equilibrium volume (L)  
- \( m \) = mass of dry adsorbent (g)

Isotherms for all three samples were carried out in the pH range 4–9. This method was repeated for As(V) concentrations 200, 400, 500, 750, 1000 and 2000 µg L⁻¹. A summary of the conditions is given in Table 5.5.

5.3.5 Mini-column experiments

5.3.5.1 Initial experiments

Approximately 0.2 g NN sample (150–300 µm) were weighed on a Sartorius BP210D balance, accuracy ±0.0005 g and transferred into a 1 mL nominal capacity empty solid phase extraction (SPE) column containing a 20 µm polyethylene frit (Thames Restek, Windsor). A PTFE valve was attached to the bottom of the column and deionized water added. A vacuum was
Figure 5.8. Arsenic uptake capacity in pH range 4–9: (a) Sample NN, (b) sample COM, and (c) sample VL.

Table 5.5. Summary of final experimental conditions.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Sample value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (µm)</td>
<td>150–300</td>
</tr>
<tr>
<td>pH range</td>
<td>4–9</td>
</tr>
<tr>
<td>Concentration range (µM)</td>
<td>0–30</td>
</tr>
<tr>
<td>Volume (mL)</td>
<td>490</td>
</tr>
<tr>
<td>Mass of adsorbent (mg)</td>
<td>5</td>
</tr>
<tr>
<td>Reagents used to control pH</td>
<td>0.1M NaOH, HCl</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25 ± 1</td>
</tr>
</tbody>
</table>
applied to remove any air trapped in the adsorbent pores and any air bubbles in the bed were also removed. Another frit was added to the column after pre-treatment to promote an even flow distribution. The diameter of the column was 5.6 mm and the wetted bed height of adsorbent was 8 mm (bed volume was 0.2 cm³).

A column adapter was attached to the top of the column to allow PTFE tubing to be fitted into the column. The column was fed at a flow-rate of 3.8 mL h⁻¹ at room temperature with 500 µg L⁻¹ As(V) solution at pH 4 via a Watson-Marlow MHRE 22 multi-head peristaltic pump. This As concentration value was chosen as As levels of this order are found in aquatic environments. An empty 6 mL SPE cartridge was used as an additional reservoir of feed.

Prior to the column being attached, the feed solution was fed through the tubing to remove any impurities from the rig. The effluent was fed to a sample collector, controlled by a Mitsubishi Fxo 14 PLC containing borosilicate glass test tubes. The samples were collected every fifty minutes and the effluent was analyzed for arsenate, using a SpectraAA 200 graphite furnace GTA 100 attached to a Perkin Elmer atomic absorption spectrophotometer. The pH of each sample was measured on a Mettler Toledo 340 pH probe calibrated at pH 4 and 10. A similar experimental method was used for a column containing COM sample.

No evidence of As breakthrough was observed after 35–40,000 bed volumes of 500 µg L⁻¹ As(V) solution had been passed through the two columns. Hence, a new set of experiments to test all three iron oxide samples was completed with a 0.133 mmol L⁻¹ initial concentration at a neutral pH. Although such a high level of As concentration is unlikely to be found in aquatic environments, it was necessary to increase the concentration to enable experiments to be carried out within a week. The flow rate was also increased slightly to 4.7 mL h⁻¹ for sufficient sample to be collected for analysis.

For all subsequent column experiments, the same conditions were used (see Table 5.6).

5.3.5.2 Regeneration

An experimental procedure was developed to regenerate the loaded iron oxide samples. At the end of each experiment, 500 BV (100 mL) deionized distilled water was fed to the rig, to remove any remaining impurities. Thereafter, 0.1 M NaOH was fed at 4.7 mL h⁻¹ for 8 hours, samples were collected every 30 minutes.

5.4 RESULTS AND DISCUSSION

The uptake loading was determined in batch mode in the pH range 4–9 up to a maximum solution concentration of approximately 28 ± 4 µmol L⁻¹. The data were fitted to Langmuir and Freundlich isotherms. The monolayer values calculated from the Langmuir model were

<p>| Table 5.6. Mini-column operating parameters. |</p>
<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (µm)</td>
<td>150–300</td>
</tr>
<tr>
<td>Mass of adsorbent (mg)</td>
<td>200</td>
</tr>
<tr>
<td>Column diameter (cm)</td>
<td>0.56</td>
</tr>
<tr>
<td>Bed height (cm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Bed volume (cm³)</td>
<td>0.2</td>
</tr>
<tr>
<td>Flowrate (mL h⁻¹)</td>
<td>4.7</td>
</tr>
<tr>
<td>Bed volume/h</td>
<td>24</td>
</tr>
<tr>
<td>Superficial liquid velocity (m s⁻¹)</td>
<td>6.63 × 10⁻⁵</td>
</tr>
<tr>
<td>Empty bed contact time (min)</td>
<td>2.52</td>
</tr>
<tr>
<td>Time per sample tube (min)</td>
<td>50</td>
</tr>
<tr>
<td>pH range</td>
<td>7.6–7.8</td>
</tr>
<tr>
<td>Concentration (µmol L⁻¹)</td>
<td>133.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>22 ± 2</td>
</tr>
</tbody>
</table>
compared to those determined experimentally. The effect of pH and ferric oxide structure on the uptake loading was studied in order to elucidate possible adsorption mechanisms. In column mode, the material was challenged with a 133.5 µmol L⁻¹ As solution to determine the capacity and breakthrough curve characteristics.

5.4.1 Arsenic adsorption isotherms

Arsenic adsorption isotherms in the pH range 4–9 are shown in Figure 5.8. Correlation is not straightforward since a cursory examination of the data by eye suggests the possibility of two domains. Data points could be described by two straight lines of different slope that intersect at a solution concentration of about 0.002–0.003 mmol L⁻¹ (see for example Fig. 5.8a). This may be attributed to As speciation and the complex binding mechanisms at adsorption sites. Nevertheless, we have attempted to correlate the data using the Langmuir (eq. 5.2) and Freundlich (eq. 5.3) models and the derived correlation coefficients are given for each granular ferric hydroxide in Tables 5.7 and 5.8. The theoretical values of monolayer coverage calculated by the Langmuir model can be compared to the equilibrium value, experimentally determined at three pH values, namely 4, 7 and 9 (see Table 5.7).

\[
\text{Langmuir model: } q = \frac{a b c}{1 + b c} \quad (5.2)
\]

\[
\text{Freundlich model: } q = k c^n \quad (5.3)
\]

Experimental points are fitted to the Langmuir curves in Figure 5.8. The Langmuir model underpredicts the monolayer coverage value, a, for all materials across the pH range. At low pH, the values in Tables 5.7 and 5.9 are comparable. The difference between the experimental value and predicted value increases with increasing pH.

Table 5.7. Parameters for the Langmuir model \(a\) (mmol g⁻¹) and \(b\) (L mmol⁻¹) and correlation coefficients \(R^2\) for all samples for arsenate adsorption.

<table>
<thead>
<tr>
<th>pH</th>
<th>NN</th>
<th>COM</th>
<th>VL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>R²</td>
</tr>
<tr>
<td>4</td>
<td>1.21</td>
<td>180</td>
<td>0.986</td>
</tr>
<tr>
<td>5</td>
<td>0.908</td>
<td>174</td>
<td>0.987</td>
</tr>
<tr>
<td>6</td>
<td>0.641</td>
<td>223</td>
<td>0.975</td>
</tr>
<tr>
<td>7</td>
<td>0.626</td>
<td>138</td>
<td>0.992</td>
</tr>
<tr>
<td>8</td>
<td>0.584</td>
<td>102</td>
<td>0.997</td>
</tr>
<tr>
<td>9</td>
<td>0.578</td>
<td>81</td>
<td>0.987</td>
</tr>
</tbody>
</table>

Table 5.8. Parameters for the Freundlich model, \(k\) (mmol g⁻¹) (L mmol⁻¹)\(^{1/n}\) and \(n\), and correlation coefficients \(R^2\) for all samples, for arsenate adsorption.

<table>
<thead>
<tr>
<th>pH</th>
<th>NN</th>
<th>COM</th>
<th>VL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k</td>
<td>n</td>
<td>R²</td>
</tr>
<tr>
<td>4</td>
<td>10.71</td>
<td>1.74</td>
<td>0.964</td>
</tr>
<tr>
<td>5</td>
<td>8.63</td>
<td>1.69</td>
<td>0.959</td>
</tr>
<tr>
<td>6</td>
<td>5.08</td>
<td>1.88</td>
<td>0.972</td>
</tr>
<tr>
<td>7</td>
<td>5.69</td>
<td>1.65</td>
<td>0.974</td>
</tr>
<tr>
<td>8</td>
<td>4.91</td>
<td>1.6</td>
<td>0.979</td>
</tr>
<tr>
<td>9</td>
<td>4.56</td>
<td>1.56</td>
<td>0.956</td>
</tr>
</tbody>
</table>
The changes in the type of As complex binding with the surface are dependent on surface loading (number of available sites) and pH. The Langmuir model does not take into account the degree of crystallinity, the change in speciation or changes in the surface charge and can therefore only provide a limited fit of the data.

The surface of iron oxide is either positively or negatively charged, depending upon the pH of the system. It is interesting to note that Lin and Wu 2001 found that the Freundlich and Langmuir models fitted the isotherm data for amphoteric activated alumina, although the latter gave a better fit.

5.4.1.1 Effect of pH
It was found that As uptake decreases as the pH increases (see Fig. 5.8). Driehaus et al. (1998) also found that arsenate adsorption decreased with increasing pH for granular ferric hydroxide. Similar results were also found for two-line ferrihydrite (Raven et al. 1998) and goethite (Hingston et al. 1971).

Under most pH conditions, arsenate is present as a negative species. The isoelectric point (IEP) for the adsorbents is near neutral, in the pH range 7–8. The surface is, therefore, positively charged at pH 4 and will attract anions. For protonated anions such as arsenate, ligand exchange may be accompanied by a deprotonation at the surface, resulting in bidentate inner-sphere bonding (two bonds with the iron oxide surface; see equations 5.1 and 5.2) (Stumm and Morgan 1981). Figure 5.9 illustrates both monodentate and bidentate bonding using arsenate complexes.

\[
\text{FeOH} + \text{H}_2\text{AsO}_4^- (aq) \rightleftharpoons \text{FeH}_2\text{AsO}_4^- + \text{OH}^-(aq) \quad (5.4)
\]

\[
\text{FeH}_2\text{AsO}_4^- (aq) \rightleftharpoons \text{FeHAsO}_4^{2-} + \text{H}^+ (aq) \quad (5.5)
\]

As the pH increases, the degree of positive surface charge decreases, lowering the attractive forces towards anionic species. Neutral adsorption occurs through proton dissociation from an acid surface. Adsorbed species obtain a proton from solution to equilibrate with the surface.

<table>
<thead>
<tr>
<th>pH</th>
<th>q (mmol g(^{-1}))</th>
<th>NN</th>
<th>COM</th>
<th>VL</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.3</td>
<td>1.17</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.89</td>
<td>0.77</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.77</td>
<td>0.7</td>
<td>0.64</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.9. Maximum loading values for arsenate.

Figure 5.9. Arsenate surface complexes (Davis et al. 1978).
solution. At pH > IEP there is some As adsorption despite the mutual repulsion between the negative surface and anionic species. Hence, the energy gained by the surface in forming new bonds with the anion must be greater than the repulsive forces, for any adsorption to occur. In addition, the speciation of arsenate changes from \( \text{H}_2\text{AsO}_4^- \) to \( \text{HAsO}_4^{2-} \), increasing the negative charge of the species. Removal at higher pH by specific adsorption is possible, if the undissociated acid donates a proton to the surface hydroxyl group to form water that can be displaced by the anion (Westall 1980):

\[
\equiv\text{FeOH} + \text{HAsO}_4^{2-} (\text{aq}) \rightleftharpoons \equiv\text{FeHAsO}_4^{2-} + \text{OH} (\text{aq}) \quad (5.6)
\]

\[
\equiv\text{FeHAsO}_4^{2-} + \text{H}_2\text{O} \quad (5.7)
\]

A cationic counter-ion, e.g., \( \text{Na}^+ \) would be attracted to the surface at pH > IEP and balance the negative charge due to \( \equiv\text{FeHAsO}_4^{2-} \). Lower capacity compared to site availability is due to the bidentate surface formation and electrostatic repulsion.

5.4.1.2 Effect of material

Sample NN has the highest removal capacity for As (\( \sim 1 \text{ mmol g}^{-1} \)) whereas COM and VL give a value of approximately 0.9 mmol g\(^{-1}\). Specific surface area does not appear to affect the uptake capacity, since sample NN possesses a specific surface area greater than VL, but smaller than COM. The degree of crystallinity however, appears to have some bearing on the isotherm results.

Waychunas et al. 1995 determined that bidentate ligands were the primary species on akaganeite with very little monodentate bonding. Higher quantities of monodentate coverage were evident on amorphous material, such as ferrihydrite, but less common in more crystalline polymorphs, i.e. goethite and akaganeite (Waychunas et al. 1993). Hence a higher capacity would be expected in materials that are more amorphous. Some authors maintain, however, that crystal structure has no effect on adsorption capacity (Davis et al. 1978, Pierce and Moore 1982).

5.4.2 Mini-column experiments

5.4.2.1 Sorption studies

The uptake of arsenate ions and the pH profile of samples NN, COM and VL are shown in Figure 5.10. The performance of sample NN is given in Figure 5.10a. Breakthrough of arsenate ions occurs at about 500 BV solution passed and there is a shallow rising curve. This is probably due to the relatively high feed flow-rate (19 BV h\(^{-1}\)). The corresponding pH profile is unusual since the pH value rises slightly from about 6–7.5 in the range 0–500 BV solution passed and then drops sharply to about 6.6 to coincide with breakthrough of arsenate ions. This sharp drop in pH could indicate a change in the type of bonding mechanism. At near neutral conditions, there is an equal amount of \( \text{HAsO}_4^{2-} \) and \( \text{H}_2\text{AsO}_4^- \). The presence of \( \text{HAsO}_4^{2-} \) increases the likelihood of bidentate bonding with the iron oxide surface. The pH profile reflects the arsenate breakthrough curve above 500 BV and slowly attains the pH value of the feed solution, i.e., pH 7.6–7.8.

The arsenate breakthrough curves for samples COM and VL are shown in Figures 5.10b and 5.10c. Breakthrough also occurs at about 500 BV but there is evidence of a slight increase in the observed breakthrough capacity of these two adsorbents compared to NN. The pH profiles for COM and VL are more typical—the initial pH of the effluent falls to about pH 4 and remains steady until breakthrough of arsenate occurs. Thereafter, the pH rises steadily to reflect the shape of the arsenate breakthrough curve and attains a plateau value corresponding to the feed pH, i.e. 7.6–7.8.

One possible difference between the samples is the equilibrium pH of each material in water and its chloride capacity. With increasing chloride content the equilibrium pH drops. Paterson and Rahman 1983 also found the pH of the wash-water for akaganeite was acidic, approximately pH 3. The chloride present in the pores and on the surface slowly leaches into
the solution as hydrochloric acid. The difference in pH could account for the slightly higher breakthrough values of samples COM and VL over NN, as a lower pH would increase the positive charge on the iron oxide surface and the attractive forces would increase. This effect would not be so pronounced in batch mode, as the pH was adjusted regularly to compensate for any HCl released for the surface.

5.4.2.2 Regeneration of mini-columns
The regeneration efficiency of the column runs was determined using 0.1 M NaOH. Prior to elution, the columns were washed with 500 BV (100 mL) of deionized distilled water. The regenerant was fed to the columns via a Watson-Marlow pump and the same flowrate was used as in the adsorption runs, i.e. 4.7 mL h⁻¹. The time required for each elution sample test tube was set to 30 minutes in order to collect sufficient sample for analysis.

An indication of elution efficiency for each adsorbent is given in Table 5.10. The elution efficiency was determined by dividing the arsenate ions eluted by the amount of arsenate

Figure 5.10. Breakthrough curves, concentration 0.133 mmol L⁻¹ As and pH profiles; initial pH = 7.7: (a) Sample NN, (b) sample COM, and (c) sample VL.
adsorbed in a column run using mass balance equations. The 0.1 M NaOH elution efficiency was 95–97% for each adsorbent. The elution curves are presented in Figure 5.11.

These results indicate that the granular ferric hydroxide adsorbents studied in this work can be regenerated and may be reused if desired. Only one cycle of anion loading was attempted for each sample, hence the effect of recycling on uptake capacity has not been quantified. An alternative procedure is to use granular ferric hydroxide on a once-through cycle, after which the adsorbent is sent to landfill as is current practice with activated alumina (Clifford 1990). The brine used to elute As(V) is precipitated with Fe(III) salts, the resulting sludge dried to reduce the volume. The standard EP test revealed an As(V) leachate of 1.5 mg L$^{-1}$, which is acceptable ($<$5 mg L$^{-1}$).

All iron oxide samples were tested across the pH range 4–9 to determine whether Fe$^{3+}$ ions were leached into solution. 50 mL of deionized distilled water were transferred using a 50 mL pipette into three 100 mL Erlenmeyer flasks and the pH adjusted to 4, 7 and 9, respectively by the addition of 0.1 M NaOH or HNO$_3$. The pH was measured on a Mettler Toledo 340 pH probe, calibrated at pH 4 and 10. 50 mg of sample NN was weighed on a Sartorius BP210D balance, accuracy $\pm$0.0005 g and transferred to each flask. The particle size of the material used was 150–300 $\mu$m. The flasks were sealed with Parafilm and left in an orbital shaker at 22 $\pm$ 2°C for two weeks. This procedure was repeated for samples COM and VL, i.e. 9 samples in total. Thereafter, the supernatant solution from each flask was tested for the presence of Fe$^{3+}$ ions using a Dionex 4500i ion chromatograph with gradient pump and conductivity detector.

Neither sample NN nor COM released any Fe$^{3+}$ and sample VL only slightly dissolved [0.04 mg L$^{-1}$ Fe(III) was detected]. The threshold limit value of Fe$^{3+}$ in drinking water is 0.3 mg L$^{-1}$ (75/440/EEC 1975). This is a distinct advantage over activated alumina that dissolves liberating about 3% aluminum on regeneration (Ghosh and Yuan 1987).
5.5 CONCLUSIONS

SEM images show that all the materials discussed in this work are robust and granular, not aggregated. A commercially available sample of granular ferric hydroxide of undisclosed structure, COM and the laboratory prepared samples, NN and VL, have a more powdery surface than the synthetic akaganeite. The latter appears to show some surface material, probably NaCl, formed as a by-product of the reaction. Nucleation and growth of akaganeite occurs most rapidly at pH 1.5. As the pH of the reaction solution increases, the peaks indicated by XRD analysis become broader, indicating a decrease in crystallinity. There is a similarity between the COM, sample VL and the pure sample of akaganeite. The XRD output signals for COM and VL are stronger with more distinct peaks, implying a higher degree of crystallinity. The peaks do not exactly match up, indicating that there are probably two phases present in the sample. The quantity of chloride in the final product also affects the width of XRD peaks. Sample VL contains the most chloride and has the strongest intensity and most distinct peaks, COM has intermediate crystallinity and chloride content and sample NN possesses the lowest chloride content and has a broad XRD peak, indicating that it is amorphous. The presence of other phases, particularly in the sample VL may be due to the change in pH throughout the reaction procedure. The pH was not controlled, but approached a value of 5.5. It is likely that akaganeite was formed initially and at pH > 5 hematite formation began since hydroxide ions compete more effectively with chloride ions for surface sites.

BET surface area analysis shows that all samples have a well developed specific surface area in the range 200–300 m² g⁻¹ and are predominantly mesoporous. The difference in porosity is probably due to the lack of pH control during sample VL preparation resulting in a wider pore size distribution.

There is little evidence to show that the freeze/thaw method of dewatering is advantageous for As adsorption based solely on adsorption performance. For practical purposes, a satisfactory material is synthesized by the ambient temperature route.

Adsorption of arsenate ions from water has been studied in both batch and mini-column experiments. Uptake capacities have been determined for all three iron oxide materials studied. Adsorption increased with decreasing pH, in the range 4–9. The highest uptake capacity occurred at pH 4, where the granular ferric hydroxide surface possesses the greatest positive charge.

Langmuir and Freundlich isotherms were fitted to the adsorption data. The Langmuir model gave a slightly better fit despite its limitations that are discussed in detail. Empirical models, such as Langmuir and Freundlich, do not take into account the nature of the complexation at the iron oxide surface nor allow for the effect of the electric double layer. It is postulated that there are different binding mechanisms for arsenate that are affected by surface loading and pH. At low loading, the proportion of monodentate bonds increases as there is less competition for surface sites. As the concentration increases, bidentate bonds are preferred as they are more stable and release the most electrostatic energy. This might explain why there are two domains to the isotherm depending on concentration, marked by a transition from monodentate to bidentate bonding. Furthermore, bidentate binding is preferred at low pH, whereas monodentate complexes become more evident as pH increases. The formation of bidentate complexes at the surface reduces the number of available sites, hence the capacity for arsenate is lower.

The degree of crystallinity appears to have an affect on the uptake capacity. Sample NN had a higher uptake capacity than samples COM and VL. This is probably due to the nature of the sites available on more crystalline material that favors bidentate bonding.

Limitations of the experimental mini-column runs restricted the influent concentration and mass of sorbent used and this resulted in non-optimum operating conditions. The flow-rate was necessarily high to enable sufficient sample to be collected. The pH profile of sample NN was different to the other two samples and this effect was attributed to a difference in
the amount of chloride present in each sample. Both samples COM and VL possessed a much higher quantity of chloride, which reduced the solution pH due to slow release of HCl. Arsenate removal from solution was achieved by all three samples of granular ferric hydroxide and the breakthrough volumes were similar suggesting that there is no real advantage in adopting the more tedious freeze/thaw preparation routine. Sample VL prepared at ambient temperature, dewatered and dried at room temperature gave equally satisfactory arsenate removal results.

Elution of each column experiment was carried out by the addition of 0.1 M sodium hydroxide. All three adsorbents were successfully eluted at an efficiency of 95–97%. The elution stage was not optimized and the adsorbent was not further challenged to determine uptake capacity after regeneration. There was no evidence that iron was significantly leached in the pH range 4–9. Sample VL liberated 0.04 mg L$^{-1}$ at pH 9, well below the EC drinking water standard. This presents a distinct advantage over activated alumina.

REFERENCES


CHAPTER 6

Arsenic removal from water using magnetites

Kaoru Ohe, Tatsuya Oshima & Yoshinari Baba

6.1 INTRODUCTION

Arsenic (As) is well known to be a toxic element (WHO 2003) and has also been classified as one of the carcinogenic chemical elements by the International Agency for Research on Cancer (IRAC) (Tchounwou et al. 2004). Exposure of the human body to arsenic through drinking water has been reported from many countries (Bhattacharya et al. 2007) such as Argentina (Bundschuh et al. 2004), Bangladesh (Watanabe 2001), China, India (Roychowdhury et al. 2005), Nepal, Vietnam (Berg et al. 2001), and Japan (Kondo et al. 1999), where large areas of groundwater are contaminated by As with concentrations ranging from 0.1 to over 2 mg L⁻¹ (Mandal and Suzuki 2002, Smedley and Kinniburgh 2002). These concentrations are higher than 0.01 mg L⁻¹, a standard recommended by the World Health Organization (WHO) (WHO 2006). Long-term consumption of drinking water contaminated with As causes, among other diseases, cancers of the skin, lung, liver, kidney and bladder (Liao et al. 2009). Thus, the As contamination in groundwater is considered a serious problem.

In nature, As exists in the −3, 0, +3 and +5 oxidation states (Baes and Mesmer 1976), mainly in the form of arsenite, arsenate, methylarsenic acid, and dimethylarsinic acid. Inorganic forms of As usually predominate over organic forms in water supplies. Two forms are common in natural waters: arsenite and arsenate, referred to as As(III) and As(V), respectively. The chemical species of arsenite in water are AsO⁻₃³⁻, HAsO⁻₂²⁻ and H₂AsO⁻₃, while the chemical species of arsenate are AsO⁺₅⁵⁻, HAsO⁺₄²⁻ and H₂AsO⁺₅. Various technologies have been used for As removal from water, such as coagulation (Hering et al. 1997), ion exchange (Wasay et al. 1996), adsorption and reverse osmosis (Nig 2002). Although coagulation methods are simple, they produce a large amount of wet sludge and thus their efficiency is questionable. Adsorption is another simple method and this has been focused on as an efficient and cost effective alternative.

Many papers have demonstrated that iron oxides have a high affinity for As(III) and As(V) (Sigg and Stumm 1981, Hiemsta and Van Rijmsdijk 1999, Guo and Chen 2005, Disit et al. 2003). Magnetite (Fe³⁺Fe⁷⁻O₄) is an iron oxide comprising Fe(II) and Fe(III), with a molar ratio of 1:2, and is well known for having magnetic properties and thus can be separated using magnets. Magnetite is also well known as a functional material in various fields, such as adsorption, catalysis, semiconductors, medical science, etc. Ohe et al. (2005) reported that magnetite effectively adsorbs not only As(V) but also As(III). It is anticipated that both the surface charge of magnetite, i.e. the point of zero charge, and surface area are very important for the effective removal of As because the adsorption of As(III) and As(V) onto magnetite depends upon the pH, and a high surface area increases the number of adsorption sites. On the basis of these facts, we have conducted fundamental studies on the adsorption of As on a number of magnetites prepared under various conditions and some of these studies are reviewed in this chapter.

6.2 SURFACE HYDROXYL GROUP AND SURFACE CHARGE

Metal ions on metal oxide surfaces are not fully coordinated. When a metal oxide is exposed to water, these vacant coordination sites are occupied by water molecules through
chemisorption (Dzombak and Morel 1990). Surface hydroxyl groups are formed by the dissociation of the water molecules.

Most metal oxides exhibit amphoteric behavior in water. The hydroxyl groups on oxide surfaces can bind and release protons and this reaction generates a charge on oxide surfaces. The amphoteric surface reactions can be described as

\[
\text{MOH}^0 + \text{H}^+ \Leftrightarrow \text{MOH}^+_1
\]

\[
\text{MOH}^0 \Leftrightarrow \text{MO}^- + \text{H}^+
\]

where MOH\(^0\), MOH\(^+_1\) and MO\(^-\) represent neutral, positively charged and negatively charged surface sites, respectively. As shown in equations 6.1 and 6.2, the addition of acid to an oxide suspension causes an excess of protons at the surface (positive charge) and the addition of base causes a proton dissociation (negative charge).

### 6.3 ADSORPTION OF As(III) AND As(V) ON MAGNETITE

Generally, there are two types of magnetite preparation methods: a dry method and a wet method. In the case of the dry method, mixed powdered materials were calcined and ground. This method has a high productivity but the particles have diverse forms and the particle sizes are neither uniform nor homogenous. On the other hand, the magnetite prepared in solution by the wet method is uniform and homogenous, hence it is superior to the magnetite prepared by the dry method. Therefore, we prepared magnetite by the precipitation process using the wet method (Ohe et al. 2005).

The magnetite was prepared by dropping an aqueous sodium hydroxide solution into an aqueous solution comprised of a mixture of FeCl\(_2\) and FeCl\(_3\) in a molar ratio of 1:2 at room temperature. The aqueous sodium hydroxide solution was added until the pH was maintained as high as 12. The black colored particles obtained were found to be magnetically active and were identified using X-ray diffraction analysis to be crystalline magnetite with an inverse spinel structure. The pH\(_{\text{pzc}}\) of the magnetite was found to be 6.0 (Table 6.1), which was consistent with that of the magnetite prepared by Sun et al. (1998). The specific surface area of the magnetite, calculated using the Brunauer-Emmett-Teller (BET) method by N\(_2\) gas adsorption at 77 K, was found to be 90 m\(^2\) g\(^{-1}\). As the surface of the magnetite is amphoteric, the surface is positively charged at pH < 6.0 and negatively charged at pH > 6.0.

Figure 6.1 shows the distribution ratio D versus equilibrium pH for the adsorption of As(III) on magnetite. The distribution ratio of the chemical species of As(III) is shown in Figure 6.2. The distribution ratio was obtained using the H\(_3\)AsO\(_4\) dissociation constants, pK\(_{a1}\) = 9.2, pK\(_{a2}\) = 12.1 and pK\(_{a3}\) = 13.4 (Meng et al. 2000). As seen from these figures, the decrease in the distribution ratio of the chemical species of As(III) at pH values greater than 6.0 is attributable to the formation of anionic species. As mentioned above, the surface on the magnetite is negatively charged at pH > 6.0. The decrease of the distribution ratio is also attributable to the surface charge. The distribution ratio of the chemical species of As(III) showed high performance at pH values less than 6.0 where the chemical species of As(III) is mainly a neutral molecule, H\(_3\)AsO\(_4\).

Figure 6.3 shows a plot of the distribution ratio D versus equilibrium pH for As(V) adsorption on magnetite. The distribution ratio of As(V) chemical species obtained using the

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Specific surface area (m(^2) g(^{-1}))</th>
<th>pH(_{\text{pzc}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_3)O(_4)</td>
<td>90</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Table 6.1. Specific surface area and pH\(_{\text{pzc}}\) of the synthetic magnetite (Ohe et al. 2005).
Figure 6.1. Logarithm of distribution ratio $D$ versus equilibrium $p$H for the adsorption of As(III) on magnetite (Ohe et al. 2005).

Figure 6.2. Chemical species of As(III) as a function of $p$H obtained using dissociation constants of $H_3AsO_3$ (modified from Meng et al. 2000).

Figure 6.3. Logarithm of distribution ratio versus equilibrium $p$H in the adsorption of As(V) on magnetite (Ohe et al. 2005).
$H_2\text{AsO}_4$ dissociation constants, $pK_{a1} = 2.2$, $pK_{a2} = 6.8$ and $pK_{a3} = 11.6$ (Meng et al. 2000) is shown in Figure 6.4. The distribution ratio of As(V) showed an optimum value in the range of pH 4–5. As seen in Figure 6.3, the adsorption behavior of As(V) is different from that of As(III). The difference is attributable to the different chemical properties of the individual species of As(III) and As(V). The chemical species of As(V) existing in the aqueous solution is mainly $H_2\text{AsO}_4^-$ in the range pH 4–5 as illustrated in Figure 6.4. The experimental results indicated that below pH 6, As(V) was adsorbed through the electrostatic force between the positively charged surface of the magnetite and $H_2\text{AsO}_4^-$. Above pH 6 the distribution ratio sharply decreased. As(III) was adsorbed on the magnetite at higher pH, around pH 8, whereas As(V) was poorly adsorbed at the same pH. The decrease of As(V) adsorption at higher pH is due to the electrostatic repulsion between As(V), existing as anions, and the negatively charged magnetite surface. At pH $< 4$, the decrease of As(V) may be attributable to the dissolution of magnetite in acidic solution. As(V) is hardly adsorbed at around pH 11, while As(III) shows a higher distribution ratio than As(V). This result suggested that As(III) can be selectively separated from a mixture of As(III) and As(V) in the alkaline range. Figure 6.5 illustrates the selective separation of As(III) from a mixture of As(III) and As(V) at an initial pH of 10.5. As seen from Figure 6.5, only As(III) was selectively adsorbed on the magnetite from a mixture of As(III) and As(V).

![Figure 6.4](image1.png)

**Figure 6.4.** Chemical species of As(V) as a function of pH obtained using dissociation constants of $H_2\text{AsO}_4$ (modified from Meng et al. 2000).

![Figure 6.5](image2.png)

**Figure 6.5.** Selectivity of As(III) adsorption on magnetite from a mixture of As(III) and As(V) (Ohe et al. 2005).
solution containing both As(III) and As(V) in a molar ratio of 1:1. The adsorption of As(III) was higher than that of As(V) when the molar ratio of As(III)/As(V) equaled 5:1 and 10:1. The adsorption of As(V) was higher than that of As(III) from the mixture when the molar ratio of As(III)/As(V) equaled 25:1. These results suggested that the selective separation of As(III) from a mixture of As(III) and As(V) can be performed only when the molar ratio of As(III)/As(V) equals 1:1.

The adsorption capacities and the equilibrium constant were determined by plotting the adsorption isotherms for As(III) and As(V) on magnetite as depicted in Figures 6.6a and 6.6b, respectively. These values and the correlation coefficients are presented in Table 6.2. As seen from these results, the adsorption capacity for As(III) is higher than that of As(V). Different researchers reported that the adsorption of As(V) on ferric oxides, such as goethite and amorphous iron oxide, is greater than that of As(III) (Meng et al. 2000, Dixit and Herin 2003). From these results, it is expected that the magnetite is an effective As(III) adsorbent.

Reuse of the magnetite requires the desorption of As, which was done using aqueous sodium hydroxide solutions of 0.01 to 5 mol L\(^{-1}\) as an eluent because As was not adsorbed on the magnetite in the region of higher pH, as suggested by Figures 6.1 and 6.3. It was found that As(V) was quantitatively desorbed from As(V)-loaded magnetite using aqueous sodium hydroxide solution with a concentration of 0.1 mol L\(^{-1}\). As(III) was also quantitatively desorbed from As(III)-loaded magnetites using an aqueous sodium hydroxide solution of 1 mol L\(^{-1}\). Consequently, the aqueous sodium hydroxide solution was found to be a suitable eluent for the desorption of both As(III) and As(V).

### 6.4 ADSORPTION OF As(III) AND As(V) BY MF\(_2\)O\(_4\) (M = Co, Ni, Zn AND Mg)

Considering that MF\(_2\)O\(_4\) has similar chemical properties to magnetite, we prepared a series of adsorbents using a co-precipitation method (Ohe et al. 2007b). M(NO\(_3\))\(_2\) (M = Co, Ni, Zn

![Figure 6.6. Adsorption isotherm of (a) As(III) and (b) As(V) by magnetite (at 303 K) (Ohe et al. 2005).](image)

<table>
<thead>
<tr>
<th>As(III)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent</td>
<td>(Q_{\text{max}}) (mmol g(^{-1}))</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 6.2. Langmuir isotherm fitting parameters of the magnetite (Ohe et al. 2005).
and Mg) and Fe(NO$_3$)$_3$ were mixed at the molar ratio of 1:2. NiFe$_2$O$_4$ and ZnFe$_2$O$_4$ (Ni-F and Zn-F) were prepared and calcined at 773 K. MgFe$_2$O$_4$ (Mg-F) was prepared using the method reported by Chen et al. (1999). Mg-F500, 800 and 1000 were prepared by calcinations at 773, 1023 and 1273 K, respectively. The composition ratio (M/Fe), specific surface area and pH$_{pzc}$ for these materials are shown in Table 6.3.

These pH$_{pzc}$ of MFe$_2$O$_4$ were found to be similar to those of the magnetite except for Mg-F. The specific surface area of Mg-F adsorbents decreased with increasing calcination temperature.

The effect of pH on the adsorption of As(III) by Co-F, Ni-F, Zn-F, Mg-F500, 800 and 1000 is shown in Figure 6.7a. It was observed that the percentage of As(III) adsorbed depended upon the equilibrium pH. Over 70% of the As(III) was adsorbed in the region of pH 4–10, except by Mg-F800 and 1000. The adsorption of As(III) by Ni-F and Zn-F was inferior to that on magnetite at pH 7. The adsorption of As(III) by Co-F was superior to that on magnetite in the region of high pH. Mg-F800 and 1000 showed low adsorption due to the lower specific surface area of these materials. Figure 6.7b shows a plot of the adsorption percentage of As(V) against equilibrium pH on the MFe$_2$O$_4$ adsorbents. The adsorption of As(V) rapidly decreased with increasing pH. The adsorption behavior on Ni-F and Zn-F was also similar to that on the magnetite. Co-F mostly adsorbed As(V) at pH 8, whereas the adsorption of As(V) gradually decreased at pH > 8. As seen in Table 6.3, the pH$_{pzc}$ of Co-F was 7.1, which was higher than that obtained for magnetite (Ohe et al. 2005). Mg-F500 mostly

Table 6.3. Molar ratio of M/Fe, pH$_{pzc}$ and specific surface areas of adsorbents (Ohe et al. 2007b).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>M/Fe$^1$</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>pH$_{pzc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-F</td>
<td>0.51</td>
<td>131</td>
<td>7.1</td>
</tr>
<tr>
<td>Ni-F</td>
<td>0.52</td>
<td>–</td>
<td>6.6</td>
</tr>
<tr>
<td>Zn-F</td>
<td>0.44</td>
<td>–</td>
<td>6.5</td>
</tr>
<tr>
<td>Mg-F500 (773 K)$^2$</td>
<td>0.50</td>
<td>107</td>
<td>10.0</td>
</tr>
<tr>
<td>Mg-F800 (1073 K)$^2$</td>
<td>0.42</td>
<td>26</td>
<td>9.4</td>
</tr>
<tr>
<td>Mg-F1000 (1273 K)$^2$</td>
<td>0.50</td>
<td>&lt;4</td>
<td>6.8</td>
</tr>
</tbody>
</table>

$^1$M/Fe means a molar ratio of metal ion to total Fe.

$^2$Calcinations thermodynamic temperature.

Figure 6.7. Adsorption percentage of (a) As(III) and (b) As(V) versus equilibrium pH with Co-F, Ni-F, Zn-F, Mg-F500, 800 and 1000 (Ohe et al. 2007b).
adsorbed As(V) at pH 10, however the magnetite hardly adsorbed As(V) at the same pH. The difference of adsorption behavior of As(V) with Mg-F500 and the magnetite was attributed to the difference in their pH_pzc. Most of the equilibrium pH values during the adsorption test using Mg-F500 and Mg-F800 were found to be around pH 10. This was attributed to a solubility of Mg from Mg-F500 and Mg-F800. Around 5–12 wt% of Mg in these Mg-F compounds dissolved in solution. In contrary, this result also suggests that magnesium hydroxide exists in Mg-F500 and Mg-F800. It was also learnt that Mg-F1000 was not entirely soluble. The level of Mg is not limited in the WHO guidelines (WHO 2006) since Mg is not considered a toxic element. However increased exposure to magnesium causes some diseases, such as diarrhea and urethral calculus. Therefore Mg-F may not to be recommended for use as an As adsorbent in groundwater.

Metal ions in MFe_2O_4 containing Co(II), Ni(II) and Zn(II) were not found to be soluble at a pH higher than 6.5, 6.2 and 5.9, respectively. According to the WHO guidelines (WHO 2006) concentrations of Ni in drinking water should not exceed 0.07 mg L^{-1}. The level of Zn is not limited by the WHO guidelines (WHO 2006). The guidelines show that the concentration of Zn is problematic when it exceeds 3 mg L^{-1}. The concentration of Zn in tap water can increase due to the dissolution of Zn included in water pipes. In the case of Co, no data on the limits in drinking water was available. Therefore, there should be no problems in using MFe_2O_4 as As adsorbents at pH > 6.5.

The adsorption capacities and the equilibrium constants of As(III) and As(V) on Co-F, Mg-F500 and Mg-F800 are listed in Table 6.4. It was found that the adsorption capacities of As(III) and As(V) with Co-F were 0.85 and 0.52 mmol g^{-1}, respectively. The adsorption capacities of Co-F for As(III) and As(V) were approximately 2–3 times higher than those of magnetite. The adsorption equilibrium constant of Co-F for As(III) was also higher than that of magnetite.

Mg-F500, 800 and 1000 prepared by different calcination temperatures had different specific surface areas as shown in Table 6.3. The adsorption isotherms of As(III) onto Mg-F500, 800 and 1000 were fitted to the Langmuir model, except for Mg-F1000 which hardly adsorbed As(III). The order of their adsorption corresponds to the specific surface area. The decrease in As adsorption is also related to the decrease in the number of hydroxyl groups on the adsorbent surface due to dehydration and condensation that occurred at high temperature.

6.5 ADSORPTION OF AS(III) AND AS(V) ON MAGNETITE CONTAINING Ce(III) AND Zr(IV)

Zirconium oxide and cerium oxide have been investigated for the removal of As (Imai et al. 1987, Suzuki et al. 2000). It is expected that Ce(III) or Zr(IV) introduced into the magnetites will enhance the affinity toward As(III) and As(V). Zhang et al. (2003) reported good As(V) removal using an adsorbent prepared with Ce(IV) and Fe(III). Ohe et al. (2009b) prepared the adsorbents as magnetites containing Ce(III) and Zr(IV) (CeMAG and ZrMAG) with the molar ratio of Fe(II):Fe(III):Ce(III)/(Zr(IV)) = 1:2:0.2. The specific surface areas of

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>As(III)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q_{max} (mmol g^{-1})</td>
<td>K_{ad} (L mmol^{-1})</td>
</tr>
<tr>
<td>Co-F</td>
<td>0.85</td>
<td>7.24</td>
</tr>
<tr>
<td>Mg-F500</td>
<td>0.48</td>
<td>7.22</td>
</tr>
<tr>
<td>Mg-F800</td>
<td>0.13</td>
<td>1.51</td>
</tr>
</tbody>
</table>
ZrMAG and CeMAG, were higher than those of the magnetite (Table 6.5). The pH\text{pzc} values of ZrMAG and CeMAG as shown in Table 6.5 were higher than that of the magnetite (6.0) (Ohe et al. 2005), ZrO\textsubscript{2} (6.7) (Parks 1965) and CeO\textsubscript{2} (hydrous) (6.75) (Parks 1965). These results indicated that ZrMAG and CeMAG are not a physical mixture of ZrO\textsubscript{2} or CeO\textsubscript{2} and magnetite. The surface of these adsorbents is positively charged at pH < 7.0.

The adsorption behavior for As(V) is shown in Figure 6.8a. The adsorption of As(V) on CeMAG was similar to that on ZrMAG, which is in turn similar to the adsorption by the magnetite. The distribution ratio of As(V) at pH 7–8 was higher than that of magnetite. According to Table 6.5, the surface of the adsorbents is positively charged at pH < 7.0. As(V) exists as H\textsubscript{3}AsO\textsubscript{4}\textsuperscript{−} at pH < 7.0, which is favorable for adsorption of As(V) through an electrostatic interaction. The adsorption of As(V) decreased with increasing pH. Since the surface of the adsorbents is negatively charged at pH > 7.0, electrostatic repulsion occurred between adsorbent and As(V). In contrast, the amount of As(III) adsorbed on ZrMAG and CeMAG is almost constant in the pH range 4–9 as shown in Figure 6.8b, though the adsorption of As(III) using the magnetite decreased at pH > 7. The difference in the optimum pH for As(III) is due to difference of the surface states of ZrMAG and CeMAG when compared to the magnetite.

6.6 ADSORPTION OF AS(III) AND AS(V) BY Ti(IV)-INTRODUCED MAGNETITE

It is expected that titanium(IV)-introduced magnetites probably also have some enhanced properties, such as surface area, point of zero charge of the surface, etc., relative to standard magnetite. These magnetites containing Ti(IV) were prepared with FeCl\textsubscript{2}, FeCl\textsubscript{3} and TiCl\textsubscript{4} using different molar ratios such as 1:2:0.5 (TiMAG0.5), 1:2:1 (TiMAG1) and 1:2:3

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>M/Fe\textsuperscript{1}</th>
<th>Specific surface area (m\textsuperscript{2} g\textsuperscript{−1})</th>
<th>pH\text{pzc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeMAG</td>
<td>0.06</td>
<td>122</td>
<td>7.0</td>
</tr>
<tr>
<td>ZrMAG</td>
<td>0.05</td>
<td>113</td>
<td>7.0</td>
</tr>
</tbody>
</table>

\textsuperscript{1}M/Fe means a molar ratio of metal ion to total Fe.

Figure 6.8. Logarithm of the distribution ratio of (a) As(V), (b) As(III) versus equilibrium pH for CeMAG and ZrMAG (Ohe et al. 2009b).
(TiMAG3), respectively, at pH 11 (Ohe et al. 2008). Their pH$_{pzc}$ and specific surface areas are shown in Table 6.6. Generally, the amorphous iron oxide has a high surface area and a large number of surface active sites. The surface area and active sites decrease greatly with increasing crystallinity (Pena et al. 2005). TiMAG1 had a very high specific surface area. Figure 6.9a shows the effect of pH on the adsorption of As(III). The adsorption of As(III) by TiMAG1 was similar to that of magnetite. This result was also similar to that of TiMAG0.5 and TiMAG3. As(III) was adsorbed when the equilibrium pH was between 3 and 8. The adsorption percentage of As(III) decreased at pH values greater than 8, where the first proton of arsenious acid begins to be dissociated. Since As(III) predominantly exists as a neutral molecule in the range pH 3–8, it appears that the adsorption percentage of As(III) decreased as the amount of H$_3$AsO$_4$ decreased. Therefore, H$_3$AsO$_3$ is considered to be the adsorbed species. The relationship between adsorption percentage of As(V) and pH is shown in Figure 6.9b. The pH dependence of As(V) adsorption by TiMAG1 was similar to that of MAG0.5 and TiMAG3. The optimum pH for the adsorption of As(V) on all Ti-introduced adsorbents was in the region of pH 3–6, and the adsorption percentage of As(V) sharply decreased beyond this pH range. From Figure 6.9b, the percentage of As(V) adsorbed decreased when the pH was greater than 6, where the second proton of arsenious acid begins to be dissociated. Since As(V) is predominantly present as a monoanion at pH 3–6, H$_3$AsO$_4$ is considered to be the adsorbed species. As seen from the surface charge state shown in section 6.2, the surface of the adsorbents is positively charged at pH values below the pH$_{pzc}$. As(V) was expected to be adsorbed on the adsorbents through an electrostatic force. At pH > 7, the predominant species is HAsO$_4^{2-}$ and the surface of the adsorbents is negatively charged. The decrease in adsorption is due to the electrostatic repulsion between

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>M/Fe</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>pH$_{pzc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiMAG 0.5</td>
<td>0.16</td>
<td>180</td>
<td>7.8</td>
</tr>
<tr>
<td>TiMAG1</td>
<td>0.31</td>
<td>237</td>
<td>5.8</td>
</tr>
<tr>
<td>TiMAG3</td>
<td>0.91</td>
<td>80</td>
<td>4.6</td>
</tr>
</tbody>
</table>

$^{1}$M/Fe means a molar ratio of metal ion to total Fe.

Figure 6.9. Logarithm of the distribution ratio of (a) As(III), (b) As(V) against equilibrium pH in the adsorption on TiMAG0.5, 1 and 3. (Ohe et al. 2008).
the As(V) anions and the negatively charged surface of the adsorbent. It is a great advantage that TiMAG0.5 and TiMAG1 could be operated at about pH 7, which is the natural pH of many groundwaters. The adsorption isotherms for As(III) and As(V) were correlated with the Langmuir isotherm model in order to determine the adsorption capacity ($Q_{\text{max}}$) and the adsorption equilibrium constant ($K$) for each adsorbent. These corresponding fitting parameters and the correlation coefficients are presented in Table 6.7. The maximum adsorption capacities of As(III) and As(V) with TiMAG1 were greater than those of TiMAG0.5 and TiMAG3. Figure 6.10 shows the correlation of adsorption capacities and specific surface area. TiMAG1 is considered to have a large number of adsorption activity sites because TiMAG1 has very high specific surface area. TiMAG1 exhibited a higher affinity for As(III) and As(V) than nano-TiO$_2$ (Pena et al. 2005, Jing et al. 2005) and magnetite (Ohe et al. 2005). Titanium oxide-magnetite also showed a good As adsorption capacity. The selectivity of As(III) (Fig. 6.11a) and As(V) (Fig. 6.11b) from a mixture containing nitrate, sulfate, phosphate and silicate anions, which exist in natural water, was investigated using TiMAG1. In each adsorption test nitrate and sulfate were not adsorbed on TiMAG1 at all. The adsorption behavior of As(V) was found to be very similar to that of phosphate and the adsorption of both species decreased with increasing pH. Contrarily the adsorption of silicate increased with increasing pH. The sequence of the selectivity series for the anions tested at pH 8 is silicate $>>$ As(V) $>$ phosphate. On the other hand, the adsorption of As(III) at pH $> 7$ was greater than that of phosphate. Silicate was adsorbed less than As(III) in the pH range 4–11. The sequence of the selectivity series for the anions tested at pH 8 is As(III) $>$ silicate $>>$ phosphate. It can be expected that the most toxic As species, As(III), is effectively and selectively removed from groundwater containing phosphate using TiMAG1.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$Q_{\text{max}}$ (mmol g$^{-1}$)</th>
<th>$K_{\text{ad}}$ (L mmol$^{-1}$)</th>
<th>$R^2$</th>
<th>$Q_{\text{max}}$ (mmol g$^{-1}$)</th>
<th>$K_{\text{ad}}$ (L mmol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiMAG 0.5</td>
<td>0.86</td>
<td>5.98</td>
<td>0.99</td>
<td>0.80</td>
<td>60.7</td>
<td>1.00</td>
</tr>
<tr>
<td>TiMAG1</td>
<td>1.20</td>
<td>11.4</td>
<td>0.99</td>
<td>0.85</td>
<td>6.54</td>
<td>0.99</td>
</tr>
<tr>
<td>TiMAG3</td>
<td>0.39</td>
<td>1.74</td>
<td>0.98</td>
<td>0.27</td>
<td>2.68</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Figure 6.10. Adsorption capacities of As(III) and As(V) versus specific surface area of TiMAG (Ohe et al. 2008).
6.7 ADSORPTION OF As(III) AND As(V) BY HIGH SURFACE AREA Fe₃O₄ (MEBWx)

Magnetites effectively adsorb As(III) and As(V). Wakui and co-workers reported the extraction of As(V) using ultrafine magnetite (Wakui et al. 2002) and the adsorption of As(V) using a novel composite adsorbent that consists of magnetite and a porous acrylate copolymer (Wakui et al. 2005). The maximum capacity for As(V) was 0.05 mmol g⁻¹. As(III) and As(V) were adsorbed using spherical porous silica covered with magnetite (Ohe et al. 2007a). The adsorption of As(III) and As(V) was tested using magnetite nanoparticles by Mayo et al. (2007). They reported that the magnetite nanoparticle size affects the adsorption of As(III) and As(V). The high surface area greatly enhanced the adsorption capacity for As(III) and As(V). Ohe et al. (2009a) prepared high surface area Fe₃O₄ (MEBW0, 60 and 120) using an alcohol/water mixture as the solvent and amine as the alkaline solution. The adsorbent was prepared using Fe(II), Fe(III), ethylenediamine, water and 1-butanol in a molar ratio of 1.05:2.7:(120-x):x (x = 0, 30, 60, 90, 120). The reaction was carried out at 333 K. The resulting precipitate was separated using a magnet and then dried using a freeze drier after washing with 50 wt% aqueous ethanol solution. The adsorbents were named as MEBWx. Their characteristics are shown in Table 6.8. The specific surface areas of MEBW0, 60, and 120 were 96.8, 173, and 245 m² g⁻¹, respectively. The specific surface area of MEBW0 prepared in water (without 1-butanol) was the same as that of magnetite. The specific surface areas increased with increasing ratio of 1-butanol to water. These results indicated that the specific surface area is dependent on the molar ratio of 1-butanol to water and not on the difference of the alkaline reagents used.

The adsorption of As(III) and As(V) versus the equilibrium pH for MEBW120 was the same as that as magnetite. The adsorption isotherm experiments for As(III) and As(V) were

![Figure 6.11. Adsorption percentage of anions from a mixture containing (a) As(III) and (b) As(V) versus equilibrium pH by TiMAG 1 (Ohe et al. 2008).](image)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>pHₚzc</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEBW0</td>
<td>96.8</td>
<td>6.5</td>
</tr>
<tr>
<td>MEBW60</td>
<td>173</td>
<td>6.8</td>
</tr>
<tr>
<td>MEBW120</td>
<td>245</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Table 6.8. Specific surface area and pHₚzc of adsorbents (Ohe et al. 2009a).
carried out at 303 K by varying the initial concentrations of As(III) and As(V), respectively. The adsorption capacity and the adsorption equilibrium constant are shown in Table 6.9. The adsorption capacities of As(III) and As(V) with mebW120 are 0.962 and 0.557 mmol g\(^{-1}\), respectively. These results are superior to the adsorption capacities of the magnetites with lower surface areas. Figure 6.12 shows the plots of the adsorption capacity of magnetites for As(III) and As(V) against their specific surface areas. These results showed the linear relationship between adsorption capacity and specific surface area. In other words, increasing the specific surface area increases the adsorption capacities. The magnetite prepared in 1-butanol has been successfully applied to the removal of As(III) and As(V) from water.

### Table 6.9. Langmuir isotherm fitting parameters as adsorption capacity \((Q_{\text{max}})\), adsorption equilibrium constant \((K_{\text{ad}})\) and correlation coefficient \((R^2)\) of adsorbents (Ohe et al. 2009a).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>As(III)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_{\text{max}}) (mmol g(^{-1}))</td>
<td>(K_{\text{ad}}) (L mmol(^{-1}))</td>
</tr>
<tr>
<td>MEBW0</td>
<td>0.56</td>
<td>10.1</td>
</tr>
<tr>
<td>MWBW60</td>
<td>0.78</td>
<td>12.0</td>
</tr>
<tr>
<td>MEBW120</td>
<td>0.96</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>37.9</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>28.9</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Figure 6.12. Adsorption capacities of As(III) and As(V) versus specific surface area of MEBWx (Ohe et al. 2009a).

### 6.8 CONCLUSIONS

Magnetite, one of the iron oxides, is an environmentally friendly material. As described in this chapter, magnetites can be used for the removal of not only As(V) but also of As(III). Magnetite can be prepared with a high surface area and optimum pH\(_{\text{pzc}}\) by introducing metal ions into the materials. The adsorption of As(III) and As(V) was investigated using these magnetites. ZrMAG and CeMAG could be operated without pH control. Calcining the magnetites at high temperature caused a decrease in their specific surface area which was accompanied by a decrease in the adsorption of As(III) and As(V). The magnetites prepared in a mixed 1-butanol/alcohol solution had a high surface area. The adsorption capacity for As(III) and As(V) also increased with increasing surface area of the magnetites. The adsorption capacities for As(III) and As(V) showed a linear correlation with specific surface area.
It is expected to be feasible to develop magnetites with high surface areas which will have an enhanced adsorption capacity for As(III) and As(V) from contaminated natural water.

REFERENCES


CHAPTER 7

Study of the long term stability of ferric iron—arsenic precipitates

Nadejda Dimitrova & Valentin Nenov

7.1 INTRODUCTION

Arsenic (As) is one of the most toxic metals occurring in natural ecosystems. The major cause of human As toxicity is from contamination of drinking water from natural geological sources (Ratnaike 2003). Natural contamination of groundwater by As has become a threatening problem in many parts of the world, especially in areas where groundwater is the only or major drinking water source. However, groundwater contamination is often caused by agricultural activities, where As is used for the production of insecticides and herbicides. Areas, which are close to mining activities or smelters, have also been found to contain elevated As concentrations. Arsenic is mainly present in waters in its inorganic forms. Inorganic As occurs with two main oxidation states in natural waters, such as As(V) and As(III). Arsenates are the predominant species in oxygenated water, whereas arsenite species predominate under anoxic or reduced conditions (Fields et al. 2000). As(III) is more toxic and more difficult to be removed by the conventionally applied physicochemical treatment methods (Jekel 1994) than As(V) (Pontius et al. 1994).

The principal methods used for As removal from contaminated water are coagulation/direct filtration, ion exchange, adsorption on iron oxides or on activated alumina, iron-oxide coated sand and reverse osmosis (Kartinen and Martin 1995, EPA 2000). These methods usually require a preliminary oxidation step, for the transformation of As(III) to As(V), in order to achieve efficient arsenite removal (Jekel 1994, Viraraghavan et al. 1999). As(III) oxidation is usually performed by the addition of chemical reagents, such as, potassium permanganate, hydrogen peroxide or ozone (Jekel 1994, Molnar et al. 1994, Kim and Nriagu 2000).

During the last 10–15 years, apart from the conventional treatment methods, a biological method for removing As has been developed (Katsoyiannis and Zouboulis 2002). This method is based on the presence of certain species of indigenous bacteria in groundwater, which are capable of oxidizing and removing iron and manganese. Specifically, by this method As(III) can be efficiently treated, without any additional use of chemicals required for As oxidation.

However, precipitation has been the dominating technique for As removal for a number of years (Patterson 1985). The wide use of this technique can be explained on the basis of its technological and design simplicity and its applicability to wide ranges of As concentrations. It was proved that precipitation based on use of Ca(OH)₂ for As precipitation, is not acceptable as the residual concentration is several times greater than the permitted level (Robins 1985). In addition, their studies of As-containing sediments show that the compound Ca₂(AsO₄)₂ is unstable for long term deposition because the chemical reaction with CO₂ leads to formation of CaCO₃ with simultaneous release of As.

Coagulation of As(V) by Fe(III) salts has been found to be promising in removing As from water. In the late 1980s it was shown that the effect of the Fe/As ratio on As precipitation can stimulate a re-evaluation of the effect of ferric salts on As removal. Krause et al. (1987) have shown that at molar ratio Fe/As = 4, the solubility of the precipitated sediment is 100–1000 times lower than the stoichiometric FeAsO₄. Similar results were obtained by Kontopoulos et al. (1988) who showed that the optimal conditions are at a molar ratio, Fe/As = 4 and pH 3–5. Maosui (1989) reported excellent precipitation results at Fe/As = 100 and pH = 7.
By our studies in the early 1990s we tried to define optimal values of pH and Fe(III)/As(V) molar ratio for maximum inclusion of As in the solid phase and to resolve discrepancies in the literature on the optimal conditions of As(V) precipitation. In addition, we have set out to assess the stability of the residual sediments as a function of Fe/As molar ratio, pH and initial concentration of As. Our experiments, carried out over a wide pH range (pH 2–8) and range of molar ratio Fe (III)/As(V) = 4–10 showed that the lowest residual As and iron concentrations result when the molar ratio Fe(III)/As(V) is 7, and pH = 5 at an initial As concentration of 3775 mg L\(^{-1}\).

The results of solubility tests on sediments at initial As concentration of 3775 mg L\(^{-1}\) have shown that at Fe(III)/As(V) ≥ 6 and pH of precipitation of 5, the amount of As removed in the solubility tests are below the limit of detection (Nenov et al. 1992).

In order to determine the optimum conditions for As(III) removal, different concentrations of Fe\(_{2}(SO_{4})_{3}\) were added. Depending on the pH of the solution, this salt hydrolysis to several Fe(III) hydroxy-complexes and colloidal Fe(III) hydroxide. Three different molar ratios Fe(III)/As(III) were tested. On the basis of the observed data, it was found that pH 9 is the optimum for As(III) removal for all examined molar ratios. It was also found that an increase of molar ratio Fe(III)/As(III) from 7 to 9 (at the optimum pH) results in slight improvement of As removal [0.42 mg L\(^{-1}\) was the lowest encountered As(III) concentration], while the remaining Fe(III) in the supernatant solution after filtration was found to be lower than 0.2 mg L\(^{-1}\).

For this reason, it was decided to carry out some additional experiments by changing the molar ratio of Fe(III)/As(III) up to 14, but at constant pH 9. It was found that the residual As(III) concentrations were practically unaffected, remaining around 0.13 mg L\(^{-1}\), while the residual Fe(III) started to increase, by increasing the molar ratio above 11.

When the leaching test of EPA was applied, the examination of the pH influence and the different molar ratio Fe(III)/As(III) on the resolubilization of As(III) and Fe(III) from the filtered solids showed clearly that the precipitates obtained at pH 9 and molar ratio equal to 11 possess very low solubility. The residual concentrations of As(III) and Fe(III) were 0.045 mg L\(^{-1}\) and 0.78 mg L\(^{-1}\), respectively (Nenov et al. 1994).

The experiments with wastewater from the copper industry show that both species, As(III) and As(V) can exist in wastewater, i.e. the removal of As from waters representing a mixture of these species is of interest for the practice. Batch experiments were carried out at initial As concentration of 3775 mg L\(^{-1}\) As(total), as the ratio As(III)/As(V) was 1:1. The experiments were carried out at three different molar ratios, Fe(III)/As(total) = 7, 9 and 11 and pH of precipitation was 5, 7 and 9. The solubility of the obtained precipitates was studied by the modified leaching test of EPA of Ham (Ham et al. 1979). The results obtained show that the crucial factor concerning the effectiveness of As precipitation is pH and the lowest residual As was encountered at pH 9 and molar ratio Fe(III)/As(total) of 11 (Nenov et al. 1998).

According to our view, the mechanism of As(V) removal is based on the fact that at pH = 5 (the optimal pH of precipitation), the predominant form is H\(_{3}\)AsO\(_{4}\)\(^{−}\) (see Fig. 7.4). During the simultaneous precipitation of As(V) and Fe\(_{2}(SO_{4})_{3}\) by NaOH an environment for ionic sorption process is created, i.e., condition for an electrostatic bond, resulting in formation of stable chemical compounds of As(V), Fe(III), and SO\(_{4}\)\(^{2−}\).

Concerning As(III) precipitation, we suppose that within the pH range of 2–8 a molecular adsorption and coprecipitation are the predominant mechanisms of As uptake because for this pH interval As(III) exists mostly in its non-dissociated form (H\(_{3}\)AsO\(_{4}\)). At pH higher than 9 a considerable part of As(III) is in H\(_{2}\)AsO\(_{4}\)\(^{−}\) (Kartinen et al. 1995) which creates conditions for partial ionic sorption of As(III). Namely, pH = 9 is the optimal value of pH for As(III) precipitation by ferric sulfate. The fact that As(III) precipitates are more unstable compared to As(V) rests on the hypothesis of the above mechanism. In addition, it is well known that physical mixtures (in our case result of molecular sorption and coprecipitation) are unstable in conditions of dissolution. According to our view the reason for the shift of the optimal conditions for precipitation of mixed forms towards higher molar ratios and higher pH is that ionic sorption occurs for the both As forms at higher pH (Nenov et al. 1997).
The purpose of this study is to evaluate the long term stability of ferric iron-arsenic precipitates.

7.2 MATERIALS AND METHODS

During our studies within the period from 1990–2001, we have collected a large number of precipitates obtained at conditions of non-stoichiometric precipitation of As(V), As(III) and the As mixed forms by ferric sulfate.

The stability of precipitates was studied by evaluating their solubilization at different pH using a modification of an EPA-USA approved leaching test (Ham et al. 1979). Two grams of solid were dispersed in 200 mL distilled water and the pH was adjusted to desired value (pH = 3, 5, 7 and 9) by addition of 1 N NaOH or 1 N HCl at ambient temperature. Samples were subjected to continuous reciprocal shaking. The pH was readjusted every 24 h. If within 48 h period the pH was not changed, the procedure of pH adjustment was stopped. Samples were filtered using 0.45 \( \mu \)m porosity membrane and the filtrate was analyzed for As and Fe content. Arsenic was measured photometrically using the standard silver diethyldithiocarbamate method (APHA et al. 1989) while Fe(III) was measured using the standard photometrical method with 1,10-phenanthroline (APHA et al. 1989).

The initial conditions of precipitation and the age of some precipitates are given in Table 7.1. All listed precipitates were formed at optimal or very close to optimal conditions for removing As(V), As(III) or their mixed forms.

7.3 RESULTS AND DISCUSSION

The results of the solubility tests applied for nine year-aged ferric arsenate precipitates are shown in Tables 7.2–7.5. The tests which were carried out at pH = 3, 5, 7 and 9 indicate lowest
Table 7.1. Conditions of precipitation and precipitates age.

<table>
<thead>
<tr>
<th>Precipitate number</th>
<th>As, Ionic form</th>
<th>As, Initial conc., mg L⁻¹</th>
<th>Molar ratio, Fe/As</th>
<th>pH of prec.</th>
<th>Precipitate age, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As(V)</td>
<td>1919</td>
<td>6</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>As(V)</td>
<td>5638</td>
<td>6</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>As(V)</td>
<td>3775</td>
<td>6</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>As(V)</td>
<td>3775</td>
<td>6</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>As(III)</td>
<td>3775</td>
<td>11</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>As(III) + As(V) (1:1)</td>
<td>3775</td>
<td>11</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>As(III) + As(V) (1:1)</td>
<td>3775</td>
<td>11</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>As(III) + As(V) (1:1)</td>
<td>3775</td>
<td>11</td>
<td>9</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 7.2. Solubility of precipitate obtained at molar ratio Fe(III)/As(V) = 6, pHₚᵣ = 5, initial concentration of arsenic Cₐᵣ = 1916 mg L⁻¹. Precipitate age: 9 years.

<table>
<thead>
<tr>
<th>Solubility test pH</th>
<th>Cₐᵣ (mg L⁻¹)</th>
<th>C₉ᵣ (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.107</td>
<td>2.460</td>
</tr>
<tr>
<td>5</td>
<td>&lt;0.020</td>
<td>0.701</td>
</tr>
<tr>
<td>7</td>
<td>0.109</td>
<td>0.200</td>
</tr>
<tr>
<td>9</td>
<td>9.516</td>
<td>0.751</td>
</tr>
</tbody>
</table>

Table 7.3. Solubility of precipitate obtained at molar ratio Fe(III)/As(V) = 6, pHₚᵣ = 5, initial concentration of arsenic Cₐᵣ = 5638 mg L⁻¹. Precipitate age: 9 years.

<table>
<thead>
<tr>
<th>Solubility test pH</th>
<th>Cₐᵣ (mg L⁻¹)</th>
<th>C₉ᵣ (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.014</td>
<td>12.721</td>
</tr>
<tr>
<td>5</td>
<td>0.048</td>
<td>0.600</td>
</tr>
<tr>
<td>7</td>
<td>0.055</td>
<td>0.383</td>
</tr>
<tr>
<td>9</td>
<td>8.067</td>
<td>0.634</td>
</tr>
</tbody>
</table>

Table 7.4. Solubility of precipitate obtained at molar ratio Fe(III)/As(V) = 6, pHₚᵣ = 4, initial concentration of arsenic Cₐᵣ = 3775 mg L⁻¹. Precipitate age: 9 years.

<table>
<thead>
<tr>
<th>Solubility test pH</th>
<th>Cₐᵣ (mg L⁻¹)</th>
<th>C₉ᵣ (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.032</td>
<td>11.464</td>
</tr>
<tr>
<td>5</td>
<td>0.034</td>
<td>0.701</td>
</tr>
<tr>
<td>7</td>
<td>0.186</td>
<td>0.818</td>
</tr>
<tr>
<td>9</td>
<td>10.059</td>
<td>0.052</td>
</tr>
</tbody>
</table>

Table 7.5. Solubility of precipitate obtained at molar ratio Fe(III)/As(V) = 6, pHₚᵣ = 7, initial concentration of arsenic Cₐᵣ = 3775 mg L⁻¹. Precipitation age: 9 years.

<table>
<thead>
<tr>
<th>Solubility test pH</th>
<th>Cₐᵣ (mg L⁻¹)</th>
<th>C₉ᵣ (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.082</td>
<td>2.829</td>
</tr>
<tr>
<td>5</td>
<td>0.048</td>
<td>0.466</td>
</tr>
<tr>
<td>7</td>
<td>0.363</td>
<td>0.718</td>
</tr>
<tr>
<td>9</td>
<td>14.225</td>
<td>0.701</td>
</tr>
</tbody>
</table>
solubility towards As at pH 5. Actually this is the optimal pH value for As(V) precipitation by Fe$_3$(SO$_4$)$_3$ (Nenov et al. 1992). Through the increasing of initial concentrations of As in the premature solution, a slight elevation of equilibrium As is found. Concerning the Fe(III) release, its lowest values are registered at pH 5 and 7. At the test pH 5, both the equilibrium As and ferric iron concentrations are lower, compared to the corresponding values of the “fresh” precipitate obtained 9 years ago (Nenov et al. 1992), i.e., the nine years aged Fe(III)-As(V) precipitates posses higher stability.

The results of the solubility of precipitates aged 8 years, obtained at initial As(III) concentration of 3775 mg L$^{-1}$, mole ratio 11 and pH$_{pr}$ = 9 are shown in Table 7.6. These values of mole ratio and pH$_{pr}$ are optimal for the precipitation of As(III). A minimal solubility is observed in precipitate exposed to the aquatic media at pH = 5 (the equilibrium concentration for As is 0.057 mg L$^{-1}$ and those for Fe(III) is 0.27 mg L$^{-1}$). The available data for the solubility of the same precipitate following its immediate formation (8 years ago) show that at the test pH = 5 the residual concentrations were 0.046 mg L$^{-1}$ (As(III)) and 0.02 mg L$^{-1}$ [Fe(III)], i.e., the solubility has increased to a certain extent. In addition, it was found that the solubility of the precipitate at test pH 3, pH 7 and pH 9 is much higher.

The solubility data of mixed As form precipitates aged 8 years, are given in Figure 7.2. These precipitates are formed at equal values of the mole ratio, Fe(III)/(As(III) + As(V)) = 11, equal initial As concentration, 3775 mg L$^{-1}$ and at three different pH of precipitation (pH$_{pr}$ = 5, 7 and 9). The precipitates exposed to the test pH 5 show lowest solubility, irrespective of pH$_{pr}$. The increase of the test pH above 5 follows to considerable elevation of As solubility. This tendency is valid at the other pH of the tests as well. The solubilities of the same precipitates tested 8 years ago at pH 5 are listed in Table 7.7. The comparison of results from Table 7.8 and Figure 7.2 shows an improved stability of the mixed As form precipitates following 8 years aging.

<table>
<thead>
<tr>
<th>Solubility test pH</th>
<th>C$_{As}$ (mg L$^{-1}$)</th>
<th>C$_{Fe}$ (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.476</td>
<td>0.533</td>
</tr>
<tr>
<td>5</td>
<td>0.057</td>
<td>0.265</td>
</tr>
<tr>
<td>7</td>
<td>0.268</td>
<td>0.433</td>
</tr>
<tr>
<td>9</td>
<td>9.153</td>
<td>0.768</td>
</tr>
</tbody>
</table>

Figure 7.2. Solubility of mixed forms precipitates at different pH: (a) residual arsenic; (b) residual Fe(III).
7.4 CONCLUSIONS

The solubility tests of ferric iron-As precipitates aged in the range of 8–9 years, performed at pH = 3, 5, 7 and 9 show:

- The extent of re-solubilization of precipitates obtained at non-stoichiometric precipitation of As by Fe$_3$(SO$_4$)$_3$, irrespective of the ionic form of As, is lowest at the test pH = 5 and highest at pH = 9;
- The stability of ferric-arsenate precipitates aged of 9 years does not change at pH = 5; This fact confirms the already made finding that the basic ferric arsenates have an extremely low solubility over a wide range of pH values (3–7) and thus are environmentally safe for disposal;
- Eight years aged ferric-arsenite precipitates show a lower stability compared to ferric-arsenates;
- The precipitates of mixed ionic forms of As, As(III) and As(V), obtained at pH of precipitation of 5 and 9 posses lower solubility at the test pH = 5, compared to the newly formed precipitate at the same conditions.

REFERENCES


CHAPTER 8

Arsenic and boron in geothermal water and their removal

Kazuharu Yoshizuka, Nalan Kabay & Marek Bryjak

8.1 INTRODUCTION

Geothermal energy is a renewable heat energy source from deep in the earth. Heat is brought to the near-surface by thermal conduction and by intrusion into the earth's crust of molten magma originating from great depth. In certain areas, water sweeping down through faults and fractures in the crust, comes in contact with this hot rock, and is heated to high temperatures. Some of the heated water circulates back to the surface and appears as hot springs and geysers. The rising hot water may remain underground in areas of permeable hot rock, forming geothermal reservoirs. These reservoirs, which may reach temperatures of more than 350°C can provide a powerful source of energy. If a geothermal reservoir is sufficiently close to the surface, the heated water can be piped to the surface and used to produce electricity and for direct use (Barbier 2002). Some geothermal water contains large concentrations of dissolved minerals, such as sodium, calcium, sulfate, chloride, or iron. These ions have been dissolved from the minerals in the rocks that compose the geothermal reservoirs and vary as the mineral composition of the rocks varies. Concentrations of some constituents such as boron (B), arsenic (As), and fluoride (F), usually exceed those in the standards recommended for drinking water by the water authorities; thus, geothermal water that is withdrawn and used can become a disposal problem. Therefore, in many areas, reinjection of geothermal water is required.

8.2 ARSENIC AND BORON IN GEOTHERMAL WATER

Selecting an As treatment technology for remediation of geothermal waters depends on several key factors. Among these, speciation of As, initial As concentration, regulatory requirements and target treatment levels must be considered. Due to variations in As speciation and large differences in the chemistry and physical properties of geothermal waters, no single technology will adequately meet the needs of every project. Furthermore, successful remediation often requires a combination of two or more treatment technologies. There are several inorganic arsenite species [inorganic As(III); e.g., $\text{H}_3\text{AsO}_3$, $\text{H}_2\text{AsO}_4^-$, $\text{HASO}_4^-$ and $\text{AsO}_3^{3-}$] and inorganic arsenate species [inorganic As(V); e.g., $\text{H}_3\text{AsO}_4$, $\text{H}_2\text{AsO}_4^-$, $\text{HASO}_4^-$ and $\text{AsO}_4^{3-}$] in geothermal water.

Table 8.1 lists the As content of several geothermal waters in the world. Though large variation of As content is indicated in geothermal sites, extremely high As content is detected in some hot spring areas. This is linked to the mineralogical, chemical and physical characteristics of the soils, sediments and rocks in contact with these waters. In addition, the As is significantly leached from aquifers under the extremely high temperature and pressure conditions. Depending on oxidation-reduction (redox) conditions and biological activity, groundwater and geothermal water may contain As(V) and the more toxic As(III) forms (US EPA 2002). Considering that As contamination can originate from geological materials, the remediation of these materials is usually necessary to reduce As concentrations in associated geothermal waters. In some cases, however, geothermal water contamination is so severe that affordable and effective remediation is not possible. The physical and chemical characteristics of geothermal waters will affect the selection of reliable treatment technologies to work effectively under the high temperature condition. Alaerts and Khouri (2004) identified several factors...
that affect the costs and feasibility of treating As in geothermal water. The lowering of As drinking water standards (maximum contaminant level, MCL) from 50 to 10 µg L\(^{-1}\) in many countries has resulted in increasing demands for additional removal technologies when geothermal waters are used for drinking and cooking.

High-As geothermal waters are sometimes used to heat clean river water for greenhouses, indoor swimming pools and other facilities (Okada et al. 2004). If As could be removed from the geothermal waters, they could be directly utilized for recreation, business, agriculture, washing and drinking (Gallup 2007).

Table 8.1. Worldwide arsenic contents in geothermal waters.

<table>
<thead>
<tr>
<th>Site</th>
<th>Total dissolved As (µg L(^{-1}))</th>
<th>Other information</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kalloni drainage basin, Lesvos, Greece</td>
<td>41.1–90.7</td>
<td>pH = 6.56 (6.33–6.79)</td>
<td>Aloupi et al. (2009)</td>
</tr>
<tr>
<td>Kalikrati area, Chalkidiki, Greece</td>
<td>4.2–35.8</td>
<td>pH = 6.73 (6.65–6.8)</td>
<td>Aloupi et al. (2009)</td>
</tr>
<tr>
<td>Yangbajing geothermal power plant, Tibet, China</td>
<td>5700</td>
<td>[B] = 119 mg L(^{-1}) [F] = 19.6 mg L(^{-1})</td>
<td>Guo et al. (2008)</td>
</tr>
<tr>
<td>Rehai geothermal field, Yunnan Province, China</td>
<td>43.6–687</td>
<td>[Sb] = 0.38–23.8 µg L(^{-1})</td>
<td>Zhang et al. (2008)</td>
</tr>
<tr>
<td>Aksios area, Northern Greece</td>
<td>3.0–68.8 [predominately As(III)]</td>
<td>pH = 7.5–8.2 [HCO(_3)] = 4–6 mM [B] = 0.14–0.28 mg L(^{-1})</td>
<td>Katsoyiannis et al. (2007)</td>
</tr>
<tr>
<td>Kalikrati area, Northern Greece</td>
<td>3.6–74.6 [predominantly As(V)]</td>
<td>pH = 6.7–7.5 [HCO(_3)] = 6–12 mM [B] = 0.11–1.58 mg L(^{-1})</td>
<td>Katsoyiannis et al. (2007)</td>
</tr>
<tr>
<td>Chalkidiki, area, Northern Greece</td>
<td>1–1843 [predominately As(V)]</td>
<td>pH = 5.8–8.1 [HCO(_3)] = 6–17 mM [B] = 0.04–6.50 mg L(^{-1})</td>
<td>Kouras et al. (2007)</td>
</tr>
<tr>
<td>Bath Spring, Yellowstone National Park, USA</td>
<td>1560 (32% as trithioarsenate)</td>
<td>pH = 9.0</td>
<td>Planer-Friedrich et al. (2006, 2007)</td>
</tr>
<tr>
<td>Hot spring Ojo Caliente, Yellowstone National Park, USA</td>
<td>1500 (51% as trithioarsenate)</td>
<td>pH = 7.5</td>
<td>Planer-Friedrich et al. (2006, 2007)</td>
</tr>
<tr>
<td>Kawerau geothermal field, New Zealand</td>
<td>38</td>
<td>[Cl] = 50 mg L(^{-1})</td>
<td>Mroczek (2005)</td>
</tr>
<tr>
<td>Norris Geyser Basin, Yellowstone National Park, USA</td>
<td>2500</td>
<td>pH = 3.1</td>
<td>Langner et al. (2002)</td>
</tr>
<tr>
<td>Hot Creek, Eastern Sierra Nevada, USA</td>
<td>750–1400 [max 73% as As(III)]</td>
<td>[B] = 10 mg L(^{-1})</td>
<td>Wilkie and Hering (1998)</td>
</tr>
<tr>
<td>Beppu hot spring, Oita, Japan</td>
<td>210–1360</td>
<td>pH = 2.6–7.9 [F] = 0.53–1.64 mg L(^{-1})</td>
<td>Yoshizuka et al. (2010)</td>
</tr>
<tr>
<td>Hachoubaru geothermal power plant, Oita, Japan</td>
<td>3230</td>
<td>pH = 8.0</td>
<td>Yoshizuka et al. (2010)</td>
</tr>
<tr>
<td>Obama hot spring, Nagasaki, Japan</td>
<td>550</td>
<td>[B] = 33.9 mg L(^{-1}) [F] = 3.76 mg L(^{-1})</td>
<td>Yoshizuka et al. (2010)</td>
</tr>
<tr>
<td>Kizildere geothermal power plant, Denizli, Turkey</td>
<td>853</td>
<td>pH = 7.9</td>
<td>Kabay et al. (2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[B] = 14.9 mg L(^{-1}) [F] = 1.27 mg L(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH = 9.0–9.2 [B] = 18–20 mg L(^{-1}) [F] = 15.36 mg L(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>
The majority of Earth’s B occurs in the ocean with an average concentration of 4.5 mg L\(^{-1}\) (WHO 1998). The natural B content of groundwater is usually low. The B content of surface water can be significantly increased as a result of leaching from rocks and soils containing borates and borosilicates. Concentration of B in groundwater throughout the world varies widely from <0.3 to >100 mg L\(^{-1}\) (WHO 1998). Average surface water concentration of B is about 0.1 mg L\(^{-1}\) but concentrations vary greatly, depending on B content of local geologic formations and anthropogenic sources of B. The presence of appreciable quantities of B, both in drinking and irrigation water deteriorates the quality of water. Therefore, WHO recommends in its guides for the quality of drinking water, a value with a maximum of 0.5 mg L\(^{-1}\) based on the NOeL (no-observed-adverse-effect-level) (Prats et al. 2000).

Normally B is present in two different chemical forms. The predominant form is boric acid \([H_3BO_3\text{ or } B(OH)_3]\). Two boric acid types exist in the free state, metaboric (HBO\(_2\)) and orthoboric (H\(_3\)BO\(_3\)). Each type may be converted to the other by either hydration or dehydration at certain conditions. In solution, metaboric acid converts rapidly to orthoboric acid due to hydration. Boric acid in solution dissociates weakly to form monoborate and some polyborates, depending on temperature, concentration and pH. The primary species at the acidic and basic extremes are B(OH)_3 and B(OH)_4\(^-\), respectively (Ooi et al. 1996). At low concentration (<0.025 M as B), B(OH)_4\(^-\) is the only significant species in the solution, while at higher concentrations polyborates-triborates, tetraborates and pentaborates-along with B(OH)_3, may exist (Lou et al. 1999).

Boric acid is a very weak acid with an equilibrium constant (pKa) value of 9.2. At a pH < 7, B is present in its non dissociated form (boric acid) and at a pH > 10.5, it is present in the dissociated borate form. The exact percentage of boric acid and borate in any aqueous system is basically dependent on pH. The element B exists in equilibrium as the borate monovalent anion B(OH)_4\(^-\) at higher pH and as non-ionized boric acid B(OH)_3 at lower pH. The dissociation of boric acid in water can be described by the chemical equilibrium reaction between two species (MEDRC-04-AS-004, 2007):

\[
B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad \text{pK}_a = 9.2 \text{ at } 25^\circ C
\]

Between pH 6 and 11 and at high concentration (>0.025 mol L\(^{-1}\)), highly water soluble polyborate ions such as B\(_2\)O\(_5\)(OH)\(_4\), B\(_3\)O\(_5\)(OH)\(_4\)\(^-\) and B\(_4\)O\(_5\)(OH)\(_4\)\(^-\) are formed (WHO 1998). There are two opinions about the formation of trimer borate. Due to the ring type of structure of trimeric hydroxyborate B\(_3\)O\(_6\)(OH)\(_4\), and its high solution stability, the first reaction was suggested to form B\(_3\)O\(_6\)(OH)\(_4\) (Edwards 1953):

\[
2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O
\]

while the second reaction is as follows (Mesmer 1972):

\[
2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3(OH)_{10}^-\]

and leads to the formation of B\(_3\)(OH)\(_{10}\)^-. At high B concentrations, the formation of tetraborates is suggested by the following reaction (Cotton 1980):

\[
2B(OH)_3 + 2B(OH)_4^- \rightleftharpoons B_4O_5(OH)_{12}^- + 5H_2O
\]

The formation of pentaborate is given below (Ross 1967):

\[
4B(OH)_3 + 2B(OH)_4^- \rightleftharpoons B_5O_6(OH)_{14}^- + 6H_2O
\]
8.3 TECHNOLOGIES FOR REMOVAL OF ARSENIC AND BORON SPECIES

8.3.1 Arsenic removal

Adsorption involves the removal of contaminants by causing them to attach onto the surfaces of solid materials (adsorbents) and is widely used in water treatment technologies. Sometimes the adsorbed solute is called the adsorbate (Krauskopf and Bird 1995). Adsorption often involves ion exchange (Eby 2004). For example, adsorbed As oxyanions will replace other anions on the surface of the adsorbent.

Adsorbents are sometimes suspended in the separator to adsorb As contaminants from water. More commonly, however, 0.3–1.0 mm diameter adsorbents or ion exchange granules, fibers, or other materials are packed into columns or filters (Clifford and Ghurye 2002, Greenleaf et al. 2006). The materials are large enough to facilitate permeability and water flow while still providing sufficient surface area for numerous adsorption and ion exchange sites. Other desirable properties of adsorbents and ion exchange media include (1) ability to rapidly and effectively remove large amounts of both As(III) and As(V) before regeneration or disposal, (2) capability of being regenerated, (3) high durability in water, and (4) reasonable costs. Nevertheless, few, if any, adsorption and ion exchange systems adequately achieve all of these goals.

Selecting an appropriate adsorption or ion exchange technology strongly depends on the characteristics of the contaminated water, including its total dissolved solids (TDS) content, pH, redox conditions, microbial activity, the presence of any organic and inorganic species that might interfere with treatment, and the concentrations of the As species. For example, very acidic waters may corrode alumina adsorbents, thus decreasing the number of active adsorption sites and reducing the effective life spans of the adsorbents (US EPA 2002, Prasad 1994).

For As, adsorption onto inorganic solids is generally more convenient than chemical precipitation/co-precipitation methods and less expensive than ion exchange resins or membrane filtration (Kim et al. 2004). In contrast to precipitation/co-precipitation that produce large volumes of sludge that are difficult to dewater (Deliyanni et al. 2003a, b), adsorption and ion exchange columns usually produce relatively few waste and can often be regenerated. Adsorption and ion exchange technologies are most often used with low TDS waters where As is the only significant contaminant or as final step after precipitation/co-precipitation (US EPA 2002). Adsorbents and ion exchange materials are more vulnerable to chemical interferences when compared to precipitation/co-precipitation methods for the removal of As from water (US EPA 2002). Some interfering chemicals directly compete with As species for adsorption and ion exchange sites. Two prime examples are phosphate (PO$_4^{3-}$) and silicate (SiO$_4^{4-}$), which have the same tetrahedral structure as arsenate (AsO$_4^{3-}$). Due to these similarities, phosphate and silicate desorb As(V) from sorbents such as iron (hydr)oxide, aluminum (hydr)oxide and silica over a wide pH range, or at least hinder the adsorption of As(V) onto these materials (Clifford and Ghurye 2002, Zhang et al. 2004, Smith and Edward 2005, Violante et al. 2006). While carbonates (H$_2$CO$_3$, HCO$_3^-$ and CO$_3^{2-}$) mainly present in geothermal waters often have little or no effect on As(V) adsorption, evidence suggests that they may interfere with As(III) adsorption due to their similar trigonal molecular structures (Stollenwerk 2003). The cost of adsorption and ion exchange systems would depend on the concentration and speciation of the As contaminants, regeneration and disposal requirements for the spent media, water flow rates, and the overall chemistry of the water, which controls fouling mainly caused by organic materials and silica (SiO$_2$).

Table 8.2 lists the studies on the As removal from geothermal waters. Adsorption by inorganic materials are mostly used for removal of As. Tyrovola et al. (2006, 2007) carried out the adsorptive removal of As(III) and As(V) with zerovalent iron. In the presence of water and oxygen, zerovalent iron rapidly oxidizes. Depending on pH, the number of oxygen molecules (O$_2$), the presence of bacteria and other aqueous conditions, the oxidation of zerovalent
iron may produce a wide variety of compounds, including lepidocrocite $[\gamma$-FeO(OH)], sulfate $[4\text{Fe(OH)}_2\cdot2\text{FeOOH}\cdot\text{FeSO}_4\cdot4\text{H}_2\text{O}]$ and carbonate [possibly $\text{Fe(II)}\cdot\text{Fe(III)}\cdot\text{OH}_2\cdot\text{CO}_3\cdot2\text{H}_2\text{O}$], mackinawite ($\text{Fe}_9\text{S}_8$), magnetite ($\text{Fe}_3\text{O}_4$), maghemite ($\gamma$-Fe$_2$O$_3$), and amorphous ferrous sulfide (FeS) (Gu et al. 1999). These oxidation products are largely responsible for sorbing and/or coprecipitating As from water. De Carlo et al. (1985) and Buisson et al. (1979) carried out the As removal by adsorptive bubble flotation using iron flocculant. They successfully removed both As(III) and As(V) from geothermal waters by the adsorptive bubble flotation technology.

Okada et al. (2004) used a superconducting magnet as part of a treatment system that reduced As concentrations from 3400 [mostly as As(III)] to 15 $\mu$g L$^{-1}$ in geothermal waters from Kakkonda, Japan. Before magnetic treatment, the As was entirely oxidized to As(V) with hydrogen peroxide. Fe(III) sulfate was then added to the water at pH 4 to coprecipitate the As(V) with paramagnetic iron (oxy)(hydr)oxides and magenetics wire meshes were used to capture the precipitates.

Yoshizuka et al. (2010) have recently conducted chromatographic As removal from geothermal water. The geothermal water sampled from Hachoubaru, Japan (pH 8.0, As concentration of 3.23 mg L$^{-1}$) was fed into the adsorption column packed with granulated magnetite as shown in Figure 8.1. Figure 8.2 shows the breakthrough curve of As from the geothermal water. Arsenic in the geothermal water was slowly adsorbed and breakthrough occurred at bed volume (BV) of 200. The As concentration was less than 0.01 mg L$^{-1}$ up to a bed volume of 200 with this chromatographic operation.

### Table 8.2. Methods for arsenic removal from geothermal water.

<table>
<thead>
<tr>
<th>Method</th>
<th>Separation media</th>
<th>Species</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption/coprecipitation</td>
<td>Zerovalent iron</td>
<td>As(III), As(V)</td>
<td>Laboratory study, effect of NO$_3^-$ and PO$_4^{3-}$</td>
<td>Tyrovola et al. (2007)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Hydroxyapatite-based ceramics</td>
<td>As(III), As(V)</td>
<td>Laboratory study, XANES measurement</td>
<td>Nakahira et al. (2006)</td>
</tr>
<tr>
<td>Adsorption/coprecipitation</td>
<td>Zerovalent iron</td>
<td>As(III), As(V)</td>
<td>Laboratory and field pilot studies, effect of temperature, NO$_3^-$ and PO$_4^{3-}$</td>
<td>Tyrovola et al. (2006)</td>
</tr>
<tr>
<td>Adsorption/magnetic separation</td>
<td>Magnetite</td>
<td>As(III), As(V)</td>
<td>Laboratory study</td>
<td>Okada et al. (2004)</td>
</tr>
<tr>
<td>Adsorptive bubble flotation</td>
<td>Colloidal ferric hydroxide</td>
<td>As(III), As(V)</td>
<td>Quantitative removal above pH 6.5</td>
<td>De Carlo et al. (1985)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Chelating resin with mercapto groups</td>
<td>As(III)</td>
<td>Laboratory study</td>
<td>Egawa et al. (1985)</td>
</tr>
<tr>
<td>Adsorptive bubble flotation</td>
<td>Iron flocculant</td>
<td>As(V)</td>
<td>Laboratory study</td>
<td>Buisson et al. (1979)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Granulated magnetite</td>
<td>As(III), As(V)</td>
<td>Laboratory study of chromatographic removal</td>
<td>Yoshizuka et al. (2010)</td>
</tr>
</tbody>
</table>
8.3.2 Boron removal

Water contamination by B is a widespread environmental problem since even a low level of B present in irrigation water can damage the plant growth. The World Health Organization has established a guideline value of 0.5 mg L$^{-1}$ of B as limit for drinking water (Sabarudin et al. 2005). A minimum B concentration in irrigation water is required for some metabolic activities of plants, such as cellular multiplication and the metabolism of nucleic acids. Deficiency in B level will result in poor budding, excessive branching, and in general, inhibits plant growth. On the other hand, B concentration in irrigation water which is only slightly higher than the minimum will be negative for plant growth and will exhibit signs of “B poisoning” - yellowish spots on the leaves and the fruit, accelerated decay, and ultimately plant expiration (Boncukoglu et al. 2004). Therefore, removal of B from water and wastewater is a crucial problem for environmental control. There is no easy method for removal of boric acid and borates from aqueous solution. As has already been stated in the literature, conventional sedimentation and biological treatment methods remove B poorly from water. Also, coagulation-precipitation methods are not effective and not feasible for this purpose (Nadav 1999). Table 8.3 displays various possible approaches for reduction of B level.
8.3.2.1 Removal of boron by sorption methods

Sorption is most widely used method to remove B from water and wastewater. Activated carbon, activated alumina, hydrous cerium oxide and hydrous lanthanum oxide have a high performance for B among the inorganic adsorbents (Ooi et al. 1996). Karahan et al. (2006) used some clays and nonylammonium chloride modified clays as adsorbents for the removal of B from aqueous solution. Fly ashes (Polat et al. 2004, Ozturk et al. 2005), natural adsorbents (Inukai et al. 2004, Smith et al. 1998) and some other inorganic adsorbents (Ay et al. 2007, Seyhan et al. 2007, Seki et al. 2006, Yurdakoc et al. 2005, Ozturk and Kavak 2004, 2008) were reported to be effective materials for removal of B from water. (Polat et al. 2004) developed a new methodology for removal of B from seawater collected from the Gulf of Eilat (Red Sea) and from the Mediterranean Sea by coal and fly ash. The results showed a significant reduction of B concentration in seawater after interaction with different types of coal and fly ash.

Ooi et al. (1996) screened 46 kinds of inorganic and 12 kinds of organic adsorbents for their B adsorption in residual brine after salt production from seawater. They reported that hydrous cerium oxide, hydrous zirconium oxide and N-glucamine type resin with N-methyl(polyhydroxyl) amino groups showed a high adsorption capacity (above 5 mg g$^{-1}$) for B (Ooi et al. 1996). Yurdaçoç et al. (2005) performed a study to investigate the B sorption with Siral 5, 40, and 80 in a batch system. Also, the adsorption behavior of B was studied using a chitosan resin derivated with N-methyl-d-glucamine (CCtS-NMDG) (Sabarudin et al. 2005). The CCtS-NMDG resin showed high ability in B sorption with the capacity of 2.1 mmol g$^{-1}$ (Sabarudin et al. 2005). Inukai et al. (2004) synthesized N-methylglucamine-type cellulose derivatives to obtain an adsorbent for B(III) with a high adsorption rate.


Simonnot et al. (2000) have reviewed the methods of B removal from drinking water. Among them, they have also pointed that the use of B selective resins is the most efficient one. Commercially available B selective chelating ion exchange resins are prepared from macroporous poly(styrene-co-divinylbenzene) by functionalization with

### Table 8.3. Boron removal technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>B-Removal (%)</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening</td>
<td>Insignificant</td>
<td>Batch tests of calcite precipitation</td>
<td>Kitano et al. (1978)</td>
</tr>
<tr>
<td>Coagulation</td>
<td>&lt;28%</td>
<td>Typical removal &lt;10%</td>
<td>Borax (1996)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>up to 90%</td>
<td>High carbon doses needed</td>
<td>Choi et al. (1979)</td>
</tr>
<tr>
<td>Reverse osmosis (RO)</td>
<td>43–78%</td>
<td>Survey of 8 operating RO plants</td>
<td>Magara et al. (1996)</td>
</tr>
<tr>
<td>Ion exchange resin</td>
<td>&gt;99%</td>
<td>pH of produced waters &lt;4.5 for 600 bed volumes</td>
<td>Nadav (1999)</td>
</tr>
<tr>
<td>Two pass RO with pH adjustment</td>
<td>up to 90%</td>
<td>Best removal at pH 10.5</td>
<td>Prats et al. (2000)</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>&gt;90%</td>
<td>Cost of 0.15 USD per m$^3$</td>
<td>Turek et al. (2007)</td>
</tr>
<tr>
<td>Boron chelation</td>
<td>&gt;80%</td>
<td>N-methyl-D-glucamine</td>
<td>Smith et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>&gt;98%</td>
<td>Mannitol</td>
<td>Geffen et al. (2006)</td>
</tr>
</tbody>
</table>
N-methyl-D-glucamine (NMG) (1-amino-1-deoxy-D-glucitol) (Fig. 8.3) (Senkal and Bicak 2003).

NMG groups capture B through a covalent attachment and an internal coordination complex formation as shown in Figure 8.4 (Marston et al. 2005). It was reported that B liberating hydrolysis is relatively easy at pH less than 1.0 and therefore, relatively high acid concentrations of acid are required for the complete and rapid elution of the boric acid from B selective resin (Marston et al. 2005). Marston et al. (2005) mentioned that extra acid is required in the elution step since the NMG functional group is linked to styrenic backbone. It was noted that larger amount of acid is required for the elution stage than required for hydrolysis alone. The acid is needed to accommodate the appetite of the tertiary amine group for hydronium ion while it reacts with acid to form a conjugate acid salt. Only after bridging nitrogen atoms of NMG groups are protonated, can excess acid accumulate around the bound cis diol-borate ester complex to facilitate the B liberating hydrolysis reaction (Marston et al. 2005).

Badruk et al. (1999a, b) reported on the preliminary results of batch-mode and column-mode studies for B removal from wastewaters of Kizildere geothermal power plant using N-methyl-D-glucamine type resins. Column-mode removal of B from geothermal wastewaters was performed using Diaion CRB 02 N-methyl-glucamine-type chelating resin for ten sorption-washing-elution-washing-regeneration-washing cycles in Kizildere geothermal field, Denizli, Turkey (Kabay et al. 2004b).

Column-mode recovery of B from acidic eluate solution was performed using weak base anion exchange resin Diaion WA 30 according to acid-retardation technique (Kabay et al. 2004b). Also, the comparative results obtained using different N-glucamine type resins (Purolite S108, Diaion CRB01, Diaion CRB 02) and column performances of these resins for B removal from geothermal wastewater were reported elsewhere (Kabay et al. 2004a). Boron selective resins Diaion CRB02 and Dowex XUS 43594.00 have been also tested for

Figure 8.3. The structure of boron selective chelating resin containing NMG group (Marston et al. 2005).

Figure 8.4. Binding mechanism of boron by NMG type chelating resin (Marston et al. 2005).
B removal from model seawater. These resins exhibited a good performance for B removal from model seawater (Kabay et al. 2007) and elimination of B from natural seawater reverse osmosis permeate (Kabay et al. 2008a). Elsewhere, fibrous sorbents based on polypropylene and viscose fibers grafted with polystyrene and glycidylmethacrylate and functionalized with N-methyl-D-glucamine were compared with commercially available B selective ion exchange resins. Fibrous sorbents showed much faster sorption kinetics compared to ion exchange resins. They were able to tolerate very rapid specific flow rates with only small drop in B breakthrough capacity. But sorption capacity of fibrous adsorbents was lower than that of ion exchange resins. They were also much easier to regenerate. For example, a viscose based sorbent was easily regenerated with diluted (0.1 mol L\(^{-1}\)) hydrochloric acid. A viscose based sorbent also exhibited the highest B breakthrough capacity among the fibrous sorbents studied (Parshova et al. 2007). The effect of ionic strength of solution on B transfer by ion exchange resins was investigated using B selective ion exchange resins Diaion CRB02, Dowex XUS.43594.00 and Purolite S108. Ionic strength of the solution affected kinetic performance of the resins although the nature of the electrolyte species did not influence the kinetic performance of the resins (Yilmaz et al. 2007).

The optimum resin amount was found as 2 g resin L\(^{-1}\)-geothermal water for B removal from geothermal water using B selective chelating ion exchange resins Diaion CRB 02 and Dowex (XUS 43594.00) (Yilmaz-Ipek et al. 2009). Both ion exchange resins were found to be effective for B removal from geothermal water. Also, it was found that the breakthrough capacity of Dowex (XUS 43594.00) resin decreased when the feed flow rate was increased due to the decrease in contact time (Yilmaz-Ipek et al. 2009).

Glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-DVB (divinyl benzene) terpolymer beads have been prepared and used as support for preparation of B selective resins. The resulting resin has been demonstrated to be an efficient sorbent for removal of B (Bicak et al. 2001). Polymer supported iminodipropylene glycol functions have been shown to be efficient in chelation with boric acid and can be used for removal of boric acid at trace levels (Senkal and Bicak 2003).

8.3.2.2 Removal of boron by reverse osmosis (RO)

Desalination by reverse osmosis is an efficient and reliable technology for production of drinking water from seawater and brackish water. Seawater contains B at a concentration of approximately 5 mg B L\(^{-1}\). In most cases, rejection of B by RO is not sufficiently high and around 1.5 mg B L\(^{-1}\) is normally found in permeate.

With high rejection RO membranes, the recommended level of B (0.5 mg L\(^{-1}\)) in drinking water by WHO can be obtained in the RO permeate if raw water is not acidified. However, to conduct the process under these conditions requires particular attention to proper chemical pretreatment step and removal of Ca and Mg ions that are mostly responsible for membrane scaling phenomenon. The rejection of non-ionized boric acid by RO is low due to its smaller size and lack of electric charge. Boron rejection by RO membranes is affected by pH, permeate flux and temperature (Busch et al. 2003, Koseoğlu et al. 2007, 2008, Guler et al. 2009). Boron is rejected by RO membranes at a level of 100% when the solution pH reaches a value of 10.5, and is in the range of 40–60% for solution of pH varying between 5.5 and 9.5. It was reported that improvement of B rejection was obtained with increased operating pressure (Prats et al. 2000, Koseoğlu et al. 2007, 2008, Guler et al. 2009) and for the system when pH of the second stage RO permeate was adjusted to 9.5 (Rodrigues-Pastor et al. 2001). A number of process configurations have been proposed to achieve low B concentration in RO permeate. Some of them involve RO treatment of first-pass permeate at elevated pH and/or application of B-selective ion exchangers (Redondo et al. 2003, MEDRC-04-AS-004, 2007).

The detailed studies showed that B rejection by RO membranes is related to the pH of solution and closely follows the dissociation ratio of boric acid. When dissociation ratio depends also on water salinity it is understandable why seawater shows the higher rejection values for B than brackish or geothermal water. With increased salinity, the equivalent dissociation ratio shifts to lower pH (MEDRC-04-AS-004, 2007).
The recent experiments on B removal from geothermal water have been done using cross-flow flat sheet reverse osmosis system. The chemical composition of geothermal water sampled from Izmir region, Turkey is summarized in Table 8.4. Figure 8.5 shows the percent rejection of B from the geothermal water using BW 30 RO membranes. Boron rejection increased following an increase in applied pressure within the ranges from 10–15 to 25–30 bar. Average salt rejection value was 98.5% at 30 bar while respective value for B was about 83%.

8.3.2.3 Removal of boron by other membrane processes
Several other membrane processes such as nanofiltration (Dydo et al. 2005), polymer enhanced ultrafiltration (Melnik et al. 1999, 2005, Turek et al. 2005, Yazicigil and Oztekin 2006, Oren et al. 2006), donnan dialysis (Ayyildiz and Kara 2005), and electrodeionization (Wen et al. 2005) have been used for B removal. Kabay et al. (2008b) studied the B removal by electrodialysis as a function of solution pH, applied voltage, feed flow rate, and initial B concentration in the feed. Electrodialytic treatment of B containing wastewater with univalent permselective membranes was tested to obtain optimum B removal conditions by Turek et al. (2007, 2008). Shimada et al. (2007) examined removal of B from aqueous solution with polyvinyl alcohol membranes under the conditions where one side of membrane was kept acidic and the other alkaline (pH 10). The borate ions formed a complex with the membrane, and the chemical potential gradient compelled borate transport (Shimada et al. 2007). Donnan dialysis was investigated as a new method for regeneration of B selective resins (Bryjak et al. 2007).

8.3.2.4 Solvent extraction with complexing agents (diols)
Boric acid/borate reacts with chemical compounds containing multiple hydroxyl groups (polyols), such as mannitol, generating anionic complexes at the neutral pH of water. With

<table>
<thead>
<tr>
<th>Cations</th>
<th>Concentration (mg L$^{-1}$)</th>
<th>Anions</th>
<th>Concentration (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>366</td>
<td>Cl$^-$</td>
<td>188</td>
</tr>
<tr>
<td>K$^+$</td>
<td>26.3</td>
<td>NO$_3^-$</td>
<td>N.D.</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>26.2</td>
<td>SO$_4^{2-}$</td>
<td>109</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>4.00</td>
<td>F$^-$</td>
<td>4.45</td>
</tr>
<tr>
<td>pH</td>
<td>8.6</td>
<td>HCO$_3^-$</td>
<td>622</td>
</tr>
<tr>
<td>EC (µS cm$^{-1}$)</td>
<td>1770</td>
<td>TDS (mg L$^{-1}$)</td>
<td>885</td>
</tr>
<tr>
<td>Salinity (%)</td>
<td>0.7</td>
<td>B (mg L$^{-1}$)</td>
<td>10.7</td>
</tr>
</tbody>
</table>

N.D.: not determined.

Figure 8.5. Boron rejection as a function of time: Effect of applied pressure on boron removal from geothermal water by RO (Oner et al. 2009).
carbohydrates and most polyols possessing 1,2-diol systems, the borate ion forms anionic mono (1:1) and bis (1:2) diol-monoborate species. The stability of the borate complex formed is strongly dependent on the type of diol, namely 1,2 or 1,3-diols. If the diol involves the -OH groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated B, a strong complex will be formed. The borate esters are formed and dissociated spontaneously in a variety of pH dependent equilibria. Due to the release of protons during complexation there is a concomitant decrease of pH which tends to reverse the reaction and thus, in order to maintain stable complexes there is a need to avoid pH decrease. The amount of acidification produced upon the addition of polyol is proportional to the extent of borate ester formation (Geffen et al. 2006).

8.3.2.5 Adsorption-Membrane Filtration (AMF) hybrid process for removal of boron
The recent achievements in ‘materials science’ offer new types of sorbents and binding agents. This includes polymer and ceramic sorbents, chelating and ion exchange resins, coordinating and complexing agents. They can be prepared and modified to establish an outstanding selectivity towards some particular components that can appear even in minor quantities. The combination of the advanced binding agents with their separation on membranes reveals many advantages compared to the conventionally used systems. The main benefit of the AMF method is the higher efficiency and lower costs of the hybrid process as compared with the classical column sorption in the fixed bed mode. At first, the sorbents may be prepared as very fine particles, which increase the interface area and results in enhancement of the process rate. Secondly, synergetic effects may achieve the high process intensity when sorbent is concentrated nearby the membrane surface (Koltuniewicz et al. 2004). Recent knowledge about membrane processes enables the high productivity of the process to be reached despite of the very small size of sorbent particles (Kabay et al. 2006, Yilmaz et al. 2006). The integrated system includes two separation loops, as shown in Figure 8.6.

![Flow sheet of adsorption-membrane filtration integrated system](image)

Figure 8.6. Flow sheet of adsorption-membrane filtration integrated system (Kabay et al. 2006, 2009).
Loop 1: Binding of boron (B) on a specific sorbent (S) is followed by separation of (BS) complex from the geothermal water (GW) by means of microporous membrane. The process is controlled by balancing of fluxes. Pure water (W) is the main product while (BS) passes to the regeneration second loop.

Loop 2: Splitting of the complex (BS) onto the free sorbent (S) and boron (B) followed by membrane separation is carried out on this stage. This step allows reusing the sorbent and offers the concentrated brine.

Figure 8.7 shows the mass balance in the AMF system. Boron comes from the feed 1—with flux J_f and concentration C_f(B). Feed is mixed with suspension of B selective resin 2—flux J_s(in), concentration of solid X(in) that carries q(in) of B. Boron is removed from the system in three different ways: on sorbent 3—J_s(out), X(out), q(out), in solution 4—J_s(out), C_p(B) and in permeate 5 J_p, C_p(B). After balancing the flows in the whole system and after making the following assumptions:

- J_s(in) = J_s(out),
- X(in) = X(out),
- J_f = J_p,
- Concentration of B in liquid of suspended resin stream is the same as in permeate,
- In the sorption loop, the residence time of resin is long enough to reach the B sorption equilibrium,
- Due to delivery of fresh suspension, dilution caused by water is negligible

one gets the general balance equation: B inlet = B outlet:

\[ J_f C_f + J_s \text{ (in) } X(\text{in}) q(\text{in}) = J_p C_p + J_s \text{ (out) } X(\text{out}) q(\text{out}) + J_s \text{ (out) } C_p \]

After some mathematical transformations the above equation becomes:

\[ (C_f - C_p)/C_f = ([J_s X(\text{out})/(J_f)] q(\text{out})/C_f) \]

where the terms in brackets represent the process parameters that affect separation efficiency. They are as follows: volume flux of suspension (J_s), concentration of solid particles (X) and flux of feed phase (J_f). Hence, the efficiency of B removal can be expressed as:

\[ -C_p \propto A J_s X(J_f) - B; \quad C_p \propto B - A J_s X(J_f) \]
where \( A \) and \( B \) are the process constants. This simple approach allows one to control the concentration of \( B \) in the permeate. Now, one is able to say that reduction of \( B \) concentration in permeate is possible by two ways: (1) by an increase of the suspension replacement rate or (2) by a decrease the feed delivery. The trivial approach—the increase of solid contents in the suspension—can serve as the safety vent of the AMF process (Kabay et al. 2009). The effect of process parameters on \( B \) removal efficiency is shown in Figure 8.8. It can be noted that the efficiency of hybrid process is improved significantly when one makes higher the rate of sorbent suspension delivery and decrease permeate flux.

Kabay et al. (2006) investigated the efficiency of adsorption-membrane filtration hybrid process for \( B \) removal from model solution and compared it to the ion-exchange process. Elsewhere, evaluation of a sorption-submerged membrane hybrid process using N-methyl glucamine chelating resins for \( B \) removal from the solution was reported (Yilmaz et al. 2006). Kinetic performance of \( B \) selective resins in a seeded microfiltration system was investigated in order to explore the efficiency of adsorption-membrane filtration hybrid process (Yilmaz-Ipek et al. 2007). The suitability and performance of adsorption-membrane filtration hybrid process technology was also investigated for \( B \) removal from seawater and reverse osmosis permeate (Kabay et al. 2008c, Bryjak et al. 2008). Elsewhere, \( B \) selective ion exchange resins Diaion CRB 02 and Dowex-XUS 43594.00 were used for \( B \) removal from geothermal water by ion exchange-submerged microfiltration hybrid process. The effect of various parameters such as resin particle size, flow rate, and resin concentration on \( B \) removal was investigated (Kabay et al. 2009).

8.4 CONCLUSIONS

Geothermal waters may contain some toxic elements such as \( B \) and As which are mostly at higher concentrations than recommended for drinking water by the water authorities; thus, geothermal water that is withdrawn and used can become a disposal problem. In this chapter, various methods for removal of As and B from water have been reviewed. Special emphasis was given to the treatment of geothermal waters containing As and B. Selecting an appropriate technology for As removal strongly depends on the characteristics of the contaminated water, including its total dissolved solids (TDS) content, pH, redox conditions, microbial activity, the presence of any organic and inorganic species that might interfere with treatment, and the concentrations of the As species. Adsorption methods by inorganic materials were mostly used for As removal. Granulated magnetite exhibited a good performance for column-mode removal of As from geothermal water containing 3.23 mg L\(^{-1}\) As, giving
a breakthrough at BV of 200 at a concentration of 0.01 mg L$^{-1}$ As. The use of B selective chelating ion exchange resins containing N-methyl-glucamine is defined to have still the highest importance among several methods of B removal from water. The adsorption-membrane filtration hybrid process for B removal from geothermal water was suggested as an alternative method to traditional column-mode ion exchange operation with fast sorption kinetics.

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CHAPTER 9

Arsenic removal from potable water: Point-of-use, point-of-entry and municipal experiences

Paul Sylvester, Teresia Möller & Owen Boyd

9.1 INTRODUCTION

Arsenic (As) is a widely distributed element within the earth’s crust with an average abundance of approximately 2 mg per kg and may occur in drinking water due to contact between the groundwater and As-rich sediments and rocks (Greenwood and Earnshaw 1984). The consumption of drinking water containing even relatively low levels of As over long periods of time has been shown to be deleterious to human health (Kapaj et al. 2006, Steinmaus et al. 2000, Smith et al. 1999). A range of diseases have been linked to As exposure via drinking water and include cancers, dermal lesions, and skin diseases. This has been particularly acute in Bangladesh and West Bengal, India where well waters may contain As concentrations as high as several hundred micrograms per liter. This link between As exposure due to the consumption of contaminated water and human health has prompted the USA Environmental Protection Agency (EPA) to lower the Maximum Contaminant Level (MCL) for As in drinking water from 50 µg L\(^{-1}\) to 10 µg L\(^{-1}\). This lower level came into force in January, 2006 and affected an estimated 4000 municipal authorities and several million private wells in the United States. Although private domestic wells are not covered by federal regulations, local laws governing the water quality are starting to appear in some states (e.g., New Hampshire) which often mandate that during real estate transactions, the quality of the water must meet federal regulations. These local laws and a growing consumer awareness of the adverse health effects associated with the consumption of As-tainted water have spurred sales of water treatment systems among residential and small business customers.

Arsenic occurs in drinking water in two major oxidations states: As(V), arsenate and As(III), arsenite. There may also be low levels of organic As species, but in most waters these are present at insignificant concentrations. The actual species present in solution will depend upon the redox conditions and the pH. In oxygen-rich waters, As(V) will be the predominant oxidation state with \(\text{H}_3\text{AsO}_4\) and \(\text{HAsO}_4^{2-}\) being the main anions present (Berdal et al. 2000) at typical drinking water pH values. Under more reducing conditions, As(III) species are stable with undissociated \(\text{H}_2\text{AsO}_3\) predominating at pH values less than 9. Arsenic speciation has a large effect on the efficacy of As adsorbents since the capacity for arsenite is generally less than 20% of the capacity for arsenate.

9.2 ARSENIC REMOVAL USING ADSORBENTS

The use of adsorbents has proved an effective method to remove As from drinking water and a wide range of media are commercially available. Many of these granular metal oxide based media have a very high affinity for arsenate and a negligible affinity for other common anions, such as sulfate and chloride, which means that they have operational lives measured in tens of thousands of bed volumes in many cases. However, a major drawback, which can cause operational problems, is the low structural stability of most granular adsorbent media. In use, the media requires regular backwashing to remove fines generated from the breakdown of the granules (Chen et al. 2008). In some cases the poor structural strength of the media leads
to a significant attrition loss during operation. For instance, at a system operating in New Hampshire which used a granular iron oxide media, it was recently reported that between 46 and 59% of the total volume of media was lost as fines during the backwash (Cumming et al. 2009). This complicates system design and reduces system reliability, especially for small systems and domestic water treatment, where skilled operators are usually not available. This mechanical deficiency spurred the development of new materials which had improved structural stability. Hybrid adsorbents are materials that combine the As removal capacity of a granular media with the ruggedness of a traditional polymeric ion exchange resin bead. These media are ideal for use in simple fixed bed applications and typically require minimal maintenance. As is the case with the majority, if not all, of the adsorbents utilized for As removal, the spent hybrid media pass the United States Toxicity Characteristic Leaching Procedure (TCLP) which means that they can be disposed of in a non-hazardous waste landfill.

9.2.1 Hybrid adsorbents

ArsenX™ was a first generation hybrid inorganic/organic sorbent that was developed by SolmeteX for the removal of As from drinking water (Sylvester et al. 2007). This media consists of hydrous iron oxide nanoparticles impregnated into 300–1200 µm durable polymeric anion exchange resin beads and is based upon the concept invented by Sengupta (Sengupta and Cumbal 2007, Cumbal and Sengupta 2005) and was developed into a commercially viable product by the research team at SolmeteX. The small size of the hydrous iron oxide particles and the high porosity of the polymer substrate ensure that reaction kinetics associated with As uptake are rapid and the As removal capacity is high. This means that a column of ArsenX™ only requires a contact time of between 2 and 3 minutes for optimum As uptake as opposed to the 5 minutes required for most granulated iron media. This translates to a small system footprint which is an important criterion for low volume water systems such as point-of-use (POU) and point-of-entry (POE) devices where space is often limited. An alternative iron oxide based hybrid media was also developed by SolmeteX, via the direct impregnation of an anion exchange resin bead using a concentrated solution of ferric chloride, FeCl₃ (Sylvester and Möller 2008). However, despite the fact that the product contained a high level of iron, field pilot testing showed the product to be relatively sensitive to the effect of As interferants in water making it unsuitable for commercial applications. Continued media development has resulted in a new, more effective second generation hybrid media, LayneRT. This product is similar to ArsenX™ but the base bead allows for a greater iron content than that of ArsenX™ and consequently an improved As adsorption capacity. A comparison of the properties of ArsenX™ and LayneRT is shown in Table 9.1.

Although the two media physically look very similar, the performance in dynamic column experiments is significantly different. This has been attributed predominantly to the more open, porous nature of the base bead in LayneRT which allows greater access to the hydrous iron oxide surfaces. The two media were evaluated in small column experiments in the laboratory using synthetic water. In addition to these two media, a recently developed hybrid media developed by Lanxess, Lewatit FO36, was also evaluated. This is a similar hybrid media in appear-

<table>
<thead>
<tr>
<th>Property</th>
<th>ArsenX™</th>
<th>LayneRT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer substrate</td>
<td>Strong base macroporous bead</td>
<td>Strong base macroporous bead</td>
</tr>
<tr>
<td>Iron content, mg g⁻¹</td>
<td>250</td>
<td>320</td>
</tr>
<tr>
<td>(dry weight)</td>
<td>58–61</td>
<td>61–63</td>
</tr>
<tr>
<td>Moisture content, %</td>
<td>300–1200</td>
<td>420–1200</td>
</tr>
<tr>
<td>Size range, µm</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Bulk density, g L⁻¹</td>
<td>Opaque mustard spheres</td>
<td>Chocolate brown spheres</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
arsenic but consists of iron oxide particles on a weak base anion exchange resin as opposed to a strong base anion exchange resin. Also, the particle size of the Lewatit FO36 media is a uniform 350 µm in diameter which is considerably smaller than the average diameter of ArsenX* or LayneRT, (500–600 µm). This may improve the reaction kinetics but is also likely to result in an increased pressure differential across the media bed in any system.

Small Pyrex glass columns (9 mm diameter and 14 cm length) containing about 8 mL (6–6.5 g) of media sample were used in the dynamic column runs. Synthetic NSF-53 challenge water (Table 9.2) spiked with 300 µg L⁻¹ As(V) at pH 7.5 ± 0.2 was pumped down flow through the column with an empty bed contact time (EBCT) of 3 minutes. All column experiments were run until a minimum of 10 µg L⁻¹ As(V) was detected in the column effluent. Samples of the effluent from the column were taken at regular intervals and analyzed for As in order to monitor As breakthrough.

Arsenic analyses were performed using a PSA 10.055 Millennium Excalibur instrument based on As hydride formation followed by atomic fluorescence spectrometry. Five As standards (2, 5, 10, 20 and 30 µg L⁻¹) in addition to the blank were used to calibrate the system. Samples with As concentrations greater than 40 µg L⁻¹ were diluted prior to analysis. At this linear range the accuracy of the analysis is ±1–2 µg L⁻¹. Any drift in the calibration curve was checked by re-running the As standards every 25 samples and recalibrating if necessary.

It can clearly be seen that the dynamic capacity of LayneRT is almost three times greater than that of ArsenX* (Fig. 9.1). The performance of Lewatit FO36 is intermediate between ArsenX* and the LayneRT. It is also interesting to note that the Lewatit FO36 has a lower As bleed than the LayneRT during the duration of the dynamic column studies. This fact

<table>
<thead>
<tr>
<th>Species</th>
<th>As</th>
<th>Na⁺</th>
<th>SiO₂</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>PO₄³⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>pH⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg L⁻¹</td>
<td>0.3</td>
<td>153</td>
<td>20</td>
<td>12</td>
<td>40</td>
<td>0.79</td>
<td>~150</td>
<td>179</td>
<td>0.12</td>
<td>47</td>
<td>9.0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

* pH adjusted to 7.5 using HCl.

Figure 9.1. As breakthrough curves of ArsenX, FO36 and LayneRT to 10 µg L⁻¹ using NSF-53 challenge water at pH ~7.5 in small scale laboratory column tests. Influent As(V) concentration was 300 µg L⁻¹.
can be attributed to the smaller bead size of this media which leads to more rapid adsorption kinetics and faster intraparticle As diffusion rates.


9.3 SYSTEM DESIGNS

A number of specific designs for simple, reliable water treatment systems have been developed around the desirable properties of the hybrid media.

9.3.1 Household systems

Simple, low-maintenance single faucet point-of-use (POU) applications and point-of-entry (POE) systems designed to treat the water for an entire house or a small building complex are very effective in maintaining As concentrations below the current United States drinking water limit of 10 µg L⁻¹. Since November 2005, 1,157 SolmeteX As removal systems designed around the ArsenX® (and more recently, LayneRT) As-removal media, have been installed. Due to the similar physicochemical properties of ArsenX® and LayneRT, the two media can be used in the POE and POU devices interchangeably.

The bulk of the SolmeteX household systems have been installed in the northeast of the United States in the New England area. In this region, more than 40% of the population relies upon private wells for their source of drinking water and there are large geographic areas affected by elevated As in the groundwater. Typically, the levels of As encountered are below 50 µg L⁻¹ but many wells contain As levels above 100 µg L⁻¹. The highest recorded level of As at a customer site found to date by the SolmeteX laboratory was 447 µg L⁻¹ at a private well in Epping, New Hampshire (Möller et al. 2009).

The SolmeteX POU system contains 4.5 L of media in a single column and is designed to treat a water flow of up to 2 gallons (7.6 liters) per minute (Figure 9.2). Depending upon the water chemistry, an operational life of several years can be expected since the average water use at a single faucet in the USA is only 10.9 gallons (41.2 liters) per person per day (AWWARF 2000). The standard POE system is a lead-lag device with each tank containing 1 cubic foot (28.3 liters) of media and is designed for flows up to 10 gallons (38 liters) per minute (Fig. 9.3). Each system is accompanied by a water monitoring program which has allowed SolmeteX to track the performance of the installed systems. For the POU systems, samples from the influent and treated water are periodically taken and analyzed at SolmeteX. The results data is provided to the customers and dealers so that any As breakthrough can be monitored and the systems replaced when they have expired. A similar program is also in place for the larger POE systems but in addition to the influent and treated water, a sample from between the two columns is taken. This allows the lead column to be replaced when As exceeding the MCL is detected at the midpoint of the system. When the lead column is replaced, the lag column is moved to the lead position and fresh media placed in the lag position ensuring maximum efficiency of operation while still maintaining As-free water from the system.

The life of the POE and POU systems strongly depends upon a number of factors including water pH, As concentration, As oxidation state, water consumption and competing species (e.g. silica, phosphate). To date, the longest operational POE system has processed 287,264 gallons (1,087,300 liters) of water over a period of almost three years with no As detected in the water exiting the lead column. This is equivalent to 38,400 bed volumes, based
on the volume of media in a single column. The influent As concentrations at this site ranged from 15–17 $\mu$g L$^{-1}$ over this time, with a water pH of 6.8. The water chemistry at this site is ideally suited to adsorption and a long bed life would be expected.

9.3.2 Small pre-engineered systems

For larger applications, SolmeteX has developed a range of pre-engineered systems (PES), designed for flows up to 300 gallons (1140 liters) per minute. These also use a lead-lag design and are intended for applications such as condominium complexes or small housing developments where a simple, robust system is required that needs minimal maintenance.
and generates no waste. A prototype PES system is shown in Figure 9.4. A similar system was installed at Turkey Hills Apartments, Connecticut in June 2007. It was designed to treat water at a maximum flow rate of 50 gallons (189 liters) per minute and operated smoothly with no problems for 14 months (~5,000,000 gallons) until As was detected above 10 µg L\(^{-1}\) after the lead tank. At this point, the media in the lead bed was replaced and the system reconfigured so that the old lead bed was in the lead position and the new media was in the lag bed. After this first media change-out in August 2008, this system has continued to run with minimal maintenance. The influent As concentration at Turkey Hills varied between 12 and 18 µg L\(^{-1}\) over this period according to the routine analyses performed by SolmeteX.

9.4 INTERFERING COMPONENTS AFFECTING ARSENIC ADSORPTION

The adsorption of As(V) and As(III) at iron hydroxide surfaces is mostly ligand exchange with Fe-OH\(_2^+\) and Fe-OH\(^-\) groups. Both adsorption mechanisms are strongly dependent on pH, but while the capacity for As(V) decreases as pH increases, the capacity for As(III) is relatively constant over the typical drinking water pH range of 6.5–8.5. In general, adsorption of As is the highest at lower pH values.

Silica typically has a strong interfering effect on the adsorption of As, especially at elevated pH values, due to silica polymerization and coating of the surface and the adsorption sites on the iron hydroxides. At neutral pH, silica is predominantly present as an uncharged Si(OH)\(_4\) molecule and will not be strongly attracted to the iron oxide surface. At higher pH values, however, significant dissociation and polymerization of silica occurs to produce negatively charged species, such as Si(OH)\(_3^+\), Si\(_2\)(OH)\(_5^-\) and other polymeric anionic species which are strongly bound to the iron hydroxide surfaces (Davis et al. 2002, Smith and Edwards 2005). The interfering effect of silica becomes particularly significant at pH values above 8.0 and SiO\(_2\) concentrations greater than 20 mg L\(^{-1}\) (Möller and Sylvester 2008).

Phosphate is another key water component that interferes with As adsorption. The affinity of iron oxide surfaces for phosphate is very similar to that for arsenate due to the similar aqueous chemistry of these two species. The dissociation constants for H\(_3\)AsO\(_4\) [As(V)] are
close to those of orthophosphoric acid, $\text{H}_3\text{PO}_4$. In general, phosphate can be expected to compete with As adsorption at a ratio of almost 2:1 (Meng et al. 2002, Michaud 2008).

Vanadium is present in most groundwaters at concentrations of 0.010 mg L$^{-1}$ and greater and is also adsorbed by many As selective media. Consequently, it competes with As for available adsorption sites on the iron oxide surfaces and elevated levels can decrease the As capacity of the media.

9.5 CONCLUSIONS

Hybrid As adsorption media have been shown to be excellent for use in small and medium systems. The operating data obtained on the installed systems have demonstrated that the units are reliable and the media has an acceptable As capacity over a wide range of water chemistries. However, system life has been found to be very variable due to variations in the water chemistry over a relatively narrow geographical area. Customer feedback regarding the installed units has been positive and operational problems associated with the POE, POU and PES systems have been minimal. Improvements to the core hybrid media are expected to increase system life and improve the economics of As removal.

ACKNOWLEDGEMENTS

The authors thank Debanjali Bagchi, Ed Morassi, Kevin Osborn and Dick Goulston (SolmetEX, Northborough, USA) for assistance in collecting the laboratory data and design of the POU, POE and PES systems and Victor Nigro Jr. (Stafford Springs, Connecticut, USA) for providing information on the PES system at Turkey Hills, CT.

REFERENCES


Section III
Membrane processes and applications in arsenic removal
CHAPTER 10

Review of membrane processes for arsenic removal from drinking water

Alberto Figoli, Alessandra Criscuoli & Jan Hoinkis

10.1 INTRODUCTION

Arsenic (As) is a natural tasteless and odorless element, existing in the earth’s crust at average levels of between two and five thousands micrograms per kg (parts per million). Arsenic is highly toxic to humans, who are exposed to it primarily from air, food and water.

The weathering of rocks leads to the release of As into different environments, such as soils, groundwater, rivers, and atmosphere.

Arsenic-related health problems were first recognized in the early 1980s in West Bengal, India, although that was first acknowledged a decade later in Bangladesh. However, acute and chronic exposure via drinking water has been also reported in other countries, especially Argentina, USA, India, Mexico, Mongolia, Thailand and Taiwan, where a large proportion of groundwater is contaminated with As at levels from 100 to 2000 µg L⁻¹.

The contamination of groundwater by As can be considered a serious threat to man all over the world. It can also enter the food chain, either through potable water or edible plants that have absorbed As (Mandal and Suzuki 2002). Human exposure is also caused by the presence of As in many foods, such as meat, fish, poultry, grain and cereals. However, in these foods, it is mainly present in organic forms, which are less toxic than inorganic As (i-As). Drinking water, after food, represents a secondary source of i-As in the human system (Caceres et al. 2005, Smedley et al. 2002).

Long-term exposure to i-As may cause a wide range of health effects, including skin lesions such as hyperkeratosis and pigmentation changes, circulatory disorders, diabetes and cancers of the bladder, lung, kidney and skin (National Research Council, 2001). Consequently, in recent years, authorities have taken a more stringent attitude to As in the environment and the new standard on the maximum contaminant level (MCL) of 10 µg L⁻¹ As in drinking water, recommended by the WHO (WHO 1998), was accepted both within the European Union (European Commission Directive 98/83/EC 1998) and in the USA by the EPA (US Environmental Protection Agency 2001). However, in some countries, such as Bangladesh, the MCL of As in drinking water is still 50 µg L⁻¹.

In order to comply with the new maximum contaminant level, numerous studies have been undertaken in order to improve established treatments or to develop novel treatment technologies for removing As from contaminated surface and groundwater. Among the available technologies applicable for water treatment, membrane technology has been identified as a promising technology to remove As from water, as reported in recent reviews of Uddin et al. (2008) and Shih et al. (2005).

10.2 ARSENIC SPECIES IN WATER

The chemistry of As is a very extensive subject. Arsenic occurs in both inorganic and organic forms in natural water. Inorganic As is the result of dissolution from the respective mineral phase, such as arsenalite (As₂O₃), arsenic oxide (As₂O₃) or realgar (As₂S₂); it may be present
in two oxidation states: arsenate [As(V)] or arsenite [As(III)] (Hem et al. 1992). Dominant As species are a function of pH and redox potential (Eh).

Arsenate is the thermodynamically stable form of the inorganic species and it generally predominates in surface waters. Arsenite is favored under reducing conditions, such as in anaerobic groundwater.

The chemical behavior of the two forms is different. Arsenite cannot be removed from water effectively. The effective removal of As from water requires the complete oxidation of As(III) to As(V).

In the pH range of 4 to 10, the As(III) compounds are neutral in charge, while the As(V) compounds are negatively charged. As(V) is found in arsenic acid $H_3AsO_4$ (Ning et al. 2002):

$$H_3AsO_4 \overset{P_{K_1}}{\rightleftharpoons} H_2AsO_4^- + H^+ \overset{P_{K_2}}{\rightleftharpoons} HASO_4^{2-} + 2H^+ \overset{P_{K_3}}{\rightleftharpoons} AsO_4^{3-} + 3H^+$$

where:

$$K_1 = 5.10^{-3} \quad pK_1 = 2.3$$
$$K_2 = 4.10^{-5} \quad pK_2 = 7.08$$
$$K_3 = 4.10^{-10} \quad pK_3 = 11.5$$

As(III) is found in arsenious acid $H_3AsO_3$:

$$H_3AsO_3 \overset{P_{K_0}}{\rightleftharpoons} H_2AsO_3^- + H^+ \overset{P_{K_2}}{\rightleftharpoons} HASO_3^{2-} + 2H^+ \overset{P_{K_1}}{\rightleftharpoons} AsO_3^{3-} + 3H^+$$

where:

$$K_0 = 6.10^{-10} \quad pK_0 = 9.2$$
$$K_2 = 1.10^{-14} \quad pK_1 = 12.3$$

The removal efficiency for elimination of As from water for As(III) is poor compared to that for As(V) by any of the conventional technologies.

In addition to geochemical factors, microbial agents can influence the oxidation state of As in water and can mediate the methylation of i-As to form organic As compounds. Microorganisms can oxidize arsenite to arsenate, reduce arsenate to arsenite or even to arsenine ($AsH_3$). Organic arsenical compounds, such as dimethylarsinic and methylarsonic acid, were reported to have been detected in surface water more often than in groundwater (Ning et al. 2002).

10.3 MEMBRANE PROCESSES

In general, the application of membrane techniques in environmental protection involves a number of advantages, principally the following:

- low energy consumption,
- no addition of chemical substances required,
- easy to scale up,
- separation carried out in a continuous mode,
- possibility to easily join membrane with other unit processes (hybrid processes),
- separation carried out in mild environmental conditions.
The intrinsic properties of membrane operations make them good candidates for reaching the goals of a process intensification strategy.

There are also some disadvantages, for example a decrease of capacity effected by concentration polarization and membrane fouling and the limited lifetime of membranes and their low selectivity for a given separation problem. Furthermore, membranes, in particular polymeric ones, are in many cases characterized by limited chemical or thermal resistance. However, continuous efforts in research are leading to significant improvements of the membrane performance.

Different membrane technologies are employed in As removal. Pressure-driven processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF) have been studied most commonly. The solution to be treated is usually passed across the filter membrane (crossflow), whereby the pressure gradient forces the water through the membrane, while retaining particulants down to solutes. Table 10.1 shows the properties of the different pressure-driven membrane processes. MF can be used to remove bacteria and fine particles, whereas UF can also retain colloids and viruses. Separation by MF and UF is usually described via mechanical sieving. NF and RO rely on rejection based on molecular size, in which the mass transport is commonly described by solution-diffusion models (Baker 2004). As far as ions are concerned, NF only has high rejection efficiency for multivalent ions. RO is also very efficient in rejecting all categories of ions including monovalent species. In membrane separation, electric fields and thermal energy can also be used as driving forces in techniques such as electrodialysis and membrane distillation, respectively. Studies on the treatment of water containing As by membrane distillation and, generally, by membrane contactors, are reported and discussed in section 10.3.3.

In many cases, one membrane process can be integrated with another one to produce water of even higher quality. In these processes, the membrane can be viewed as a barrier between contaminated and purified water streams. The separation of the two streams often allows for operation with no or minimal chemical water pre-treatment, which otherwise can form deleterious by-products. However, in physical membrane processes, inorganic anions are not destroyed. They are concentrated and the concentrate disposal can be costly and difficult to permit in many cases. Therefore, post treatment of the concentrate stream or hybrid membrane-assisted technologies capable of converting anionic contaminants to harmless products is highly desirable.

One of the major advantages of membrane processes over adsorption is that removal efficiencies are relatively less affected by the chemical composition and pH of the feed.

The feasibility of a combination of flocculation and microfiltration has been studied in several publications. Brandhuber and Amy (1998) investigated the efficiency of As removal by MF coupled with ferric chloride pre-treatment in bench-scale studies. Chwirka et al. (2004), Ghurye et al. (2004), Wickramasinghe et al. (2004) and Han et al. (2002), also studied coagulation with ferric chloride and ferric sulfate and MF for removal of As. The studies demonstrated that a membrane pore size of around 0.2 μm is usually necessary in order to

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Typical pore size (nm)</th>
<th>Operating pressure (bar)</th>
<th>Flux range $1 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>50–10000</td>
<td>&lt;2</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>1–100</td>
<td>1–10</td>
<td>10–50</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>&lt;2</td>
<td>10–25</td>
<td>1–12</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>&lt;2</td>
<td>15–80</td>
<td>0.02–1.5</td>
</tr>
</tbody>
</table>
achieve a high degree of As removal, whereby the removal effectivity depends on coagulant
dose, pH and ferric counter-ions.

Table 10.2 shows the performances of As removal by various membrane processes, based
on the work reported by Kartinen and Martin (1995).

In 2005, Shih et al. illustrated an interesting overview of As removal by pressure driven
membranes. In this chapter, the two membrane techniques that show the higher removal
arsenic [As(V)] efficiencies (>95%), reverse osmosis (RO) and nanofiltration (NF), will be
described in detail. Figure 10.1 shows a typical model of an RO and NF system. The per-
formance of membrane contactors for treating water containing As will be also presented
and discussed in this chapter.

10.3.1 Reverse osmosis (RO)

Reverse osmosis is a well-established technology in desalination of brackish water and sea-
water, to produce potable water. Most RO membranes have an asymmetric structure with
a thin dense top polymer layer supported by a porous sublayer which gives the membrane
mechanical stability.

The RO membranes discriminate on the basis of molecular size and solubility and due to
the properties of the separating dense layer, with very high (close to 100%) rejection of low-
molecular weight solutes such as inorganic salts or small organic molecules.

The treated water stream may lack the right balance of dissolved minerals, however it
can be easily readjusted by adding natural salts. Another disadvantage of RO is the energy
consumption, due to the high-pressure need to force the solvent (water) through the dense
membrane. Moreover, the osmotic pressure has to be overcome. In the case of seawater, for
example, the osmotic pressure is about 25 bar. The choice of the membrane material is also

<table>
<thead>
<tr>
<th>Removal efficiencies (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total As</td>
</tr>
<tr>
<td>RO</td>
</tr>
<tr>
<td>NF</td>
</tr>
<tr>
<td>ED</td>
</tr>
<tr>
<td>UF</td>
</tr>
</tbody>
</table>

Figure 10.1. Typical scheme of RO and NF membrane system.
very important, since it must have a high affinity for the solvent (water) and a low affinity for the solutes.

The separation of toxic anionic species can be strongly influenced by the presence of non-toxic components, such as hardness (i.e. Ca$^{2+}$) and SO$_4^{2-}$ anions, which affect the ionic strength and therefore the osmotic pressure. Therefore, the contaminated water usually requires pre-treatment. In this context, the possibility of integrating different membrane operations is becoming quite attractive as a way of reducing the pretreatment costs and increasing the performance of the process. Membrane processes such as MF, UF and also NF are now increasingly employed as pre-treatment of the contaminated water before RO (Criscuoli and Drioli 1999).

Several studies have been performed on As removal by RO technology; the main results achieved with RO membranes are shown in Table 10.3.

Table 10.3. Main performance of RO membrane in treating arsenic-containing waters.

<table>
<thead>
<tr>
<th>Membrane and manufacturer</th>
<th>Water origin</th>
<th>Rejection (%)</th>
<th>Flux (kg m$^{-2}$ h$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DK2540F, DESAL</td>
<td>Arsenic spiked DI water, natural water</td>
<td>60–85</td>
<td>96</td>
<td>–</td>
</tr>
<tr>
<td>TFC4921, Fluid System</td>
<td>Pilot studies at various groundwater sites (USA)</td>
<td>65</td>
<td>96</td>
<td>8.9</td>
</tr>
<tr>
<td>TFC4820-ULPT, Fluid System AG 4040 4040 LSA-CPA2</td>
<td>Idem</td>
<td>75</td>
<td>99</td>
<td>8.9</td>
</tr>
<tr>
<td>Different membranes and manufactures</td>
<td>Idem</td>
<td>70</td>
<td>99</td>
<td>8.9</td>
</tr>
<tr>
<td>ES-10 (polyamide), Nitto Electric Japan</td>
<td>46–84</td>
<td>96–99</td>
<td>–</td>
<td>Ning et al. (2002)</td>
</tr>
<tr>
<td>NTR729HF (PVA), Nitto El. Japan</td>
<td>Groundwater (Japan)</td>
<td>75–90</td>
<td>95</td>
<td>4.1</td>
</tr>
<tr>
<td>HR3155 (TCA), Toyobo Co. (Japan)</td>
<td>Groundwater, Utah (USA)</td>
<td>Total As reject.</td>
<td>99</td>
<td>–</td>
</tr>
<tr>
<td>Different membranes and manufactures</td>
<td>Groundwater</td>
<td>Total As reject. up to &gt;99 average 80.2</td>
<td>–</td>
<td>Walker et al. (2008)</td>
</tr>
<tr>
<td>LE, Dow Water Solutions XLE, Dow Water Solutions</td>
<td>Arsenic spiked local tap water</td>
<td>&lt;80</td>
<td>&gt;95</td>
<td>40$^1$ 60$^2$</td>
</tr>
</tbody>
</table>

$^1$not reported; Pressure P, $^2$7.5 bar, $^3$4.5 bar, $^4$10 bar, $^5$15.2 bar.
Amy et al. (1998) performed bench-scale RO experiments using a membrane of type DK2540F manufactured by DESAL. The experiments comprised single element testing and flat sheet on lake water and on spiked deionized water. The results show very high removal efficiency for arsenate (up to 96%), but low removal efficiency for arsenite (60–85%).

Waypa et al. (1997) observed that thin-film composite-type membranes exhibit better removal efficiency of As than the cellulose-acetate type. Thin-film composite membrane also showed higher permeate flow rate and needed much lower applied pressure.

In a pilot-scale study, Brandhuber et al. (1998), reported removal efficiencies of 96–99% for As(V) and 46–84% for As(III). Pre-oxidation would guarantee, then, better removal.

Kang et al. (2000) used two types of RO membranes, ES-10 (polyamide) and NTR729HF (polynyl alcohol), manufactured by the Nitto Electric Industrial Co., Japan. The removal efficiency of arsenite was lower than that of arsenate over the pH range of 3–10. The arsenate removal by using ES-10 membrane was over 95% over all the investigated pH range. The removal of arsenite by ES-10 exceeded 75% in the pH range 3–7 and increased sharply by further increase of pH (from 7 to 10). The removal of arsenate using NTR729HF varied from around 80% at pH 3, jumping to 95% with increasing pH up to 10. The removal efficiency of arsenite was about 20% at pH 3, 5, and 7. These results indicate that the effect of solution pH indeed affects the removal efficiency of As.

Ning et al. (2002) concluded in an overview publication that in the commonly high arsenic oxidation state, As(V), arsenic can be effectively removed by RO, whereas the As(III) removal needs special attention by operating RO at sufficiently high pH.

The Environmental Technology Verification Program operated by the US EPA used the TFC-ULP RO membranes from Koch Membrane Systems to test the removal of As from drinking water. The average As concentration of the feed water was 60 µg L⁻¹ and the membrane system reduced the total As concentration to around 0.9 µg L⁻¹ in the permeate water. This result showed total As removal efficiency of around 99% (Koch 2001).

Gholami et al. (2006) examined a model water with As(V) by using a commercial RO membrane (2521 TE, CSM, Co. Korea) in a pilot plant set-up. The effects of As concentration, pressure, pH and temperature on the membrane performance were studied. The results showed that under optimal conditions (13–14.5 bar, 0.2–0.5 mg L⁻¹ As(V), 25–30°C and pH 6–8) the removal efficiency was −99%. Walker et al. (2008) examined the performance of different household RO systems and factors associated with As removal efficiency in 59 households in Lahontan Valley (Western Nevada, USA). Lahontan Valley is an area where naturally-occurring As concentrations commonly exceed 100 µg L⁻¹ in groundwater. In 2001, As concentrations in 89 of 100 wells sampled in Lahontan Valley exceeded the MCL of 10 µg L⁻¹. The study came to the conclusion that household RO systems can be an effective method to treat As contaminated water, with the majority of the RO systems removing more than 90% of the As. However, treatment with RO failed to lower As concentrations to safe levels when As in the well was very high. The study demonstrated that the proportion of As(III) present in groundwater was the most important factor associated with the efficiency of As removal. Several RO systems removed less than 50% of the As when As(III) was the dominant As species. However, the authors concluded that a limitation of the study was that inadequate data were available to determine the importance of other potential factors in the rejection efficiency, such as chemical factors, membrane types, and system age and maintenance history.

Deowan et al. (2008) used two types of low pressure polyamide RO membranes XLE and LE (both manufactured by Dow) in a laboratory work to study the rejection of As(V) and As(III). They prepared a model water using As spiked local tap water. It was shown that the As rejection was significantly higher for As(V) (exceeding 95%) than for As(III) (usually below 80%). With regard to As(V) the LE membrane can comply with the WHO recommended MCL 10 µg L⁻¹ up to a feed concentration of 2000 µg L⁻¹, whereas for the XLE the As values in permeate exceed the MCL at a feed concentration of around 800 µg L⁻¹. As for As(III), the As values in permeate can only be kept below the MCL up to a feed concentration of 50 µg L⁻¹. Both membranes showed a negligible pH and temperature dependency.
To date, RO processes have mostly used bulky and sophisticated units with high energy consumption. Considering the situation in developing and newly industrializing countries, such as low annual income and low electrical popularization, it seems difficult to apply traditional RO technology. Therefore, Oh et al. (2000) investigated the rejection of As by using HR3155 membrane (Toyobo Co., Ltd) made of cellulose triacetate, coupled with a bicycle pump operated at 40 bar. It was shown that the As(V) removal efficiency was over 95% and the As(III) rejection was around 55%.

Geucke et al. (2009) tested a small-scale marine RO desalinator with three different technical membranes (size 6.35 × 53.5 cm) for As(V) and As(III) removal using As-spiked local tap water. All the tested membranes were manufactured by Dow: tap water (TW), seawater (SW) and low energy (XLE) membranes. The RO pump of this system makes use of an energy recovery system taking advantage of stored energy in the high-pressure reject water that is typically wasted in conventional systems. Hence this energy is kept in the system, resulting in less work to achieve fresh water. The energy consumption per liter treated water is given between 8 and 9 Wh L⁻¹. Moreover the recovery rate is kept at only 10%, which makes the membrane process robust with regard to scaling or fouling. With two of the tested membranes (TW, SW) As(V) rejection was so high, that the permeate water quality complied with the MCL up to feed concentration of 2400 µg L⁻¹. In the case of As(III), only feed concentrations below 350 µg L⁻¹ resulted in permeate concentration below the MCL (for the SW membrane). The removal for the low-energy XLE was in agreement with the results of Deowan et al. (2008). The work of Geucke et al. (2009) aimed to eventually develop a simple and cost-effective RO water filter for developing and newly industrializing countries.

10.3.2 Nanofiltration (NF)

Nanofiltration (NF) history dates back to the seventies when RO membranes with a reasonable water flux operating at relatively low pressures were developed. Those types of “low-pressure reverse osmosis membranes” are today known as nanofiltration membranes. The main application of NF is the drinking water industry and NF membranes have been developed for softening. Hardness removal is still one of the major purposes of nanofiltration today (Van der Bruggen and Vandecasteele 2003).

NF membranes are the same as the RO membranes but with a network structure that is more open. The pressures used in NF are therefore lower than in RO, in the range of 10–20 bar. The NF membranes are usually asymmetric and negatively charged at neutral and alkaline drinking water pH. This enhances the ion rejection since the separation of anions is based not only on the different rates of their diffusion through the membrane, but also on repulsion (Donnan exclusion) between anions in the solution and the surface groups, which is higher for multi-valent anions. Therefore, similar ion rejection to RO membranes can be achieved together with higher water fluxes.

On the other hand, the NF process is much more sensitive than RO to the ionic strength and pH of source water. The membrane surface charge is mainly due to anion adsorption from water rather than fixed charged groups (as in the case of ion exchange membranes), therefore it depends strongly on bulk anion concentration (Velizarov et al. 2004).

The main works dealing with the removal of As by NF mainly from groundwater and synthetic water are discussed and reported in this section.

Urase et al. (1998) investigated the effect of pH on rejection of different species of As by using a flat sheet aromatic polyamide NF membrane supplied by Nitto-Denko Co. Ltd. Arsenate rejection was almost constant (around 90–95%) in the pH range of 3 to 10, while rejection of arsenite increased with pH, being 50% at pH 3 and 89% at pH 10. At pH 10, most of the arsenite is present in a mono-valent anion form, while at low pH the neutral form dominates because the pKa value of arsenite is 9.1. This is the same reason why As(III) was not effectively removed in another study (Vrijenhoek et al. 2000) while As(V) removal reached 90%.
The removal of As from synthetic water and surface water was investigated by Sato et al. (2002). These authors studied the performance of three types of NF membranes, ES-10 (polyamide), NTR-7250 (polyvinyl alcohol) and NTR-729HF (polyvinyl alcohol), supplied by Nitto Electric Industrial Co. (Japan), for As removal. In synthetic solutions, As rejection increased with As retentate concentration. Arsenic was removed at about 93–99% from synthetic feed waters containing between 100 and 382 µg L\(^{-1}\) As(V), resulting in permeate As concentrations of about 5 µg L\(^{-1}\). Under studied conditions, As rejection was independent of transmembrane pressures, crossflow velocity and temperature. In surface water, the mean rejection of As(V) was 95% and the co-occurrence of dissolved inorganics did not significantly influence As rejection.

In this study, the difference of the As removal efficiency between synthetic water and groundwater by nanofiltration membrane was studied. In both cases, the removal efficiency of As(V) was almost the same in all different studied membranes. In particular for synthetic water, the membrane NTR-7250 showed an As(III) rejection value of around 10%, the NTR-729HF a value of 20% and the ES-10 a rejection value of 80%. This is in agreement with their NaCl removal efficiency, which is the highest for the

Table 10.4. Main performance of NF membrane in treating arsenic-containing waters.

<table>
<thead>
<tr>
<th>Membrane and manufacturer</th>
<th>Water origin</th>
<th>Rejection (%)</th>
<th>Flux (kg m(^{-2})h(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF70 4040B, Film Tec, Dow Chemical</td>
<td>Pilot studies at various groundwater sites (USA)</td>
<td>50% 99%</td>
<td>–</td>
<td>Chwirka et al. (2004)</td>
</tr>
<tr>
<td>HL-4040F1550, Desal</td>
<td>Idem</td>
<td>20% 99%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4040-UHA-ESNA Hydraulics</td>
<td>Idem</td>
<td>30% 97%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ES-10, Aromatic polyamide (Nitto Electric Industrial, Japan)</td>
<td>Groundwater spiked with 0.6 mg L(^{-1}) As (Japan)</td>
<td>50–89% 90–97%</td>
<td>–</td>
<td>Urase et al. (1998)</td>
</tr>
<tr>
<td>NF45 Filmtec (Dow Chemical)</td>
<td>Synthetic water</td>
<td>– –90% 28.8</td>
<td></td>
<td>Vrijenhoek et al. (2000)</td>
</tr>
<tr>
<td>ES-10, (Nitto Electric Industrial, Japan)</td>
<td>Synthetic water and groundwater</td>
<td>60–80% 95% 60–80% &gt;95%</td>
<td>–</td>
<td>Sato et al. (2002)</td>
</tr>
<tr>
<td>NTR-729HF, (PVA), (Nitto Electric Industrial, Japan)</td>
<td>Synthetic water and groundwater</td>
<td>10–23% 91–94% 10–23% 95%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NTR-7250 (PVA), (Nitto Electric Industrial, Japan)</td>
<td>Synthetic water and groundwater</td>
<td>10% 86% 10% &gt;90%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>192-NF 300, Osmonics</td>
<td>Model water, surface water</td>
<td>– –93–99% 95% 39.6 37.1</td>
<td></td>
<td>Saitúa et al. (2005)</td>
</tr>
<tr>
<td>NF270 (Dow Chemical) NFc (Dow Chemical)</td>
<td>Natural groundwater</td>
<td>– 90%</td>
<td>53.9–62.6 7.3–10.9</td>
<td>Košutić et al. (2005)</td>
</tr>
<tr>
<td>NF-90 (Dow Chemical) NF-200 (Dow Chemical)</td>
<td>Tap water + As(III) and As(V)</td>
<td>65% 98%</td>
<td>51.6 58.8</td>
<td>Uddin et al. (2007)</td>
</tr>
<tr>
<td>NF90 (Dow Chemical) N30F</td>
<td>Synthetic water + As(V)</td>
<td>– &gt;91%</td>
<td>50 30–40</td>
<td>Figoli et al. (2009)</td>
</tr>
</tbody>
</table>

P = \(16\) bar, \(6.8\) bar, \(7.2\) bar.
ES-10 (99.6%) and the lowest for the NTR-7250 (70%). Removal of As(III) by all membranes also showed the same efficiency in both synthetic water and groundwater. Removal efficiencies of As(III) by NTR-729HF and NTR-7250 were <22%. However, removal efficiency of As(III) by ES-10 was higher than 75% in both water samples. Consequently, the removal of both As(V) and As(III) were not affected by source water compositions.

Saitúa et al. (2005) studied the effect of operating conditions in the removal of As(V) from water by using a spiral-wound thin film composite polyamide membrane (192-nf300) supplied by Osmonics Inc. It was found that As rejection is independent of transmembrane pressure, cross-flow velocity and temperature. Moreover, As rejection increased with As retentate concentration and removals ranging from 93–99% and 95% were obtained for synthetic feed waters and surface waters, respectively.

The removal of As from natural groundwater was also investigated by Košutic et al. (2005) by using thin-film polyamide NF membranes, NF270 and NFc (Filmtec Corporation, Dow Chemical Comp., Midland, MI). Rejection factor values of both NF membrane types for the sodium dibasic arsenate were higher (80–90%) than those for the sodium chloride (53–65%) and lower than those for sodium sulfate (>99%).

Recently, Uddin et al. (2007) studied the removal efficiency of two commercial polyamide NF membranes (NF90 and NF200) for As(III) and As(V), by analyzing the effect of the operating conditions on the rejections achievable. The feed stream consisted of tap water to which arsenate and arsenite were added. In all tests, As(V) was rejected better than As(III) and the highest removals obtained were above 98% for As(V) and around 65% for As(III).

Similar results were obtained by Figoli et al. (2009) who reported the study of As removal from synthetic water, prepared starting from As pentaoxide, by using two commercial nanofiltration membranes (NF90 and N30F). For both membranes the removal efficiency for As(V) was influenced by the operating conditions such as temperature, transmembrane pressure, pH and feed water concentration. In particular, the As rejection of the NF90 membrane was higher if compared with the N30F membrane (above 91%) for all the operating conditions investigated. The As concentration in the permeate of the NF90 membrane always resulted lower than the Bangladesh MCL (50 µg l⁻¹) while the EPA MCL (10 µg l⁻¹) was reached for initial feed As concentration in the range 100–600 µg l⁻¹. As a common trend, it was observed that an increase of pH and a decrease of operating temperature and As feed concentration determined a higher efficiency of As removal for both membranes, whereas the TMP slightly affected the As rejection of the N30F membrane (it reduced at higher TMP).

From all these studies, summarized in Table 10.4, it is evident that the efficiency of the arsenate removal from water, using NF membranes, can vary depending on the membrane module properties and the feed water composition. For this reason, further investigation on novel membrane modules and different As(V) feeds are of interest for the development of an arsenic removal strategy using NF.

10.3.3 Membrane contactors (MC)

Beside the application of “conventional” pressure-driven membrane operations for treating water containing As, in recent years the development of membrane contactors has opened other “ways of action”. Until now, few studies have been made in this field but it represents an interesting starting point for future research.

Membrane contactors are characterized by the fact that the membranes used are micro-porous hydrophobic or hydrophilic and do not take part in the separation process, simply acting as an inert barrier between phases, allowing their contact at each pore mouth while avoiding their mixing (Drioli et al. 2006). Using membrane contactors it is possible to carry out operations such as liquid-liquid extractions, gas-liquid mass transfers, and membrane/osmotic distillation.

Their potential for treating As containing waters has been investigated in several articles. Martinez Perez et al. (2007) used a PVDF hydrophobic microporous membrane (pore size of
0.22 µm) for extracting As(V) from 2M H\textsubscript{2}SO\textsubscript{4} aqueous solutions. The membrane micropores were impregnated with trioctylphosphine oxide (Cyanex 921) and tests were performed at different operating conditions and with different stripping solutions (H\textsubscript{2}O, NaOH, HCl, H\textsubscript{2}SO\textsubscript{4}, Na\textsubscript{2}SO\textsubscript{4}). Authors found that up to 94% of As(V) can be transferred in 2 hours by using Na\textsubscript{2}SO\textsubscript{4} as stripping phase.

Prapasawat et al. (2008) used hollow fiber supported liquid membranes for extracting both As(III) and As(V) from sulfate media. A commercial module—LiquiCel Extra-Flow from CELGARD LLC—equipped with hydrophobic polypropylene membranes (pore size, 0.03 µm) was used for tests. Cyanex 923 in toluene was inside the membrane micropores and acted as extractant, while water was the stripping solution. The extraction increased with the sulfuric acid content in the feed, whereas it reached a maximum at a Cyanex 923 concentration of 30% (v/v). In all cases, As(V) was extracted better than As(III) and the highest removal obtained was of about 45% and 37%, respectively. Figure 10.2 shows the principle used in both works for carrying out the extraction.

The recovery of purified water through the application of ‘direct contact membrane distillation’ (DCMD) was carried out by Macedonio et al. (2008), starting with water solutions containing both As(III) and As(V). Tests were carried out on the commercial module MD020CP-2N supplied by Enka Microdyn and equipped with polypropylene capillaries (pore size: 0.2 µm; porosity: 70%). Experiments were performed at different operating conditions by sending the feed solution (warmer) inside the fibers, while a distillate stream (colder) flowed in counter-current mode at the shell side. The trans-membrane flux increased with the feed temperature (investigated range: 25–34°C) and feed flowrate (investigated range: 100–250 L h\textsuperscript{−1}), and it did not depend on the As concentration (300–1200 µg L\textsuperscript{−1} was the concentration range considered). On average, the trans-membrane flux was of the order of 0.6 kg h\textsuperscript{−1} m\textsuperscript{−2}. In all cases the permeate did not contain As, the process, therefore, allowed to achieve a 100% rejection. Figure 10.3 depicts the DCMD process.

Qu et al. (2009) also applied direct contact membrane distillation for treating water containing As. The experiments were carried out using a module equipped with self-made capillary polyvinylidene fluoride (PVDF) membranes (pore size: 0.15 µm; porosity: 80%). Feeds containing both As(III) and As(V) at high concentrations were fed inside the capillaries while the permeate circulated at the shell side. All tests made indicated that the DCMD process had higher removal efficiencies of As than pressure-driven membrane processes, leading to an As content in the permeate lower than 10 µg L\textsuperscript{−1} until the concentration of the As in the feed was below 40 and 2000 mg L\textsuperscript{−1} for As(III) and As(V), respectively. The highest trans-membrane flux (20.90 kg h\textsuperscript{−1} m\textsuperscript{−2}) was obtained at a feed temperature of 70°C and at a feed velocity of 0.96 m s\textsuperscript{−1}.

The fact that this membrane operation is able to provide a permeate free of As even when As(III) was present in the feed solution is of extreme importance because it means that with membrane distillation the pre-oxidation step to convert As(III) into As(V) can be avoided, with consequent benefits in terms of reduced environmental impact (no use of chemicals for the oxidation step) and reduced complexity of the overall system.

More recently, membrane contactors have also been applied as a different means for oxidizing As(III) to As(V) simply using air as the oxidant agent (Criscuoli et al. 2010). The idea behind this was to try to develop a system able to efficiently oxidize As(III) without using the “conventional” oxidation agents, such as chlorine, ozone, hydrogen peroxide, etc. These present safety issues and have costly and dangerous implications for people and environments. Figure 10.4 shows the model of the system used.

Tests were carried out on a commercial microporous flat membrane (by Membrana GmbH) in polypropylene (pore size: 0.2 µm; membrane area: 40 cm\textsuperscript{2}) by varying different operating conditions. In parallel, experiments with “traditional” systems were made in order to compare the efficiency of the membrane contactor unit. Membrane contactors proved to be more efficient, giving 100% of oxidation after 16 hours. They are, therefore, interesting units to develop for obtaining the desired oxidation by using air. Table 10.5 summarizes the results achieved for the different devices after 8 hours of test.
10.4 CONCLUSIONS

Research on the development of appropriate As removal technologies for drinking water has increased in past years, mainly due to the lowering of the maximum contaminant level of As (from 50 to 10 µg L\(^{-1}\)) by the European Council Directive 98/83/EC and USEPA (2001). Membrane systems, both as single units or in an integrated scheme, can be employed to reach the new standard.
Table 10.5. Comparison among the oxidation systems analyzed. 

\[ Q_{air} = 37 \text{ L h}^{-1}; P_{air} = 1 \text{ bar}; Q_{liq} = Q_{\text{max}} = 40 \text{ L h}^{-1}; C_{As(iii)} = 0.25 \text{ mg L}^{-1}; \]

\[ V_{\text{feed}} = 40 \text{ mL}; \text{pH} = 3; T = 15^\circ \text{C}. \]

<table>
<thead>
<tr>
<th>System</th>
<th>Oxidation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane contactors</td>
<td>75</td>
</tr>
<tr>
<td>Stirrer</td>
<td>20</td>
</tr>
<tr>
<td>Bubbling</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 10.6. Main performance of membrane contactors in treating arsenic-containing waters.

<table>
<thead>
<tr>
<th>Membrane contactor type</th>
<th>Main results</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supported liquid membranes</td>
<td>Up to 94% of As(V) removal in 2 hours of test</td>
<td>Martinez Perez et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>As(V) and As(III) removals of about 45% and 37%, respectively</td>
<td>Prapasawat et al. (2008)</td>
</tr>
<tr>
<td>Direct contact membrane distillation</td>
<td>100% removals of both As(III) and As(V). Average trans-membrane flux of 0.6 L h(^{-1}) m(^{-2})</td>
<td>Macedonio et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>Arsenic content in the permeate &lt;10 (\mu) g L(^{-1}) for a broad range of high concentrated feeds [up to 40 mg L(^{-1}) for As(III) and up to 2000 mg L(^{-1}) for As(V)]; highest flux at 70°C and 0.96 m s(^{-1}) of 20.90 kg h(^{-1}) m(^{-2})</td>
<td>Qu et al. (2009)</td>
</tr>
<tr>
<td>Air-water membrane contactor</td>
<td>100% As(III) oxidation using air as oxidizing agent</td>
<td>Criscuoli et al. (2010)</td>
</tr>
</tbody>
</table>
Table 10.7 summarizes the findings from the different publications and offers a guideline for As removal via membrane treatment.

In As removal by membrane technology, the operation conditions such as membrane material, water source, and pH value of solution, affect the As removal efficiency. In particular, in RO and NF processes, on the basis of literature results, the removal efficiency for As(V) is reported to be remarkably higher than for As(III) by using membrane processes. Therefore, the use of an oxidizing agent is necessary for increasing the As removal rate if the As in the source water is primarily present as As(III). Preliminary studies on oxidation by membrane contactors using air as the oxidizing agent seem to be encouraging. This membrane process, once optimized, could represent an interesting solution for carrying out the oxidation step without the use of toxic/dangerous compounds.

Since membrane distillation is able to reject both As(III) and As(V) with the same efficiency (100%), the development of MD units with higher trans-membrane fluxes and lower energy demand would also represent a research of interest for the future. The further improvement of this membrane operation will allow to overcome the NF and RO drawback of low As(III) rejection, avoiding the pre-oxidation step.

Finally, the integration of different membrane operations could become an increasingly attractive alternative to the traditional water treatment approach, allowing the limits of the single units to be overcome and enhancing the overall performance of the process as a result.

REFERENCES


Table 10.7. Evaluation of different membrane techniques for arsenic removal.

<table>
<thead>
<tr>
<th>As type</th>
<th>MF</th>
<th>UF</th>
<th>NF</th>
<th>RO</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>_1</td>
<td>_1</td>
<td>_2</td>
<td>+/o</td>
<td>++</td>
</tr>
<tr>
<td>As(V)</td>
<td>_1</td>
<td>_1</td>
<td>_+</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

+++ very good, + good, or possibly effective, – not recommended.
1 viable option only with precipitation/coagulation as pre-step.
2 Pre-oxidation of As(III) to As(V) can achieve better performance.
3 Technique still mainly available at lab scale.


CHAPTER 11

Arsenic removal by small-scale reverse osmosis units

Jan Hoinkis, Christian Pätzold & Jochen Bundschuh

11.1 INTRODUCTION

Over the past three decades, the occurrence of high concentrations of arsenic (As) in drinking water has been recognized as a severe global public-health concern (Bhattacharya et al. 2002, Mandal and Suzuki 2002, Ng et al. 2003). The global As-contamination scenario has changed considerably in recent years, with the discovery of new As affected sites. The delayed health effects of exposure to As, the lack of common definitions and of local awareness, as well as poor reporting in affected areas are all major problems in determining the extent of the arsenic-in-drinking-water problem (WHO 2008).

Arsenic is one of the most toxic elements that exists. Humans may be exposed to As through food, water and air. Particularly, As exposure caused by groundwater used for drinking in different parts of the world has emerged as an issue of great concern. Its adverse effects depend strongly on the dose and duration of exposure. Specific dermatological effects are characteristic of chronic exposure to As. Dermatological features are melanosis (pigmentation) and keratosis (rough dry papular skin lesions). Chronic exposure to As may also cause reproductive, neurological, cardiovascular, respiratory, hepatic, haematological and diabetic effects in humans (National Research Council 1999). Inorganic As can cause skin, bladder and lung cancer (National Research Council 2001).

With regard to the toxic effects of As on humans and other living organisms, it is necessary to take into account the permissible level of As in drinking water and its chemical speciation when establishing the regulatory standards. The WHO guideline value adopted for As in drinking water is 10 µg L⁻¹ (WHO 2008). This became effective in the European Community Member States by the Council Directive from 5/12/1998. On January 22, 2001, the US Environmental Protection Agency (USEPA) adopted a new standard for As in drinking water at 10 µg L⁻¹, replacing the old standard of 50 µg L⁻¹ (USEPA 2008).

In areas where the drinking water supply contains unsafe levels of As, the main concern is to find a safe source of drinking water that complies with the national and international drinking standards for affected communities. In this regard, the issue is not only to supply As-free drinking water, but also to provide microbiologically safe water without any other contaminants (e.g., pesticides, heavy metals).

In most cases there may be a variety of technology options that can provide communities with sustainable and cost-effective safe drinking water. However, in all cases, the technologies should meet several basic technical and socioeconomic criteria such as:

- Production of the required water quality and quantities;
- Robustness and operational safety;
- No adverse effect on the environment;
- Economic feasibility;
- Institutional capacity (production and delivery of materials, training etc.);
- Social acceptance.
11.2 OBJECTIVES OF THIS CHAPTER

It is the purpose of this chapter to report on experimental results with two small-scale technical RO units for As removal from drinking water. To this end, laboratory tests were conducted using different commercially available RO membranes and As-spiked local tap water. The experiments provide a basis for developing a simple, low-cost RO desalinator for rural areas in developing countries, which can be operated decentrally by sustainable energy sources. This work was part of a project funded by the European Commission in the Asia Pro Eco Programme dealing with innovative treatment of drinking and industrial water (INNOWA 2007).

11.3 ARSENIC CHEMISTRY

In soils and natural waters, As typically occurs as weak triprotic oxyacids in the +3 and +5 oxidation states such as arsenic acid $H_{3}AsO_{4}$ and arsenu acid $H_{2}AsO_{4}^{-}$. Arsenous acid $H_{2}AsO_{3}$ dominates in reducing environment at wide range of pH values while the deprotonated $H_{3}AsO_{4}$ forms only at pH > 9.0. In oxidized environments, arsenic acid is present as $H_{2}AsO_{4}^{-}$ (pH < 7) or as $HAsO_{4}^{2-}$ (pH > 7). Arsenic acid species can form relatively stable, inner-sphere surface complexes with rock and soil constituents containing ferrous, manganic or aluminum oxy-hydroxides. The strong adsorption of As(V) on rock and soil minerals explains its lower environmental mobility. However, the neutral trivalent species bond weakly with inorganic sorbents. The trivalent As species are therefore of great environmental concern because of their high mobility and toxicity compared to As(V) compounds. Moreover, the removal efficiency of As(III) is usually lower compared to that of As(V) by any of the conventional As removal technologies.

11.4 MEMBRANE TECHNOLOGY

11.4.1 General aspects

Membrane filtration is a physical process, which typically relies on an imposed pressure gradient to force water through the membrane, while retaining particulate down to solutes (see Fig. 11.1). A variety of membrane techniques, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), may be used for As removal (for overview see Chapter 10 of this book, Figoli et al.). NF and RO have the advantage over MF and UF that they use very “dense” membranes in such a way that only a few ions and molecules can pass through the membrane; most of the others are rejected, resulting in a very high water quality. In recent years, a new generation of RO and NF membranes have been developed that are less expensive and operate at lower pressures.

11.4.2 Reverse osmosis

To date, RO membrane filtration systems have mostly used bulky and sophisticated units with high-energy consumption, which are not suitable for application on a small scale in rural areas of developing countries. However, most of the documented experience in drinking-water production using RO has been with large treatment plants in developed countries. Chapter 10 of this book (Figoli et al.), Shih (2005) and Uddin et al. (2007) give (among other membrane techniques) a review of published research work on RO for As removal. Most of the published findings on As removal deal with laboratory and small pilot research. Some time ago several companies brought small-scale marine reverse osmosis units (known as watermakers) to the market. They are applied to produce drinking water from seawater.
on boats (for overview, see Nauticexpo 2009). It is a well-proven technology, which works reliably at remote locations under difficult conditions (e.g., high salt concentration). Most of these systems have been specifically designed in terms of energy efficiency and productivity. Some of them can be powered by sustainable energy sources, such as PV or wind wheels, or can be operated manually.

11.5 EXPERIMENTAL WORK

11.5.1 Analytical method

A method in line with DIN 38405 D12 (German Standard) has been applied for As analysis. Dissolved As(V) and As(III) is converted to arsine AsH₃ by chemical reduction with KI and SnCl₂. Arsine gas is stripped into a silver diethyldithiocarbamate (SDDC) pyridine solution, forming a colored complex of arsine. The solution can subsequently be analyzed by spectrophotometry at 525 nm. In this work, a Merck Spectroquant Nova 60 spectrophotometer was applied. The standard deviation of this method had been observed as ±1 µg L⁻¹.

A liquid As(V) standard (1000 mg L⁻¹) purchased from the company Merck served as the parent solution. Arsenic trioxide As₂O₃ in powder form, also supplied by Merck, was used for the preparation of the As(III) parent solution (350 mg L⁻¹) in line with DIN 38405 D12. The arsenic trioxide was dried for 24 hours before preparing the standard solution. 0.462 g of arsenic trioxide, As₂O₃, was dissolved with 12 mL of NaOH (2 mol L⁻¹); the solution was subsequently neutralized with sulfuric acid. Finally, the solution was filled up to 1000 mL with DI water. The As(V) and As(III) parent solutions were used to spike local tap water and to prepare calibration curves.

11.5.2 Water quality

All the experiments were conducted with local tap water. The quality of the local tap water used for the experiments is summarized in Table 11.1. In order to prepare the required As-feed water, it was spiked with the parent solution of As(V) and As(III). Besides As rejection, overall salt rejection and permeate flux were also determined.
11.5.3 Materials and methods

The experiments were carried out with two technical RO units. A multi-purpose membrane testing device from the University department was used (see Fig. 11.2), supplied by Osmo Membrane Systems (OSMO 2009). The unit is fitted with a housing for a 2540 spiral wound module. Within this project a FILMTEC™ XLE supplied by Dow was applied (Dow XLE 2540 datasheet, 2009). The feed is supplied to the RO module from tank T01 with the centrifugal pumps P01 and P02 and recirculated back to T01. A small amount of water samples were taken for analysis, with the recovery kept insignificantly low. The tank T02 served as a chemicals storage tank for cleaning purposes. All data was collected by data acquisition with a PC.

A small RO desalinator type “Power Survivor™ 160E”, supplied by the Swiss company Katadyn was also used (Katadyn 2009). It is applied in marine drinking-water production on small boats. It is a robust unit that is simple to install and easy to operate and maintain (see Fig. 11.3). The membrane housing is fitted with a 2521 spiral wound module.

The “Power Survivor 160E” watermaker consists of a high-pressure, positive-displacement 316 stainless steel pump. The pump is powered by a 12 VDC electric motor. An oil-bath gearbox (drive assembly) converts the rotary motion of the electric motor to a reciprocating, linear motion for driving the pump piston. The technical data of the unit is summarized in Table 11.2. A 20 L vessel served as the feed tank. The concentrate and permeate streams were recirculated back to the feed tank. The pressure was read out at pressure gauges before and after the membrane housing. All indicated pressure values are arithmetic averages of the inlet and outlet pressure. The RO pump makes use of an energy recovery system, taking advantage of stored energy in the high-pressure reject water that is typically wasted in conventional systems. The pressurized reject water is recirculated to the back side of the piston to aid the next stroke. This energy is kept in the system, resulting in less work to achieve fresh water.

The reverse osmosis experiments were conducted with the FILMTEC™ low-pressure membrane XLE–2521 from Dow Water Solutions (Dow XLE 2521 datasheet, 2009). In addition, two other membranes were applied in the Power Survivor 160E (Dow TW and Dow SW datasheet, 2009):

- TW30 - 2521
- SW30 - 2521

All the membranes that were used during the experiments were thin-film polyamide composite membranes. XLE is an extra low-energy brackish water element for municipal and industrial applications. TW is an element for home drinking water, while SW is an element for desalination in marine applications. A hand-held unit WTW 325 was used for pH measurement and a WTW Cond 315i was utilized for electrical conductivity measurement.

Table 11.1. Average water parameters of local tap water in the city of Karlsruhe, Germany (Stadtwerke Karlsruhe 2008).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>mg L⁻¹</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg L⁻¹</td>
<td>113</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg L⁻¹</td>
<td>19.8</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>µS cm⁻¹</td>
<td>591</td>
</tr>
<tr>
<td>Hydrogen carbonate</td>
<td>mg L⁻¹</td>
<td>320</td>
</tr>
<tr>
<td>Iron</td>
<td>mg L⁻¹</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg L⁻¹</td>
<td>9.8</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg L⁻¹</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg L⁻¹</td>
<td>10.3</td>
</tr>
<tr>
<td>Sulfate</td>
<td>mg L⁻¹</td>
<td>57.3</td>
</tr>
</tbody>
</table>
11.5.4 Experiments with the technical 2540 module

All As removal tests were conducted with the Dow FILMTEC™ XLE at 25°C with As-spiked local tap water (see Table 11.1) under different conditions with regard to permeate water flux, pressure and As concentration. In Figure 11.4a, the permeate flux for the applied tap water is plotted over the applied transmembrane pressure in the investigated range. The permeate water flux at 7.5 bar, which is 47 L m⁻² h⁻¹, is in good agreement with the standard flux published by Dow, which is 51.3 ± 20% L m⁻² h⁻¹ for 500 mg L⁻¹ NaCl solution at 6.9 bar 25°C and 15% recovery (Dow XLE 2540 datasheet, 2009). Figure 11.4b gives the pressure dependency between 7.5 and 20 bar at As(V) feed concentration of 500 µg L⁻¹. The graph shows a slight decrease of the As in permeate with increasing pressure. In the whole range, the permeate concentration is below the MCL of 10 µg L⁻¹, showing a rejection of more than 99%. Figure 11.4c shows As(V) concentration in the permeate over the feed concentration at 10 bar up to 1200 µg L⁻¹. As can be seen, As permeate concentration can be kept below the MCL up to feed concentration of about 800 µg L⁻¹, showing
This result is in line with other laboratory-scale experiments carried out within the INNOWA (2009) project.

Arsenic in groundwater can also occur in its trivalent form, so experiments using As(III) were also carried out. Experience from previous bench-scale trials has shown that As rejection in the trivalent state is much less than for the pentavalent compound (see Deowan et al. 2008). Few points were therefore measured at a feed concentration of 100 µg L⁻¹. Figure 11.4d shows that As(III) concentration in permeate is above the MCL across the whole pressure range. The rejection rate is only 80–90% and hence generally much lower than for As(V). This agrees with preliminary lab-scale results using flat-sheet membranes (Deowan et al. 2008) and is in line with many other experimental findings (see chapter 8 of this book, Figoli et al.). The result can be explained as follows. All the membranes consist of polymers with negatively charged groups. A charge exclusion effect enhances the rejection of negatively charged ions such as As(V). In the observed pH range, As(III) is only neutrally charged and hence is rejected less.

11.5.5 Experiments with the Katadyn 160E

The experiments with the small-scale energy-optimized Katadyn 160E were conducted with three commercial 2521 RO modules provided by Dow (see also Geucke et al. 2009). Besides

---

Figure 11.3. The RO desalinator “Power Survivor 160E” (Katadyn 2009).

<table>
<thead>
<tr>
<th>Output</th>
<th>Power supply</th>
<th>Consumption</th>
<th>Weight</th>
<th>Membrane size (inch)</th>
<th>Dimension (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.4 L h⁻¹</td>
<td>12 VDC</td>
<td>18 A</td>
<td>16.8 kg</td>
<td>2.5” / 21”</td>
<td>Pump: 44.5 × 34.3 × 15.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Membrane housing: 64 × 8.9</td>
</tr>
</tbody>
</table>
the low-pressure XLE, which was tested within the technical unit (see section 11.5.4), two additional “denser” membranes (Dow TW, Dow SW) were investigated since the XLE had not shown satisfactory performance with As(III).

Due to the energy recovery system of the desalinator, the recovery in the system is fixed and cannot be changed, while the pressure is self-adjusting. It changes slightly with different membranes and temperatures. The tests were conducted under 4.5, 9.6 and 15.2 bar (XLE, TW and SW). The permeate water flow was 34, 32 and 31 l h⁻¹ for the XLE, TW and SW membranes, respectively. The feed flow was kept constant at 300 l h⁻¹, resulting in a recovery rate of approximately 10%. The low recovery rate avoids the membrane being clogged by scaling or fouling. Taking into account the membrane area of 1.2 m² per module, the calculated flux is 28.3, 26.7 and 25.8 l m⁻² h⁻¹, respectively. The power consumption was calculated from the measured water flow, current consumption and voltage. The power consumption increases slightly from 8.2 Wh l⁻¹ (XLE) to 9.0 Wh l⁻¹ (SW). This is in line with the increasing membrane tightness of the XLE, TW and SW membranes.

Figure 11.5 shows the three curves of As(V) in permeate, depending on the As(V) feed concentration. The findings for the Dow XLE are in line with the results from the technical RO unit (see Figure 11.4c). This membrane can only comply with the MCL up to a feed concentration of 900 µg L⁻¹. However the Dow TW and SW display an outstanding performance across the whole investigation range and comply fully with the MCL of 10 µg L⁻¹ even at feed concentration as high as 2200 µg L⁻¹.

The rejection rate for As(III) is generally much lower than it is for the As(V) (Fig. 11.6). As for the As(V), the Dow XLE shows the lowest rejection rate. At feed values of about 50 µg L⁻¹ the As in the permeate is higher than the MCL of 10 µg L⁻¹. The best performance is given by Dow SW. The permeate values are still lower than the MCL with this membrane at feed concentrations up to 300 µg L⁻¹.
The findings of experiments conducted in two small-scale technical modules indicate that the As rejection is significantly higher for As(V) than for As(III) for all of the tested RO membranes. This is in agreement with preliminary laboratory-scale screening tests and other published results. As far as the tested low-pressure RO membrane is concerned, the findings for both technical units are in good agreement. However, the As rejection performance of As(III) for this type of membrane is low. The performance of two other “denser” membranes tested in one of the technical modules is improved. As for As(III), the As values in permeate can be kept below the MCL of 10 µg L\(^{-1}\) in the tightest seawater membrane up to a feed concentration of approximately 300 µg L\(^{-1}\), whereas pentavalent As can be retained efficiently up to a feed concentration higher than 2000 µg L\(^{-1}\) without crossing the MCL level in permeate. This is also fully in accordance with the results of preliminary lab-scale screening tests. Overall, the DOW SW seawater membrane shows the best performance in As removal.

11.6 SUMMARY AND OUTLOOK

Figure 11.5. As(V) in permeate over As(V) in feed for different Dow membranes.

Figure 11.6. As(III) in permeate over As(III) in feed for different Dow membranes.
The findings indicate that, when treating underground water with high values of As(III), a pre-oxidation step might be recommended. Another viable option could be to treat the permeate by a polisher with As adsorbing media.

The results of these lab-scale investigations will serve as a preliminary step for subsequent field tests in Bangladesh and India using natural water. The findings of this work will eventually contribute to the development of a simple and cost-effective membrane RO water filter for developing and newly industrializing countries. Finally, with regard to viability, the total cost per liter drinking water has been estimated at around 0.01 Euro, due to the long life of the desalinator and the membranes.

ACKNOWLEDGEMENTS

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REFERENCES


CHAPTER 12

Potential application to remove arsenic by functional polymers in conjunction with membranes and electrooxidation processes

Bernabé L. Rivas & Julio Sánchez

12.1 INTRODUCTION

Arsenic (As) is toxic to all living organisms, thus creating potentially serious environmental concerns. The tremendous environmental impact of this highly toxic contaminating agent urges the scientific community to improve the methods for determining the level of As in water and food as well as to develop appropriate technologies to remove traces of As from drinking water, wastewaters and industrial effluents in order to reach acceptable levels.

The main As species present in natural waters are arsenate (oxidation state V) and arsenite ions (oxidation state III) related to the arsenic acid (H$_3$AsO$_4$) and arsenous acid (H$_3$AsO$_3$), respectively. However, the forms, concentrations, and relative ratios of both As(V) and As(III) in water vary significantly depending on changes in input sources, and environmental conditions such as pH and redox potential.

Several methods are used to remove traces of As from water including ion exchange resins, adsorption using especially modified chelating compounds, chemical precipitation, coagulation, and membrane processes such as nanofiltration or reverse osmosis. However, as mentioned above, the redox- and pH-controlled diversity of As species in water results in complex selectivity issues, which have yet to be fully addressed.

The first step in an efficient extraction process strongly depends on the ability to convert As(III) species into more easily extractable As(V) forms (Xu et al. 2002). The main obstacle to this conversion lies in the high irreversibility of the electrochemical oxidation of As(III) into As(V) at bare electrodes. This obstacle is the technological key which remains to be solved. In particular, in aqueous media, and in the entire pH range, the anodic oxidation of As(III) is hindered by the solvent’s oxidation resulting in a very low As(V) yield. This problem could be solved by catalytic systems that can promote the oxidation of As(III) to As(V) in the solvent’s stability domain, which is thermodynamically possible. The oxidation of As(III) could be quantitatively applied in the treatment of polluted water, by using catalysts or electrode materials possessing appropriate catalytic properties.

12.2 OVERVIEW OF POLYMERS FOR REMOVING CONTAMINANTS

In most cases, the liquid-liquid extraction, adsorption, precipitation, and other methods based on two-phase distributions can be used to separate inorganic pollutant species from both industrial waste liquids and natural waters. Although many of these methods have been developed and used successfully, application problems can emerge. Some problems are related to heterogeneous reactions and transfer phases, while others stem from the need for additional procedures, e.g. re-extraction, desorption and dissolution of solid concentrates that could contaminate the sample and complicate the analysis.

Many polymeric materials in different systems play a key role in removal of contaminating species. Water insoluble polymers are applied in the recovery of metals from aqueous solutions (Rivas et al. 2001a, b, Dicinoski et al. 2000, Trochimczuk et al. 2000). There are various natural and synthetic products that show ion exchange properties. Organic resins
are the most used as ion exchangers, where their main advantages are high chemical and mechanical stability as well as a high ion exchange capacity. These resins are widely used for water purification and demineralization and are also applied in chemical synthesis, biomedicine, pharmaceutics, food processing, hydrometallurgy, industry and agriculture (Dominguez and Benak 2001). Compared with traditional adsorbents, ion exchangers have many advantages, including the simplification of the overall preparation and ability to be manufactured in the form of filters or tissues, improving their efficiency in contact with the medium and increasing their reaction and regeneration capacity.

The development of cationic polyelectrolytes is of great importance due to their enormous potential in various fields. In addition to their use in the separation of species from water, cationic polyelectrolytes are also used in the formation of polyelectrolyte complexes with metals to be used in the modification of silica for the separation of anionic species by chromatography (Pirogov et al. 1998, Krokhin et al. 2002). These polyelectrolytes are also important in the biological field in the formation of polycomplexes used in bioseparation, biocidal compounds, and materials for medical use (Rivas et al. 2003b, Hu et al. 2003, Grapski and Cooper 2001).

Water-soluble polymers (WSP) are commercially available or can be synthesized by different routes. For use in technological applications, they should have an easy synthesis route, water solubility, adequate molecular weight distribution, chemical stability, and high affinity towards species in solution. Therefore, water-soluble polymers are increasingly being used in a variety of processes, such as water purification, oil removal, dye removal, and mineral processing. In these processes, water-soluble polymers can be used as flocculants, emulsifiers, extractants, dispersants, etc. (Hara 1993).

12.3 POLYMERS WITH THE ABILITY TO REMOVE ARSENATE

Several technologies for As removal use either membranes or polymeric adsorbents. The polymeric sorbents appear in two forms: beads or fibers. The use of fibers has become interesting as they offer higher specific surface area, smaller diameter and better elasticity. Additionally, they come in the form of filaments and other textile articles and these materials can be regenerated and reused (Zhang et al. 2008). Among the recently developed materials for As removal are the water soluble cationic polyelectrolytes that are combined with membrane filtration to remove arsenates from aqueous solutions.

While polyelectrolytes have charged functional groups, or are easily ionizable in aqueous solution, chelating polymers (polychelatogens) have functional groups capable of forming coordinating bonds with metal ions in solution. The majority of the investigated ligands present in the polychelatogens are amines, carboxylic acids, amides, alcohols, amino acids, pyridines, tioureas or imines. The most usual procedure to synthesize these polymers is radical polymerization. With a suitable choice of monomers, a polymer with determined characteristics (e.g., water solubility, bonding ability and selectivity) can be synthesized (Pizarro et al. 2007). These macromolecules can be made from homo or copolymers, and they can possess one or more functional groups in the chain. The polymers containing amino groups have been extensively studied by ultrafiltration, especially the functionalized polyethyleneimine (Rivas et al. 2003a). The most studied ligands in the case of polyelectrolyte are amines, carboxylic acids, sulfonic acids, amides, alcohols, amino acids, etc. (Geckeler 2001). Polyelectrolytes have long-range electrostatic interactions, in which the counterion tends to not specify its polyelectrolyte union and is able to move through the polymeric chain. In the short-range interactions, the counterions bind to a specific site that is associated with one or more charged groups (Manning 1984). In some cases, the intrachain interactions predominate when a dominant polymer with constant ligand concentrations exists and the distances between them are within a small range in the polymer chain (Tsuchida and Abe 1982, Geckeler et al. 1980).
Potential application to remove arsenic by functional polymers in conjunction

Both intrinsic and extrinsic variables may affect polymer interactions. The intrinsic variables, which depend on the nature of the functional groups attached to the polymer chain, determine the structure and copolymer composition. Molecular weight, polydispersity, and the degree of cross-linking also affect the interactions of polyelectrolyte versus ions in solution. The extrinsic variables that affect polymer interactions are the pH value of solution, ionic strength, and the nature of the ion in solution.

The cationic polyelectrolytes consisting of quaternary ammonium salts have a high capacity to link to oxoanions of arsenate. This interaction is between the nitrogen of the ammonium group (positively charged) and the oxygen of arsenate anion, forming a dipole according to Figure 12.1.

12.4 OVERVIEW OF LIQUID-PHASE POLYMER-BASED RETENTION TECHNIQUE

A large number of water-soluble and functional hydrophilic polymers have shown a high capacity to separate ions in solution through a membrane. This method is known as liquid-phase polymer-based retention (LPR) (Spivakov et al. 1985, Rivas et al. 2003a), and it involves the use of an ultrafiltration membrane that separates the ionic species interacting with the functional groups of water soluble polymers with high molecular weights, thus preventing them from passing through the membrane (see Figs. 12.2 and 12.3).

In the LPR experiments, the fractions of high molecular weight polymers are used in combination with membranes with a lower exclusion limit to assure that the macromolecule remains in the feed phase.

The most important physical properties of membranes are interfacial tension and interfacial adsorption. In this context, the van der Waals interactions, hydrogen bonds, electrostatic effects, charge transfer, and dipole moment play a critical role in membrane functioning. The membranes are usually made up of polycarbonate or cellulose esters, polyamides and polysulfones. The typical ultrafiltration system consists in an ultrafiltration cell, membrane, magnetic stirrer, flow switch, reservoir, and pressure source.

![Figure 12.1. Electrostatic interaction of quaternary ammonium group of cationic polyelectrolyte with oxoanion arsenate (Rivas et al. 2006).](image1)

![Figure 12.2. Ultrafiltration principle (Rivas et al. 2003a).](image2)
In order to systematize the study of polymer interactions with ions in solution using the ultrafiltration technique, two quantities should be defined: (1) retention and (2) filtering factor. Retention ($R_z$) is the fraction of ions remaining in the cell:

$$R_z = \frac{M_z}{M_z^{init}}$$  \hspace{1cm} (12.1)

where $M_z$ is the absolute amount of ions that are in the feed phase and $M_z^{init}$ is the absolute amount of ions at the start of the experiment. The subscript $z$ refers to ion valence.

The filtration factor ($Z$) is the ratio between the total volume of permeate and the volume of retentate:

$$Z = \frac{V_f}{V_o}$$  \hspace{1cm} (12.2)

Depending on the experimental data, a graph in which $R_z$ is represented as a function of $Z$ can be drawn. This chart is called the retention profile.

Different separation types can be performed using the LPR technique. In the washing method, the polymer solution is placed into the cell with an ion solution and is ultrafiltrated by eluting with pure solvent. This method is similar to the batch method diafiltration. In the enrichment method, the polymer solution is placed inside the cell and ultrafiltrated, creating a flow through the cell of liquid with an ion (Rivas et al. 2003a).

### 12.5 APPLICATION OF LPR IN ARSENATE REMOVAL

In recent times, some polymers based on ammonium salts have been studied using the LPR technique to determine their ability to remove As species in solution (Rivas et al. 2006, 2007a, b, c, 2009). The principal advantage of the method is that it is performed in homogeneous media and largely avoids the mass transfer or diffusion phenomenon that occurs in heterogeneous methods. LPR experiments use fractions of polymers with high molecular weight (100,000 Da) to interact with the anions. Poly(ether sulfone) membranes, which have an exclusion limit of 10,000 Da are used. A solution of polymer/arsenate is placed in the cell and is then washed with distilled water at constant volume and certain pH.

Water-soluble cationic polymers containing different exchanger counterions have been recently synthesized and studied (see Fig. 12.4), showing different retention capabilities. Polymeric structures with quaternary ammonium salts containing different counterions (such
Potential application to remove arsenic by functional polymers in conjunction

as methyl sulfate, chloride, bromide, and hydroxide) showed different capacities to remove arsenate from aqueous solution because the type of counterion in quaternary ammonium group influences the retention ability. However, all the polymers remove arsenates ions more efficiently at pH 8 than that at pH 6 to 4.

The inorganic species As(V) are known to coexist in an aqueous medium according the following equilibria (Rivas et al. 2007a):

\[
\begin{align*}
H_2\text{AsO}_4^- &\rightleftharpoons H^+ + H_2\text{AsO}_4^2^- & (pK_a = 2.22) \\
H_2\text{AsO}_4^- &\rightleftharpoons H^+ + \text{HAsO}_4^{2-} & (pK_a = 6.98) \\
\text{HAsO}_4^{2-} &\rightleftharpoons H^+ + \text{AsO}_4^{3-} & (pK_a = 11.53)
\end{align*}
\]

The effect of pH on arsenate retention has been studied. The removal of As(V) in the form of mono- and divalent oxoanions was determined by LPR with different cationic polyelectrolytes using the washing method in an acidic to basic pH range.

The results were expressed in a retention profile (see Fig. 12.5) for different water-soluble cationic polyelectrolytes at different pHs. In general, the As(V) is more easily retained at pH values between 6 and 9 rather than at a lower pH. At pH 3, monovalent anionic species (H₂AsO₄⁻) are in equilibrium with the coupled salt. The functional group polarity is assumed to be a parameter that controls the selectivity of ion exchange. At pH 6, the oxoanionic monovalent (H₂AsO₄⁻) and divalent (H₃AsO₄²⁻) species exist in equilibrium. The polymer interaction capacity is due to the presence of a positively charged quaternary ammonium group. These interactions are produced through the ion exchange between the counterion chloride of the quaternary ammonium salt and the arsenate anions. This explanation is corroborated by the polymers higher retention capacity at basic pH of predominantly divalent species. In this study, we used the washing method in the mole ratio polymer: As(V) of 20:1.

![Figure 12.4](image)

*Figure 12.4. Structures of the water-soluble extractant polyelectrolytes. Poly[3-(acryloylamino)propyl]trimethylammonium chloride, P(CIAPTA), poly[2-(acryloyloxy)ethyl]trimethylammonium chloride, P(CIAETA), poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate, P(SAETA), poly(ar-vinylbenzyl)trimethylammonium chloride, P(CIVBTA), poly(4-vinyl-1-methyl-pyridinium)bromide, P(BrVMP), and poly(diallyl dimethylammonium) chloride, P(CIDDA).*
The polymer removed 80–100% of the arsenate ions at pH between 6 and 9, where arsenate is an oxoanionic divalent species; at pH 3, where the species of monovalent arsenate prevail, the removal is lower than 60%.

Other assays with copolymer poly[(3-methacryloylamine) propyl]trimethyl ammonium chloride-co-acrylic acid, P(CIMPTA-co-AA), performed with different mole ratios (1:1, 1:2 and 2:1) showed differences in the arsenate removal ability (Rivas et al. 2006).

Poly[2-(acryloyloxy)ethyl]trimethylammonium chloride, P(CIAETA), and poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate, P(SAETA), have similar structures except the chloride (Cl⁻) and methyl sulfate [(OSO₂CH₃)⁻], respectively. All assays were performed using the washing method and the mole ratio polymer:arsenate of 20:1. Both polymers studied were capable of interacting and removing arsenates species at pH 8 (see Fig. 12.6). The polyelectrolytes with chlorides, such as P(CIAETA), showed greater arsenate removal...
ability than found for P(SAETA). Polymers with chloride anion have a high capacity for removal of arsenate oxoanions (100%) at basic pH.

These differences can be attributed to the easy release of the chloride anion in comparison with the methyl sulfates, which are associated with the quaternary ammonium groups. Monovalent ions (such as methyl sulfates) are strongly retained by hydrophobic sites of quaternary ammonium groups due to the difference in size, solubility and polarity. Larger and polarized ions have been reported to disrupt water local structure, allowing an easy association with the quaternary ammonium group. Specifically, monovalent ions will be polarized and better retained in comparison with chloride due to the high hydrophobicity of the anion exchanging site.

The hydrophobic nature of the monovalent anion \((\text{OSO}_3\text{CH}_3)^{-}\) that contains a methyl sulfate group (Rivas et al. 2007b), may explain this arsenate removal efficiency.

The removal was optimized by changing the mole ratio polymer:arsenate. Using the washing method with the polymers P(CIAETA) and P(CIVBTA), the influence of concentration was studied in comparison with arsenate. Different mole ratios of polymer: As(V), 31:1, 20:1, 10:1, 6:1 and 3:1 were prepared at pH 8. The results of retention R (%) of As(V) with a filtration factor of \(Z = 10\) for P(CIVBTA) and P(CIAETA) by the washing method are presented in Table 12.1. The results indicate an optimum mole ratio of 20:1 for the complete arsenate removal. The polymer presents a high recovery efficiency for the As(V) species even at high As concentrations.

Lately, a series of water-soluble polychelates have been prepared and used for one-step retention of As(III) from solution. The complex of poly (acrylic acid)-Sn, 10 and 20% by metal weight, introduced a high retention of species of As(III) at pH 8, however the molar ratio polychelate: As(III) was 400:1 (Rivas et al. 2007c).

![Figure 12.6](image_url)

Figure 12.6. Retention profile of As(V) by (a) P(CIAETA) and (b) P(SAETA) at different pH, using 30 mg L\(^{-1}\) of As(V) and mole ratio of (20:1) polymer:As(V) (1.6 \(\times\) 10\(^{-4}\) mol:8 \(\times\) 10\(^{-6}\) mol).

<table>
<thead>
<tr>
<th>Mole ratio polymer:As(V)</th>
<th>Mole of polymer</th>
<th>Mole of As(V)</th>
<th>P(CIVBTA) R(%), pH 8</th>
<th>P(CIAETA) R(%), pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(31:1)</td>
<td>(7 \times 10^{-5})</td>
<td>(2.25 \times 10^{-4})</td>
<td>70.0</td>
<td>84.0</td>
</tr>
<tr>
<td>(20:1)</td>
<td>(7 \times 10^{-5})</td>
<td>(3.45 \times 10^{-6})</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>(20:1)</td>
<td>(2 \times 10^{-5})</td>
<td>(1.00 \times 10^{-5})</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>(10:1)</td>
<td>(7 \times 10^{-6})</td>
<td>(6.90 \times 10^{-6})</td>
<td>88.0</td>
<td>59.0</td>
</tr>
<tr>
<td>(6:1)</td>
<td>(7 \times 10^{-6})</td>
<td>(1.12 \times 10^{-6})</td>
<td>77.0</td>
<td>60.0</td>
</tr>
<tr>
<td>(3:1)</td>
<td>(7 \times 10^{-6})</td>
<td>(2.25 \times 10^{-6})</td>
<td>54.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>
The enrichment method was used to determine the maximum arsenate retention capacity for the polymer. This method consists in using the maximum concentration of the polymer with arsenate anion to reach saturation. The maximum retention (enrichment method) is defined as:

\[
C = \frac{(M \times V)}{P_m} \quad (12.6)
\]

where, \(P_m\) is the amount of polymer (g), \(M\) is initial concentration of As(V) (mg L\(^{-1}\)), \(V\) is the filtrate volume (volume set) containing As(V) [mL] that passes through the membrane. The maximum retention of \(C\) was calculated in the total volume of filtrate (300 mL).

Assuming a quantitative retention of As(V), the enrichment factor \(E\) is a measure of the binding capacity of the homopolymers and is determined as follows:

\[
E = \frac{(P \times C)}{M} \quad (12.7)
\]

The results of the P(ClaETA) assays using the enrichment method to determine the maximum capacity of retention \(C\) for arsenate anions in aqueous solutions at pH 8 are shown in Figure 12.8.

![Figure 12.7. As(V) Retention profile by (a) P(CIVBTA) and (b) P(ClaETA) at pH 8, using different mole ratios of polymer:As(V).](image1)

![Figure 12.8. Maximum retention capacity C for P(CIAETA) and P(SAETA) at pH 8. Mole ratio 0.8 mmol of polymer (repeat units) per 4 mmol of As(V).](image2)
In similar conditions, the values of C were 142 µg g⁻¹ for P(CIAETA) and 75 µg g⁻¹ for P(SAETA) and the total volume of filtrate was 300 mL. Assuming quantitative retention of As(V), the enrichment factor was determined \[ E = 3.5 \text{ for P(CIAETA)} \text{ and } E = 2.5 \text{ for P(SAETA)} \]. The type of anion exchanger was an important factor in arsene retention (Rivas et al. 2007b).

### 12.6 OVERVIEW OF THE ELECTROCATALYTIC OXIDATION OF ARSENITE

Arsenic extraction efficiency strongly depends on the ability to convert As(III) species into the more easily extractable As(V) forms as the first step. The main, unsolved obstacle to this conversion lies in high irreversibility of the electrochemical oxidation of As(III) to As(V) at bare electrodes (Cox and Kulesza 1984). In particular, in aqueous media and for the entire pH range, the anodic oxidation of As(III) is hindered by the solvent oxidation, resulting in a very low As(V) yield. As(III) oxidation could be quantitatively applied for the treatment of polluted water by using catalysts or electrode materials possessing appropriate catalytic properties.

It has been established that noble metals and metal oxides can be used for this purpose, especially in the form of particles of nanometer size. Metal nanoparticles feature unique properties that arise from their high surface area and confinement of electronic states (El-Sayed 2001). The properties of materials with nanometric dimensions are significantly different from those of atoms or bulk materials. The versatility of physical and chemical properties thus afforded by metal nanoparticles makes them promising as devices with practical application in many fields, and especially in catalysis (Bonnemann and Ryan 2001). In many instances, the ability to exploit nanoparticle catalytic properties will require the morphologically controlled formation and/or highly ordered arrays of nanoparticles (Sergeev and Petrukhina 1996).

For this purpose, polymer-nanoparticle assembly provides an effective method for the controlled creation of nanocomposites. In addition to their role in assembling nanoparticles, functionalized polymers can be used to control structural parameters such as particle size and distribution. The surface of nanoparticles plays an important role in catalysis, being responsible for their selectivity and activity. Therefore, the characteristics of the stabilizing polymer (its functionalities and nanostructuring properties) are of great importance because they principally determine the state of the nanoparticles’ surface. It is obvious that future applications will require improved two- and three-dimensional manipulation of materials formed from the dispersion of nanoparticles in functionalized polymer matrices.

Electrochemical procedures for the synthesis of metal nanoparticles, although less diffuse than chemical routes, have proved to be powerful and versatile means of preparing nanoparticles for a wide range of noble and transition metals (Reetz and Helbig 1994). Moreover, electrochemical methods have proved to be effective in incorporating metal particles in either pre-deposited polymers or in growing films (Gangopadhyay and De 2000). This is especially true in the case of electron-conducting polymers modified by noble metal nanoparticles synthesized for electrocatalytic applications.

The general procedure is based on the electroreduction of metal cations or salts onto polymer film-modified electrodes. However, so far, this procedure has mainly produced materials with metal inclusions no smaller than 10 nm. The main problem is that a longer electrolysis time results in the growth of large particles as opposed to nucleating new ones. Thus, the metal particles formed are generally large, have a wide size distribution, and are largely confined to the polymer surface and unevenly distributed within the polymer matrix (Sih and Wolf 2005). Several different approaches have been tested to improve the size distribution and reduce the particle size, where these are mainly based on the use of a complexing polymer matrix or on the deposition of chemically pre-synthesized nanoparticles. However, it has been suggested that the pulsed electrochemical deposition of metal would provide control over the metal particle loading and size.
In addition to their role in assembling nanoparticles, the polymeric matrix will be responsible for increased chemical (e.g. coordinating effects) and/or physical (e.g. steric effects) stability as well as improved processability.

12.7 ELECTROLYSIS OF ARSENITE AT THE PREPARATIVE SCALE USING MODIFIED CARBON FELT ELECTRODES AND MONITORED IN-SITU BY ANALYTICAL ELECTRODES

The amount and concentration of the initial solution was 35 mL and $0.75 \times 10^{-3}$ mol L$^{-1}$ of As(III). The working electrode in the electrolysis was a C/poly-Pt$^0$ modified carbon felt macroelectrode. The voltage applied was between $+0.6$ V and $+0.8$ V vs. Ag/AgCl. The stirring during the electrolysis was 1000 rpm. The pH was measured at each point of electrolysis.

The charge applied $Q$ was determined by complete oxidation of As(III) to As(V) and the absolute amount of analyte according to Coulomb's law. The theoretical charge was calculated: $Q = \text{number electrons} \times 96500 \times \text{As(III) concentration}$ and the concentration of As(III) remnant was monitored by the in-situ control of the advancement of the electrocatalytic process to follow through the conversion of As(III) into As(V) using platinum disc electrode and C/poly-Pt$^0$ analytical modified electrode (see Fig. 12.9).

The analytical current of the As(III) remnant shows well-defined peaks for each measurement at $+0.7$ V with reproducibility and linearity in these conditions.

The electrolysis was performed on the carbon felt modified macroelectrode C/poly-Pt$^0$ in presence of organic polyelectrolytes. The poly(diallyldimethyl ammonium) chloride was used as support electrolyte. A mole ratio (polymer: As(III)) (20:1) was added to the voltammetric cell. The oxidation process took place in one compartment of the large cell with a total volume 35 mL for the initial controlled voltage ($+0.6$ V) over $0.75 \times 10^{-3}$ mol L$^{-1}$ of As(III) and initial pH of 9.5, which was periodically measured as the electrolysis advanced. The theoretical charge required for the two-electron oxidation of As(III) to As(V) for these conditions was 4.3 Coulomb. The experiment was monitored by the in-situ control of the advancement of the electrolysis for (a) C/poly-Pt$^0$ analytical modified electrode and (b) Pt disc analytical electrode. Since there was a decrease of pH during the electrolysis process, the oxidation potential needed to be increased (from $+0.6$ to $+0.8$ V) in order to obtain total oxidation of As(III). The change in pH to acidic media complicates the total electrolysis of arsenite at this

![Figure 12.9](image-url)  
Figure 12.9. Advancement electrolysis of As(III) to As(V) at the preparative scale using C/poly-Pt$^0$ carbon felt modified electrode in presence of poly(diallyl dimethylammonium) chloride as support polyelectrolyte. Decreasing peaks of direct anodic scan voltammograms of As(III) monitored in-situ between each point of electrolysis by (a) C/poly-Pt$^0$ analytical modified electrode (b) platinum disc analytical electrode.
potential application to remove arsenic by functional polymers in conjunction

voltage. Presumably, arsenite hydrolyzed species interact with acid sites of Pt\(^0\) generating H\(^+\), via acid catalysis.

12.8 OFF-LINE COUPLED ELECTROCATALYTIC OXIDATION AND LIQUID PHASE POLYMER BASED RETENTION (EO-LPR) TECHNIQUES TO REMOVE ARSENIC

Electrochemistry and membrane ultrafiltration methods (electro-oxidation and liquid phase polymer based retention technique, LPR, respectively) were off-line coupled to remove As(III) inorganic species from aqueous solutions. The main objective was to efficiently extract As species by associating a polymer-assisted liquid phase retention procedure, based on the As(V) adsorption properties of cationic water-soluble polymers, with an electrocatalytic oxidation process of As(III) into its more easily removable analogue As(V). The electrocatalytic oxidation of As(III) to As(V) was performed in the presence of different water-soluble poly(quaternary ammonium) salts acting also as supporting electrolyte, i.e., P(CIMPTA), P(CIVBTA), or P(BrVMP). After complete electrocatalytic conversion of As(III) into As(V), the mixtures were introduced into an LPR cell to remove the As(V)-polymer adducts. Using P(CIMPTA), P(CIVBTA), or P(BrVMP) ammonium salts in a 20:1 polymer:As(III) mol ratio at pH 8, complete (100%) As retention was achieved (see Fig. 12.10). Moreover, the As(V) retention efficiency turned out to be directly related to the net charge consumed during the electrochemical conversion of As(III) to As(V) (Rivas et al. 2009).

Macroscopic electro-oxidation of As(III) to As(V) at a platinum gauze electrode was performed in the presence of the polyelectrolytes P(CIVBTA), P(CIMPTA), and P(BrVMP) in unbuffered aqueous solutions. Electrolyses were performed at a constantly applied voltage between +0.8 and +0.9 V vs. Ag/AgCl until the theoretical charge required for the two-electron oxidation of As(III) to As(V) was consumed. Similar results were obtained by oxidation at +0.8 or +0.9 V, but the electrolysis time was greatly reduced at an applied voltage of +0.9 V. The initial solutions were basic (pH 9–10), but the pH decreased continuously as the consumed

Figure 12.10. Arsenic retention profile using P(CIVBTA) as supporting electrolyte and polychelatogen at pH 8, at different concentrations of As(III) in the electrolysis cell; polymer:As(III) molar ratio 20:1; solutions were previously electrolyzed onto a Pt-gauze electrode (potential applied +0.9 V vs. Ag/AgCl) up to the consumption of the theoretical charge for the complete oxidation of As(III) to As(V) (Rivas et al. 2009).
charge increased, reaching a value of 3–4 at the end of the electrolysis. The progress of the macro-scale oxidation of As(III) to As(V) could be readily judged from the height of the As(III) oxidation peak recorded at a platinum disc electrode.

Before carrying out the ultrafiltration process to remove complexed As(V) species from the electrolyzed solution, the pH was adjusted to 8 with NaOH and stirring was maintained for about 1–4 h. Several experiments were conducted using the washing method at different polymer and As concentrations and molar ratios. This is a batch-like method where a liquid sample containing the polymer and the metal ions to be separated are placed in the ultrafiltration cell at a given pH and ionic strength. This mixture is then washed with the reservoir’s water solution, which should reproduce the same pH and ionic strength values. The conditions should be those at which the ions of interest are retained and other species are removed. The resulting solutions were introduced in an ultrafiltration cell, wherein the volume was adjusted to 20 mL. Then, the samples were ultra-filtrated and washed with reservoir water at the same pH. Ultrafiltration runs were performed under a total pressure of 3.5 bar using a ultrafiltration membrane of polyethersulfone with an exclusion rating of 10,000 Da. The total volume in the cell was maintained constant during the process. Fractions of 20 mL were collected up to a total volume of 200 mL. The As concentration in the filtrate was determined by atomic absorption spectrometry. A blank assay was also performed with a solution of polymer and As(III) (20:1 mole ratio), which had not been previously electrochemically oxidized. This ratio was selected to ensure an excess of the repeat polymer unit. The results of the As(V) uptake are systematically presented as the percentage of retention $R$ (%) vs. the filtration factor $Z$ (volume of the filtrate/volume of the cell).

The combined electro-oxidation EO-LPR method avoids the use of chemical oxidants. Moreover, an important point is that the whole process can be performed in the same reactor without any additives other than the complexing polycationic polymer, which also serves as supporting electrolyte. In the conventional oxidation processes with chemical dosing, effective oxidants are free chlorine, hypochlorite, permanganate and hydrogen peroxide/Fe$^{2+}$ (Fenton’s reagent). Chlorine has the disadvantage that it leads to chlorinated byproducts, namely trihalogenmethanes, from reactions with natural organic matter. Ozone is quite effective but it is not feasible for a specific application with As(III) oxidation because it is a strong oxidant that would partly oxidize the natural organic matter. The most reasonable oxidants are KMnO$_4$ and Fenton’s reagent (H$_2$O$_2$/Fe$^{2+}$) with which the As(V) is removed by precipitation-coagulation. The H$_2$O$_2$ is applicable when the water contains some ferrous ions, but only for certain mass ratio H$_2$O$_2$/Fe$^{2+}$ and the residual H$_2$O$_2$ may not exceed 0.1 mg L$^{-1}$. The most adequate oxidant would be KMnO$_4$ for cases with a subsequent precipitation, filtration step. In the precipitation-coagulation process, the use of aluminum or ferric salts is common. Indeed, the removal of As(III) by precipitate of Fe$^{3+}$ salts was found to be only 50–60% lower than that of As(V) using the same coagulant.

A series of experiments were performed to estimate the effect of the oxidation of As(III) to As(V) species on As removal efficiency with LPR. In all these experiments, P(CIVBTA) was used as capturing and supporting polyelectrolyte. Several solutions of As(III) were oxidized at an applied voltage of +0.8 V or +0.9 V. Electrolysis was stopped after the consumption of 0.5, 1, 1.5, 1.75, and 2 electrons per As(III) species. Then, the As retention by the LPR technique was determined for each electrolyzed solution (see Fig. 12.11), and the retention factor (R) was calculated for the electrolyzed (+0.9 V) As solutions (0.5 and $1 \times 10^{-3}$ mol L$^{-1}$) containing P(CIVBTA) as polyelectrolyte as a function of the consumed charge during electrolysis. In all these experiments, the polymer: As(III) mol ratio was 20:1. After electrolysis, the pH of solutions was adjusted to 8 and As was removed by ultrafiltration.

Similar results were obtained using a lower oxidation potential (+0.8 V). The linear increase of As retention as a function of the electrolysis charge (linear regression factor $r^2 = 0.98$), reaching 100% after the consumption of 2 electrons per As(III) species, clearly demonstrates that the As removal efficiency is directly related to the oxidation of As(III) to As(V). These experiments also demonstrate that the combination of LPR with an electrocatalytic oxidation
Potential application to remove arsenic by functional polymers in conjunction

Preliminary studies indicate that these results can be improved by using electrodes modified with catalytically active materials based on nano/micro particles of noble metals (Pt, Pd and Au) or metal oxide (RuO₂), dispersed in polymer films covering the surface of carbon electrodes.

Using a modified macroelectrode with platinum particles (C/poly-Pt⁰), As(III) was electrolyzed until the complete conversion of As(III) to As(V) was achieved. The decay of the pH could be controlled because the protons generated in the electrolysis were reduced to hydrogen using the Pt basket counter electrode. The progress of the process was monitored using an in-situ analytical modified electrode (C/poly-Pt⁰), which is used as an amperometric sensor to determine the arsenite remaining.

12.9 CONCLUSIONS

Cationic polymers synthesized with different groups as anion exchangers differ in their ability to retain arsenate ions.

The liquid-phase polymer-based retention (LPR) was shown to be a convenient method to significantly retain arsenate ions in solution when using a polymer with quaternary ammonium groups.

The interaction and retention capacity for arsenate anions depends on: pH, the quaternary ammonium group’s counterion, and the polymer concentration.

The polymer P(SAETA) that contains bulky counterions (OSO₃CH₃)—which are more hydrophobic than Cl⁻ ions—showed the lowest retention capacity for arsenate ions. Thus, the nature of the anionic exchanger groups appears to be an important factor in arsenate retention by these water-soluble polymers.

The enrichment method was used to determine the maximum retention capacity C for arsenate anions in aqueous solutions at pH 8. Under similar conditions, the values of C were 142 mg g⁻¹ for P(CIAETA) and 75 mg g⁻¹ for P(SAETA). The type of anion exchanger was an important factor in arsenate retention.

The study showed that treatment with the liquid-phase polymer-based retention (LPR) technique of aqueous solutions with As previously subjected to an electrocatalytic oxidation (EO) to convert the species of As(III) to As(V) quantitatively removes the As. The use of water-soluble polymers as extracting agent for As(V) in the ultrafiltration and support
electrolytes for electrocatalytic conversion process has been demonstrated to have a decisive advantage in their application because they do not require the addition of other reagents, such as salts, in homogeneous electrocatalytic processes.

Arsenic removal was improved by using electrodes modified with catalytically active materials based on nanoparticles of noble metals (Pt, Pd), which are dispersed in polymer films covering the surface of carbon electrodes.

In the future, the challenge is to develop the EO-LPR online. Ideally, electrolysis could be performed directly inside the LPR cell or in separate reactors connected in the circuit. Another important point is the in-situ monitoring of the electrocatalytic process using these analytical modified electrodes to follow the conversion of As(III) to As(V).

ACKNOWLEDGMENTS

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Potential application to remove arsenic by functional polymers in conjunction

Section IV
Innovations in arsenic removal techniques for safe water production
CHAPTER 13

Testing of a new selective arsenic adsorbent and overview of field test data

Stefan Neumann, Reinhold Klipper, Jens Stoll, Michael Dahm, Sylvia Breuer, Brigitte Chudzik-Raeth, Sieglinde Trokowski & Chou Wei Hsin

13.1 THREAT OF ARSENIC IN POTABLE WATER SOURCES

Not all trace minerals are good for human organism: Arsenic (As) contamination in potable water supplies has become a major issue in respect to threats for human health. Arsenic in water originates from both, natural sources (geological erosion) as well as man-made pollution that contaminate ground- and surface water (e.g. mining activities, waste water discharge, etc.). The concentration of As may reach 1500 µg L$^{-1}$ in certain areas such as Western United States and Antofagasta region in northern Chile (Smedley 2002). Arsenic is known to cause diseases of the skin and different types of cancer. The World Health Organization (WHO) currently recommends a maximum As level in potable water supplies of 10 µg L$^{-1}$ (WHO 2001).

13.2 SCOPE OF THIS WORK

The scope of this work was to test a new adsorbent material, Lewatit® FO 36, on its effectiveness for removing As from water. Issues of interest were parameters such as equilibrium and operating capacity, effects of competing ions present in water supplies on As uptake, as well as adsorbent regenerability. The last part of this chapter gives an overview of operating capacities that were obtained in field tests by application of various adsorbents. These operating capacities were collected from different sources, and used as a background to judge the performance of the new Lewatit® FO 36.

13.3 PROPERTIES AND ADVANTAGES OF THE NEW HYBRID ARSENIC ADSORBENT MATERIAL

Lewatit® FO 36 is a new adsorbent material launched by LANXESS in the year 2008. It is based on a macroporous, fine beads (350 µm diameter), monodispersed, weak base anion exchanger resin that contains nano-scale particles of FeO(OH) in its pores (Fig. 13.1). The iron content is around 15% dry weight based. Since it is a composite material of two different phases, this type of adsorbent can be specified as a so called “hybrid adsorbent-material” such as described by De Marco (2003).

Hybrid adsorbent materials in general have several advantages over completely inorganic metal oxide based filtering materials. The most striking advantage is the high mechanical strength due to a “plastic” material serving as a robust backbone for the embedded soft mineral. This property assures that the particles can be hydraulically transported and backwashed, and do not collapse under situations of high mechanical stress that usually occur in a filter bed under day to day operating conditions. With Lewatit® FO 36, the production of fine particles that plug filter beds and nozzles, and cause turbidity in the outlet of the filter is inhibited. The perfectly round shape and uniform size of the particles allow a
tight packing with well defined channels in between, resulting in relatively low pressure drops and homogenous flow distribution. The outstanding stability of the polymer backbone also allows the material to be treated with aggressive chemicals without decomposition, enabling easy regeneration and cleaning operations.

Additionally, the properties of Lewatit® FO 36 are built on homogeneously shaped relatively fine beads of 350 µm in diameter. This gives the material a large specific surface, which supports mass transport, and makes the adsorption kinetics extremely fast. Due to the uniform particle size the material does not contain fine particles, which tend to plug strainers or increase the pressure drop over the resin bed.

The specific chemical and physical properties of Lewatit® FO 36 are listed in Table 13.1.

In the tests described below different samples of Lewatit® FO 36 were used. These samples were prepared by almost the same recipe and their physical and chemical properties were identical to the above (Table 13.1). The only difference in preparation was the batch size which ranged from around 1 L for R&D samples, to around 40 L for the pilot production unit, and up to several cubic meters in the technical production plant. Table 13.2 gives an overview of the different samples used.

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### Table 13.1. Chemical and physical properties of Lewatit® FO36.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional group</td>
<td>FeO(OH) + tertiary amine</td>
</tr>
<tr>
<td>Matrix</td>
<td>Crosslinked poly-styrene</td>
</tr>
<tr>
<td>Structure</td>
<td>Macroporous</td>
</tr>
<tr>
<td>Appearance</td>
<td>Brown, opaque</td>
</tr>
<tr>
<td>Stability pH-range</td>
<td>4–14</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.765 g mL⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>1.25 g mL⁻¹</td>
</tr>
<tr>
<td>Mean bead size</td>
<td>0.35 mm</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>1.1</td>
</tr>
<tr>
<td>Bed expansion</td>
<td>9.8 vol.% per m h⁻¹ at 20°C</td>
</tr>
<tr>
<td>Water retention</td>
<td>53–58 wt.%</td>
</tr>
<tr>
<td>Iron content</td>
<td>15% dry weight based</td>
</tr>
</tbody>
</table>

---

### Table 13.2. List of different samples of Lewatit® FO36 that were used for the tests described in this chapter.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;D sample A</td>
<td>Adsorption isotherm (<a href="#">Fig. 13.3</a>)</td>
</tr>
<tr>
<td>R&amp;D sample B</td>
<td>Adsorption isotherm (<a href="#">Fig. 13.3</a>)</td>
</tr>
<tr>
<td>R&amp;D sample C</td>
<td>Regeneration tests (<a href="#">Fig. 13.6</a>)</td>
</tr>
<tr>
<td>Pilot product A</td>
<td>Breakthrough curve (<a href="#">Fig. 13.4</a>); competitive adsorption tests (<a href="#">Fig. 13.5</a>); field test data indicated with [18] in Fig. 13.7.1–13.7.2</td>
</tr>
<tr>
<td>First production lot</td>
<td>Field test data indicated with [13] and [15] in Fig. 13.7.1–13.7.2</td>
</tr>
<tr>
<td>Second production lot</td>
<td>Breakthrough curve (<a href="#">Fig. 13.4</a>); Field test data indicated with [19] in Fig. 13.7.1–13.7.2</td>
</tr>
</tbody>
</table>

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**Figure 13.1.** Lewatit® FO 36 is a composite material consisting of a phase of a weak base anion exchanger material and a phase of iron oxide.
13.4 MECHANISM OF ARSENIC ADSORPTION

The adsorption of arsenate \([\text{As(V)}]\) and arsenite \([\text{As(III)}]\) on iron oxide surfaces is a relatively complex process (Cumbal 2005). A simplified mechanism for the adsorption of \text{As(V)} is postulated in Figure 13.2. This reaction is considered a condensation reaction. The adsorption can be reversed by hydrolysis under alkaline conditions. The hydrolysis of the surface complex is the basis of the regeneration-process of the exhausted material.

13.5 ADSORPTION ISOTHERM

An adsorption isotherm for a temperature of 25\(^\circ\)C was generated by measuring the static adsorption of arsenate in demineralized (demin) water. Several samples containing 250 mL of demin water and \text{As(V)} and 0.3 grams of Lewatit\textsuperscript{®} FO 36 resin dried via suction to remove only the excess moisture (water outside the beads) were prepared and vigorously shaken for 24 hours. The starting concentration of \text{As} was varied in a range of 1–100 mg L\(^{-1}\). After 24 hours the rest concentration of \text{As} in the solution was measured by atomic absorption spectroscopy (AAS). By mass balance the amount of adsorbed \text{As} was calculated. Figure 13.3 gives the results. The \text{As} uptake of Lewatit\textsuperscript{®} FO 36 is plotted against the concentration of \text{As} in the supernatant water.

![Figure 13.2](image-url)

**Figure 13.2.** Iron oxide bearing materials such as Lewatit\textsuperscript{®} FO 36 hypothetically bind arsenate by a kind of condensation reaction. The adsorption can be reversed by hydrolysis under alkaline conditions.

![Figure 13.3](image-url)

**Figure 13.3.** Adsorption isotherm for the adsorption of \text{As(V)} on Lewatit\textsuperscript{®} FO 36 at 25\(^\circ\)C and pH = 6. (Lewatit\textsuperscript{®} FO 36 Lot: R&D samples A and B).
Figure 13.3 indicates that the As uptake of Lewatit® FO 36 was a function of the equilibrium concentration. As it is quite common in adsorption tests, the equilibrium capacity increases with increasing concentration of the adsorbate in the solution. In the area relevant for potable water purification (about 0.01–0.2 mg L\(^{-1}\) of As) the equilibrium capacities ranged from 2 to 8 g L\(^{-1}\) of As adsorbed per liter of adsorbent.

### 13.6 CONTINUOUS FILTRATION TESTS

100 mL of Lewatit® FO 36 were placed in a column with a diameter of 22 mm and a bed depth of 270 mm. Water spiked with approximately 100 \(\mu\)g L\(^{-1}\) of As(V) was continuously pumped through the column at a temperature of 20°C, and at a specific flow rate of 25 bed volumes per hour (BV h\(^{-1}\)) (2.5 L h\(^{-1}\)). In the outlet of the column the As concentration was measured once a day.

The filtration tests were carried out with two different water qualities and with two different product lots: The two water types spiked with As were (1) demin water and (2) tap water from the “CHEMPARK”-facility in Leverkusen, Germany. The product lots were (1) a pilot lot produced in a 40 kg batch size and (2) the first technical production lot produced at LANXESS in Leverkusen in the year 2008. The tap water analysis indicated 160 mg L\(^{-1}\) bicarbonate, 50 mg L\(^{-1}\) chloride, 13 mg L\(^{-1}\) sulfate, 6 mg L\(^{-1}\) of silica as SiO\(_2\), 100 \(\mu\)g L\(^{-1}\) of fluoride, 60 \(\mu\)g L\(^{-1}\) of phosphorus, pH = 7.0 and TOC < 1 mg L\(^{-1}\).

It can be concluded from Figure 13.4 that the breakthrough of As occurred earlier in the case where As was adsorbed from tap water. In the filtration experiment with demin water, three times more water with As concentrations below 10 \(\mu\)g L\(^{-1}\) could be produced than in the one with tap water. The corresponding cycle times were 33 days versus 96 days. It was found that the first technical product sample had an even higher performance than the product from the pilot lot. In the case of demin water, the technical production sample delivered a cycle time of even 150 days.

By mass balance the uptake of As until the break-through point of 10 \(\mu\)g L\(^{-1}\) was calculated. The operating capacity of the pilot lot sample was 5.8 g L\(^{-1}\) in demin water and 1.9 g L\(^{-1}\) in potable water. In contrast, the first production lot sample delivered an operating capacity of as much as 8.5 g L\(^{-1}\) in demin water.

The decreased operating capacity found for the adsorption of As from tap water can be explained by the influence of co-occurring ions that compete with the As for the occupation

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![Figure 13.4](image-url)  
Filtration test to remove As(V) with Lewatit® FO 36 at 25°C from tap water and from demineralized water (Lewatit® FO 36 Lot: pilot product A and second production lot).
of active sites on the adsorbent surface. Since the tap water contained several ionic species, it was unclear which of these ions were giving the major impact. To clarify the influence of the diverse water ingredients, several tests were conducted, and the results are explained in the next section.

13.7 STUDY ON THE INFLUENCE OF WATER CONSTITUENTS ON ARSENIC ADSORPTION

Several batch adsorption tests were carried out whereby in every case 0.3 g of resin (dried via suction to remove excess moisture) was suspended for 24 h in 250 mL of an aqueous solution of As(V). In each test different amounts and types of anions were present to test their influence on As uptake. The results are given in Figure 13.5. The relative uptake of As by the resin is plotted against the relative concentration of the co-occurring anion in the solution. Thereby the relative concentration of the co-occurring ion is defined as the molar ratio of the initial concentration of this ion divided by initial concentration of As.

It can be concluded from Figure 13.5 that chloride did not have any influence on the adsorption of As since the relative adsorption stayed constant at a value of 1 over the whole range of chloride concentrations tested. In contrast, phosphate had a very strong influence on As adsorption. It can be found in Figure 13.5 that the relative adsorption already started to decrease at molar ratios of around 1. At a molar ratio of 10 phosphate already reduced the uptake of As(V) by more than 50% and extrapolated to a ratio of 100 a complete inhibition has to be expected.

Carbonate also had an effect but its influence started at molar ratios of around 100. Complete inhibition is expected at molar ratios of more than 10,000. The impact of silicate on As(V) uptake was intermediate between the impact of phosphate and the impact of carbonate. According to Figure 13.5 the impact of silicate in solutions of pH = 7 started at a As/Si molar ratio of 10. More than 50% inhibition is expected at molar ratios between 100 and 1000. Interestingly, the influence of silicate was different for pH < 7. Figure 13.5 shows no impact of silicate on As adsorption at a pH of 3.5.

The influence of pH on the impact of silicate on As adsorption is an interesting phenomenon. It has to be expected that pH also modulates the adsorption of phosphate and carbonate on Lewatit® FO 36.

Tests on the influence of pH alone on the adsorption of As(V) by Lewatit® FO 36 were carried out by suspending 0.3 g of Lewatit® FO36 in 250 mL of demin water that was spiked

Figure 13.5. Relative uptake of As by Lewatit® FO 36 in the presence of other ions plotted against the relative concentration of these ions in the initial solution. Starting concentration of As was always around 2.5 mg L\(^{-1}\). Initial concentrations of Cl\(^-\) and HCO\(_3\)^- was in a range of 0–5000 mg L\(^{-1}\) and initial concentration of SiO\(_3\)\(^2-\) and HPO\(_4\)\(^2-\) were in a range of 0–100 mg L\(^{-1}\). The pH was adjusted at pH = 7 except for one campaign, where pH was adjusted at 3.5. (Lewatit® FO 36 Lot Nr.: pilot product A).
with a starting concentration of 2.5 mg L\(^{-1}\) of As(V). The pH was adjusted by addition of suitable amounts of caustic soda or hydrochloric acid, respectively. The bottle was shaken for 24 hours in total and pH was checked. If required, the pH was re-adjusted several times during the testing. Within the 7 different adsorption tests, the pH was varied in a range from pH = 4 to pH = 9.

Figure 13.6 gives the rest concentration of As measured as a function of the pH that was adjusted in the bottle.

It can be read from Figure 13.6 that the lowest As(V) rest concentration was achieved at a pH = 6. Relative to a pH = 6 rest concentrations are raising with increasing or decreasing pH. Thus, from the perspective of looking at rest concentrations alone, it seems that there is an optimum of pH = 6 for As(V) adsorption.

Nevertheless, the removal rate of As in these tests ranged from 95 to 99% since the rest concentrations achieved were all relatively small compared to the starting concentration. This means at the same time that the As-capacity of the adsorbent does not significantly change with pH.

Hence, within the investigated pH-range the As uptake is modulated by only 4%. In contrast to that indicated in Figure 13.5, co-occurring ions can reduce As-uptake by more than 80%. Therefore, the impact of pH alone on As adsorption was relatively small compared to the effects of co-occurring ions on As-uptake of Lewatit\textsuperscript{®} FO36.

Even though the effect of pH alone on As-uptake of Lewatit\textsuperscript{®} FO36 may not be significant, it has to be considered that the pH can modulate the impact of co-occurring ions on As-adsorption. This means that in the presence of co-occurring ions the curve shown in Figure 13.6 as well as As(V) uptake of Lewatit\textsuperscript{®} FO36 is expected to show much stronger effects. To get a full picture it would be necessary to carry out adsorption tests with different co-occurring ions under different pH-conditions. It was not possible to cover this additional work within this chapter.

It can be read from Figure 13.5 that differences in pH affect As uptake in presence of silicate by more than 20%. Therefore, a significant effect of pH on As-uptake has to be expected because co-occurring ions are always present in natural waters. Following the tendency found during the tests with silicate as a co-occurring ion, it is expected, that within a range of pH from 4–9, the higher the pH the more significant will be the negative effect on As-adsorption.

13.8 REGENERATION TESTS

A filtration experiment was carried out at 30 BV h\(^{-1}\) specific flow rate with tap water containing 100 \(\mu\)g L\(^{-1}\) As. After a breakthrough at 10 \(\mu\)g L\(^{-1}\) the resin was regenerated with 3 BV of
4% NaOH at 6 BV h\(^{-1}\) followed by water rinse (6 BV). Then, a second filtration experiment was carried out with the regenerated resin followed by another regeneration and filtration cycle. It was found that leakage levels of As with regenerated resin are same as with the fresh resin but the operating capacities (OCs) decreased in each cycle. Relevant values of the operating capacities are given in Figure 13.7.

13.9 EVALUATION OF FIELD TEST DATA AND JUDGMENT OF LEWATIT\textsuperscript{®} FO 36 PERFORMANCE

Field test data were collected and evaluated within an extensive literature study. The data were collected from tests with different selective As adsorbents such as Purolite ArsenX\textsuperscript{®}, DOW Adsorbia\textsuperscript{®} GTO, GEH\textsuperscript{®} Wasserchemie GFH, LANXESS Bayoxide\textsuperscript{®} E 33, etc.

Only test reports with As(V) as major As-species were considered. The operating capacity was calculated whereby the breakthrough criterion was set at 10 \(\mu\)g L\(^{-1}\) in the outlet of a single filter in operation. The operating capacity is expressed in grams of As adsorbed per liter of material.

All the operating capacity values were plotted against the feed concentration of As since it is expected that the operating capacity is a function of the feed concentration.

Figures 13.8.1 and 13.8.2 give six different versions of this plot whereby in each plot different additional information is given:

- Plot 13.8.1a gives a general overview on all the data where the data obtained with Lewatit\textsuperscript{®} FO 36 are highlighted in the background of all other measuring points.
- Plot 13.8.1b allows differentiating between different types of products and indicates individual pH values for most of the data.
- Plot 13.8.1c allows differentiating between different types of product and indicates the concentration of silicate (SiO\(_2\)) for most of the data.
- Plot 13.8.2a allows differentiating between different types of products and indicates phosphate concentrations for most of the data.
- Plot 13.8.2b allows differentiating between different types of products and indicates specific flow rates for most of the data.
- Plot 13.8.2c indicates the source of data and refers to the list of references attached at the end of the publication as well as data given in Table 13.3.

Regarding ranges of the monitored parameters it can be stated that the majority of As feed concentrations were between 10 and 100 \(\mu\)g L\(^{-1}\) of As, only a few measurements were taken around 300 \(\mu\)g L\(^{-1}\) in the feed, and there is only one data point at 3000 mg L\(^{-1}\). The

![Figure 13.7](image_url)

Figure 13.7. Operating capacity in three cycles with two regeneration steps in between. Regeneration levels were 89 and 85%, respectively (Lewatit\textsuperscript{®} FO 36 Lot: R&D sample C).
pH ranged from 6.5 to 9. Silicate concentrations varied from 0.7 to 100 mg L\(^{-1}\). Phosphate ranged from 45 to 1400 \(\mu\text{g L}^{-1}\). Specific flow rates ranged from 10 to 120 BV h\(^{-1}\).

Some general conclusions can be drawn from Figure 13.8.1:

- Within an As feed concentration range of 10–100 \(\mu\text{g L}^{-1}\) the average operating capacity of all adsorbents is between 1 and 2 g L\(^{-1}\).
- There is a tendency to deliver higher operating capacities with increasing feed concentrations. It was observed that for every 10 \(\times\) increase of As in the feed concentration, the...
Testing of a new selective arsenic adsorbent and overview of field test data

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<th>Ads(V) feed µg L⁻¹</th>
<th>Ads(III) feed µg L⁻¹</th>
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operating capacity increases by around 1 g L⁻¹. A trend line was drawn through the data points according to this observation.

- The variation from the average trend line is approximately ±1 g L⁻¹ in operating capacity.
- FO 36 data scatters equally around the trend line in the same manner as data points from other adsorbent materials.

Through inspection of the data points in Figures 13.7.8a and 13.8.2b, including other adsorbent materials, it can be generally concluded that:

- There is no product that consistently shows results in the upper capacity area; all products show equal scattering around the average performance line.
- Scattering of data seems to be mainly caused by water composition and operating conditions.

It is difficult to find general trends within the diagrams. Tests where silicate, phosphate and pH have been in the upper range are not generally found in the low operating capacity area. Data points have to be looked at individually and checked for all parameters to explain tendencies:

- The data point (34 µg L⁻¹ As/0.26 g L⁻¹ OC) of FO 36 is below average performance but can be explained by an extraordinary high silicate concentration of 100 mg L⁻¹, high phosphate concentration of 320 µg L⁻¹ and a relatively high flow rate of 25 BV h⁻¹.
- The data point (292 µg L⁻¹ As/0.56 g L⁻¹ OC) of FO 36 is below average but can be explained by an extraordinary high flow rate of 66.5 BV h⁻¹ combined with a high pH of 8.5; other parameters were at 20 mg L⁻¹ for silicate and at 125 µg L⁻¹ for phosphate.
- The data point (66 µg L⁻¹ As/2.3 g L⁻¹ OC) of FO 36 is above average and can be explained by moderate operating conditions such as flow rate 20 BV h⁻¹; SiO₂ = 1.6 mg L⁻¹; pH = 7.3; PO₄³⁻ = 100 µg L⁻¹.

Even though the field test data do not give a clear hint on how the operating performance is connected with the operating parameters, they allow a general overview on the range of operating capacities for orientation. Also, it can be concluded that the following parameters have to be considered critical for all kind of As adsorbents: SiO₂ > 40 mg L⁻¹, PO₄³⁻ > 300 µg L⁻¹, pH > 8.5, flow rate > 40 BV h⁻¹. The effect will be strengthened in case more than one of these parameters gets into a critical range.

Hence it can be stated that the new adsorbent material, Lewatit® FO 36, is within the performance range of most other adsorbents available on the market. Furthermore, Lewatit® FO 36 and other adsorbents suffer from the same disrupting influences of competing ions in the feed water impacting operating performance.

What is still missing is a good theory to predict filter-performance based on water composition and specific flow rate. We hope that with an increased availability of data it will be possible to develop a model at least on an empirical basis.

### 13.11 CONCLUSIONS

A new selective As adsorbent material, Lewatit® FO 36, was tested. Both static and dynamic adsorption tests, as well as regeneration trials, were carried out under various conditions.

Operating capacities of up to 9 g of As per liter of resin and cycle times of up to 150 days were achieved under optimum operating conditions in a dynamic filtration test. This result indicates that the material has a high relevance for technical applications e.g. in potable water purification.

It was found that general water constituents such as Cl⁻, assumed also SO₄²⁻ and NO₃⁻, do not influence the uptake of As. In contrast, a strong influence is found from competing ions in the feed water in the following order: phosphate > silicate > bicarbonate. Also, the
pH modulates As uptake, and it was found that under conditions of pH < 7 negative effects are reduced in comparison to test results of pH > 7. Under the influence of these parameters operating capacities can be reduced by up to 80% compared to results under “optimum conditions”.

It was shown in orienting tests that the Lewatit® FO 36 adsorbent resin is regenerable in principle. The regeneration procedure was found to require optimization in order to reduce a loss of operating capacity that occurred mainly after the first cycle.

A literature study covering field tests with data of more than 40 individual filtration tests was carried out. This study allows comparing the performance of As removal under different operating conditions and comparing the performance of different adsorbent materials. Since the As uptake is modulated by different parameters at the same time, general trends are very difficult to read from these diagrams. Modeling of the adsorption process may be possible in future, when more data is available.

In general, it can be concluded that the capacity of the new Lewatit® FO 36 adsorbent material is similar to all the other selective As adsorbents. Like the others, Lewatit® FO 36 suffers from severe operating conditions. Operating conditions can be considered as severe in the case that one or more parameters exceed the following values: SiO₂ > 40 mg L⁻¹, PO₄³⁻ > 300 µg L⁻¹, pH > 8.5, flow rate > 40 BV h⁻¹.

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CHAPTER 14

Chitosan dispersed with Fe(III) oxide particles: A sorbent used for selective removal of arsenic from contaminated waters

Luis Cumbal & Marcelo Zuñiga

14.1 INTRODUCTION

Arsenic (As) is a toxic metalloid that is ubiquitous in surface water and groundwater in trivalent and pentavalent form. Ingestion of As contaminated water is a public health problem world-wide (Roychowdhury et al. 2002, Meharg and Mazibur 2003). At chronic exposure, As accumulates in the human body and high levels causes skin affections. The epidemiologic evidence of people with a long ingestion of inorganic As, via drinking water, is the sole/palm hyperkeratosis, whose main manifestation is skin pigmentation and callosities, located in hand palms and sole feet. Arsenic in water and its degree of contamination and occurrence of skin illnesses have been reported in India, Bangladesh, Taiwan, Vietnam, Argentina, and Mexico (Cebrian et al. 1994, Das et al. 1994, Frederick et al. 1994, Brown and Chen 1995, Armienta et al. 1997, Dhar et al. 1997, Smith et al. 1998, Chakraborti et al. 2002).

A number of conventional and emergent materials are used for As removal from water such as activated alumina, ion exchange resins, sand covered with iron oxides, granular ferric hydroxide, sands mixed with zerovalent iron, nanofiltration and reverse osmosis membranes, aluminum sulfate and ferric chloride coagulants, etc. Iron oxide particles are excellent materials to sorb chemical species, including metallic ions (Laxen 1983, Slavek and Pickering 1986, Music and Ristic 1992), inorganic anions (Pierce and Moore 1982, Manning et al. 1998), and some organic compounds (Matheson and Tratnyek 1994, Wang and Zhang 1997). Hydrated Fe(III) oxides (HFO) exhibit excellent properties conducive to a selective capture of trace contaminants due to its weak acid behavior. The predominance of its functional groups and its removal capacity are pH dependent ($pK_{a1} = 6.5$ and $pK_{a2} = 9$) (Dzombak and Morel 1990). For example at pH $\leq 4$, HFO particles remove arsenates with a combined effect of electrostatic and Lewis acid-base (LAB) interactions, in the pH range of 6.5 to 8.5 immobilize As by LAB interaction, and at pH $\geq 11$ capture metallic cations by electrostatic interaction (Cumbal and Sengupta 2005). The preparation methodology of HFO particles is simple; however, these tiny particles cannot be used in fixed-bed columns, permeable reactive barriers and any other plug flow configuration, since they cause high pressure loss and are not durable. Harnessing these HFO particles within supporting materials enhance their hydraulic and mechanical properties and turn them out chemically more stable. Previous studies have reported the use of various supporting materials such as sands, sodium alginate, activated carbon, etc. but the results have not been satisfactory (Benjamin et al. 1996, Min and Hering 1998, Zouboulis and Katsoyiannis 2002, De la Torre et al. 2005).

In this study, chitosan spheres were prepared, i.e., from, a biopolymer that is found in nature contained in crab shells and in cellular walls of some plants and fungi. Chitosan spheres then were impregnated with Fe(III) oxide particles and used for the removal of As from synthetic and natural waters using fixed-bed columns and in a pilot plant.
14.2 METHODS AND PROCEDURES

14.2.1 Preparation of sorbent material

The procedure consisted of the following steps:

- Grinding and screening: Chitosan granules are ground and screened to get a fraction of 250 µm particles.
- Dissolution: Chitosan particles are dissolved in a solution of 4% acetic acid and the product is stored at ambient temperature during seven days to reduce its viscosity.
- Spheres formation: From a 50 mL syringe chitosan solution is drop-wise given into a 500 mL flask containing 5% NaOH.
- Rinse and crosslinking: After 16 hours of contact with alkaline solution, spheres of chitosan are rinsed with deionized water (DI water); then they are immersed in a solution of 2.5% glutaraldehyde for six hours.
- Loading with Fe(III) oxide particles: 100 g of crosslinked chitosan spheres are submerged in a reactor containing 500 mL of 3% FeCl₃ and subsequently agitated at 40 rpm for 48 hours.
- Desorption and precipitation: Desorption and simultaneous precipitation of Fe(III) ions on the surface and pores of the chitosan spheres is carried out by contacting spheres with 5% NaOH solution.
- Rinse and wash: Chitosan spheres dispersed with Fe(III) oxides are then rinsed and washed several times with DI water to level pH at about 7.0.

14.2.2 Fixed-bed columns tests

Fixed-bed column runs were conducted using glass columns (11 mm in diameter and 250 mm length), constant-flow stainless steel pumps and Eldex fraction collectors to investigate the sorption behavior of the chitosan spheres. The ratio of column diameter to sorbent bead diameter was approximately 10:1; earlier work on chromate and phosphate removal with a similar setup and under identical conditions showed no premature leakage due to wall effects (Sengupta and Lim 1988, Zhao and Sengupta 1998). The superficial liquid velocity (SLV) and the empty bed contact time (EBCT) were recorded for each column run. For the tests, fixed-bed columns were fed with aqueous solutions containing As as a trace species (100 µg L⁻¹) and competing anions of 120 mg L⁻¹ SO₄²⁻, 90 mg L⁻¹ Cl⁻, and 100 mg L⁻¹ HCO₃⁻ at a pH around 6. Concentrations of anions and pH were chosen similar to values found in natural waters. In the second series of tests, natural waters from the Tuminguina river and from the spring of the Papallacta Lake (both from Ecuador) were used.

For regeneration of chitosan spheres loaded with As were subjected to a regenerant solution of 5% NaOH. The alkaline solution was passed through the column with a flow rate of 0.5 mL min⁻¹. For analysis, effluent samples of different volumes were collected at the column exit. Spheres were then washed with eight bed volumes of 10% acetic acid solution to bring down the pH to a value of approximately 6.3.

14.2.3 Acid digestion test

For acid digestion tests, 250 mg of chitosan spheres dispersed with HFO particles were immersed in two consecutive acidic batches (200 mL of 2N-H₂SO₄) and then placed for 48 hours in a gyratory shaker that rotated at 40 rpm. Then, samples were analyzed for total iron using the method described below. Mass balance calculations were conducted to determine iron dispersed inside the biopolymer spheres.

14.2.4 Chemical analyses

Water samples from the fraction collector, pilot plant, spring from Papallacta Lake, and Tuminguina River were analyzed for As using a Perkin Elmer hydride generator (HG) coupled
Chitosan dispersed with Fe(III) oxide particles

Chitosan dispersed with Fe(III) oxide particles to a Perkin Elmer atomic absorption spectrometer, AA100. Results of chemical analyses were validated by comparing As contents with standard solutions purchased from Sigma Aldrich. Analysis of dissolved iron, chloride, sulfate, and bicarbonate was carried out in our laboratory in accordance with procedures described in standard methods for the examination of waters and waste waters (Greenberg et al. 1998).

14.2.5 Chemicals and water

All reactive grade chemicals used in this study were purchased from Espectocrom, representative company of Sigma-Aldrich Chemicals in Ecuador. Deionized water used throughout this study was prepared in Millipore Direct-Q3 equipment. The deionized water was mainly used for making simulated contaminated water for the fixed-bed column runs and for the equilibrium tests. In addition, two types of natural water were used in this study: i) As(V), As(III), silica, and phosphorus bearing surface water from Tuminguina River, ii) water containing As(V), As(III), and natural organic matter (NOM) from the spring of the Papallacta Lake.

14.3 RESULTS AND DISCUSSION

14.3.1 Total iron dispersed within chitosan spheres

The amount of iron dispersed within the chitosan spheres was experimentally determined by the acid digestion technique. The iron content was measured using the atomic absorption spectrometer according to the analytical method Fe-4500 (Greenberg et al. 1998). As observed in Figure 14.1, the iron content varies with the loading cycle. Note that during the first and second cycles, the Fe(III) loading is about 66% of its overall content and after the fourth cycle, 33.6 mg g⁻¹ of wet chitosan is attained. The iron content in chitosan spheres is only moderate because at pH = 1.6 the amine groups of chitosan matrix are positively charged and repel Fe(III) atoms. Compared to other host materials such as sand granules (2–10 mg Fe g⁻¹ of sand) (Benjamin et al. 1996) and calcium alginate beads (3.9 mg Fe g⁻¹ of wet alginate bead) (Zouboulis and Katsoyiannis 2002), the iron content deposited into the chitosan beads is higher, however compared to iron deposited within ion exchange beads, HClX-M and HAIX-M (Cumbal 2004) is lesser (Table 14.1).

14.3.2 Fixed-bed test with synthetic water

Figure 14.2 shows the effluent concentration history of As during a sorption test using chitosan spheres loaded with Fe(III) oxides and synthetic water at pH = 6.5. Note that 50 µg L⁻¹ is reached after treating 40,000 bed volumes of water contaminated with As. The selectivity for As(V) oxyanions is due to the fact that at pH = 6.5 the reactive sites of Fe(III) oxides

![Figure 14.1. Total Fe content in chitosan spheres as function of loading cycle.](image-url)
dispersed within the chitosan spheres, are predominantly neutrally charged, and thus remove As through the combination of electrostatic and Lewis acid-base interactions as, represented by the following reactions (Sengupta 2002):

\[
\equiv \text{FeOH} + \text{H}_2\text{AsO}_4^{2-} + \text{H}_2\text{O} \xrightarrow{\text{ELEC+LAB}} \equiv \text{FeOH}_2^+(\text{H}_2\text{AsO}_4^{2-}) + \text{OH}^- \quad (14.1)
\]

\[
2\equiv \text{FeOH} + \text{HAsO}_4^{2-} + 2\text{H}_2\text{O} \xrightarrow{\text{ELEC+LAB}} \equiv (\text{FeOH}_2^+(\text{HAsO}_4^{2-})) + 2\text{OH}^- \quad (14.2)
\]

**ELEC**: Electrostatic interaction; **LAB**: Lewis acid-base interaction.

On the other hand, under ideal conditions of sorption process, amino species go by the following reactions (Niu et al. 2007):

\[
\text{QNH}_2^+ \rightarrow \text{QNH}_2 + \text{H}^+ \quad (14.3)
\]

\[
K_a = \frac{[\text{QNH}_2][\text{H}^+]}{[\text{QNH}_2^+]} \quad (14.4)
\]

\[
[\text{QNH}]_T = [\text{QNH}_2^+]+[\text{QNH}_2] \quad (14.5)
\]

From equations 4 and 5, the proportion of positively charged amino groups can be obtained using the following relation:

\[
\frac{[\text{QNH}_2^+]}{[\text{QNH}]_T} = \frac{1}{1 + \frac{K_a}{[\text{H}^+]}} \quad (14.6)
\]
where \([Q_{NH_2}]\) represents the uncharged amino group, \([Q_{NH^+}]\) is the ionized form, \([Q_{NH}]\) is the total of amino groups present in the chitosan and \(K_a\) is the dissociation constant (mol L\(^{-1}\)).

Ka values have been reported by Roberts (1992) within 10\(^{-6.2}\) and 10\(^{-7.0}\) range. Therefore, at pH = 6.5 chitosan amino groups are mainly positively charged and allow electrostatic sorption of As(V) oxyanions thus improving the capture of As species. During this experiment 2730 µg As g\(^{-1}\) of wet chitosan were removed.

Comparing with sands covered with iron oxides (Benjamin et al. 1996), modified chitosan shows a higher sorption capacity. Reactive sites of sands are only located on the external surface accordingly the capacity is diminished, while chitosan reactive locations are not only distributed externally but also they are contained within the porous structure of the spheres.

It is noteworthy to point out that this experiment was conducted using mixed chitosan (fresh and smashed). As a result, chitosan fines could produce an additional surface area and consequently could contribute to the increase of As removal capacity. Nevertheless, fines cannot be used with filters in water treatment plants due to the excessive pressure loss.

14.3.3 Fixed-bed column for treatment of natural water from Tuminguina River

To assess As removal capacity of treated chitosan spheres with natural waters, water from a dam located in the Tuminguina River was used. Concentrations of As and anions in this natural water were: 49 µg L\(^{-1}\) As\(_T\), 43.3 mg L\(^{-1}\) SO\(_4^{2-}\), 58.6 mg L\(^{-1}\) Cl\(^-\), 122 mg L\(^{-1}\) HCO\(_3^-\), 40 mg L\(^{-1}\) NOM, and pH = 6.2. The standard of 10 µg L\(^{-1}\) As\(_T\) was reached after approximately 400 bed volumes and the effluent concentration was equal to the influent (49 µg L\(^{-1}\) As\(_T\)) after 9800 bed volumes of water (Fig. 14.3). It was estimated that 180 µg As g\(^{-1}\) of wet chitosan were removed in this experiment before reaching 10 µg L\(^{-1}\). The latter value compared to the test using synthetic water is an order of magnitude lower. This phenomenon can be ascribed to the competition of natural organic matter (NOM) for the sorption sites on the Fe(III) oxides or the formation of complexes between NOM and As(III) species, favoring early elution of As from the column. Redman et al. (2002) report that the presence of organic matter provokes a slip and delay of As species from the sorption sites in natural sorbents. This is related to the occupation or obstruction of an important reactive surface fraction by NOM, causing in this way the decrease on the amount of reactive sites for capture of As.

14.3.4 Test with activated carbon column followed by a fixed-bed column for treatment of natural water from the Tuminguina River

To avoid fast As elution from the fixed-bed column when using natural water, a combination of an activated carbon pre-column followed by a fixed-bed with modified chitosan was
tested. The results show that 50 µg L⁻¹ of As are reached after passing 10,700 bed volumes of feed water. Corresponding to mass balance calculations 760 mg g⁻¹ can be removed from the raw water (see Fig. 14.4).

It is evident that the column loaded with activated carbon placed before the column with modified chitosan improves the As removal from contaminated water. Other researchers point out that activated carbon removes efficiently natural organic matter and non-polar and recalcitrant organic compounds during water and wastewater treatment (Toles et al. 1997, Matsui et al. 2004, Vieno et al. 2006).

14.3.5 **Regeneration of modified chitosan spheres**

Application of sorbents is economic when these materials can be applied repeatedly for several sorption-desorption cycles. To examine the reusability of Fe(III) chitosan spheres (Ch-HFO), a 5% NaOH solution was applied for regeneration. Figure 14.5 shows the development of As concentration during the regeneration. It is obvious that with only 10 volumes of caustic soda 89% of As can be removed from the sorbent material (673 µg As g⁻¹ of wet chitosan). The observation that As desorption was completed within 10 bed volumes, demonstrates that sorption sites of HFO nanoparticles are easily accessible within the porous structure, i.e., no pore blockage and subsequent increase of tortuosity due to the dispersion of the submicron HFO particles within the porous beads were observed. At highly alkaline pH, HFO sorption sites are all deprotonated and negatively charged. Therefore, all arsenite

---

**Figure 14.4.** Breakthrough curve of As during a run with water from a waterfall from the Papallacta Lake.

**Figure 14.5.** Concentration profile of As during regeneration of Ch-HFO spheres.
and arsenate species are displaced and regeneration is very efficient. The desorption reactions of arsenates and arsenites adsorbed on surfaces of HFO particles are expressed in the reaction scheme shown in Figure 14.6 (Cumbal 2004).

After regeneration, Ch-HFO spheres should be reconditioned with 0.3 M of acetic acid to decrease the pH. Eight bed volumes of acid solution were needed to reach pH = 5.5. After reconditioning, Ch-HFO spheres are ready to be used in another sorption cycle without any further treatment. Figure 14.7 summarizes chemical reactions of modified chitosan protonation (Cumbal 2004).

Previous studies show that resin beads impregnated with HFO particles are also regenerated with a few bed volumes of regenerant (DeMarco et al. 2003, Cumbal et al. 2003). In another study, researchers found that As immobilized on surfaces of anion resins dispersed with magnetite particles, needed around 20 bed volumes of 4% NaOH to desorb over 90% of the metalloid (Cumbal and Sengupta 2005).

14.3.6 Design, installation, and operation of a pilot plant for removal of arsenic from Papallacta Lake’s spring

For the design of a pilot plant, results of As sorption capacity of Ch-HFO obtained from fixed-bed columns, adsorption isotherms, and kinetic tests were used. The plant was calculated to supply safe water for a community of 20 people with 15 L of water/day/person (for drinking and food preparation). From sorption tests in the laboratory, an As sorption capacity of 0.5 mg g⁻¹ of wet chitosan was estimated. Further operational parameters chosen were

![Figure 14.6. Illustration of desorption mechanism of arsenic species during Ch-HFO regeneration.](image1)

![Figure 14.7. Conditioning processes of Ch-HFO spheres.](image2)
surface velocity and detention time. With these parameters, the filter to host the chitosan adsorbent was sized. Filter properties are summarized in Table 14.2.

For sizing all other components of the pilot plant, the dimensions of commercially available containers were considered. The three pumps that feed: i) raw water to the pilot plant, ii) regenerant solution to the filter, and iii) conditioning solution to the filter, were chosen with a capacity of 0.25 HP and a flow rate of around 1 L min\(^{-1}\). Table 14.3 lists the components of the plant; Figure 14.8 shows the distribution of the units.

**Table 14.2. Pilot plant: filter dimensions.**

<table>
<thead>
<tr>
<th>Technical specifications</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>L min(^{-1})</td>
<td>0.50</td>
</tr>
<tr>
<td>Height</td>
<td>cm</td>
<td>45.00</td>
</tr>
<tr>
<td>Outside diameter</td>
<td>cm</td>
<td>21.60</td>
</tr>
<tr>
<td>Inside diameter</td>
<td>cm</td>
<td>21.20</td>
</tr>
<tr>
<td>Cross section</td>
<td>dm(^2)</td>
<td>3.46</td>
</tr>
<tr>
<td>Bed height with Ch-HFO</td>
<td>cm</td>
<td>14.44</td>
</tr>
<tr>
<td>Wet density of Ch-HFO</td>
<td>g L(^{-1})</td>
<td>1000.00</td>
</tr>
</tbody>
</table>

**Table 14.3. Pilot plant components.**

<table>
<thead>
<tr>
<th>Parts</th>
<th>Volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage tank for raw water</td>
<td>4000</td>
</tr>
<tr>
<td>Storage tank for regenerant</td>
<td>250</td>
</tr>
<tr>
<td>Storage tank for used regenerant</td>
<td>250</td>
</tr>
<tr>
<td>Tank for the conditioning solution</td>
<td>50</td>
</tr>
<tr>
<td>Tank for collection of Fe(III) precipitates</td>
<td>50</td>
</tr>
<tr>
<td>Filter with activated carbon</td>
<td>10</td>
</tr>
</tbody>
</table>

![Figure 14.8. Pilot plant for arsenic removal.](image)
14.3.7 Pilot plant: First cycle of operation

Figure 14.9 shows the As concentration measured in the collection tank of the treated water during the first cycle of operation. Note that after passing 710 bed volumes of raw water 10 µg L\(^{-1}\) of As are reached while more than 2500 bed volumes can be treated without attaining 50 µg L\(^{-1}\) of As. The fast elution of As from the filter with Ch-HFO can be associated to the high concentration of As in the raw water (194 µg L\(^{-1}\)).

14.3.8 First regeneration of Ch-HFO from the pilot plant

Figure 14.10 shows the regeneration of Ch-HFO particles from the filter of the pilot plant. Only 10 bed volumes of caustic soda (50 L) were needed to remove approximately 50% of As from the Ch-HFO media. Arsenic contained in the spent regenerant was immobilized by dosing ferric chloride solutions (0.25 M to 0.50 M as Fe) (data not shown). The resulting gelatinous sludge was then dehydrated using vacuum filtration and the dried cake was disposed off in a landfill.

14.4 CONCLUSIONS

- The amount of Fe dispersed (33.65 mg Fe\(_{\text{III}}\) g\(^{-1}\) of wet chitosan) inside chitosan particles is moderate because the pH of Fe(III) solution during the dosage is low (pH = 1.6). At this pH, amino groups of chitosan matrix are positively charged and may repel Fe cations.
Compared to other host materials such as sand granules and calcium alginate beads, the iron content deposited into the chitosan beads is higher, however, compared to iron deposited within ion exchange beads is lesser. It is evident that functional groups of host materials play an important role in amount of iron deposited inside the supporting media.

- Chitosan impregnated with Fe(III) oxides shows several advantages compared to other emergent low-cost supporting materials: i) raw material availability, ii) simple preparation methodology, iii) good mechanical and hydraulic properties, iv) use in thee or four sorption-desorption cycles, and v) efficient regeneration.
- Ch-HFO spheres immobilize As species by a combination of electrostatic and Lewis acid-base interactions. Arsenic oxyanions are electrostatically linked to positively charged Fe(III) oxides while Lewis acid-base interaction forms an inner-sphere complex between As (pair of electrons donor) and HFO particles (pair of electrons acceptor).
- Experimental arrangement of an activated carbon column followed by a column with Ch-HFO provided a significant increase of the removal capacity of As from natural waters. Thus the column packed with activated carbon retains natural organic matter and avoids competition of NOM with As for sorption sites and formation of As(III) complexes that drags As to the exit of Ch-HFO filter.
- The amount of water treated (12500 L) during the first operation cycle of the pilot plant is satisfactory considering that As concentration in raw water was above 190 µg L$^{-1}$. However, treatment efficiency can be improved if the procedure for Fe(III) loading is slightly modified and if the loss of Ch-HFO beads from the filter is controlled.
- With 10 bed volumes of caustic soda moderate regeneration efficiency during the first operation cycle of the pilot plant was achieved.
- Arsenic contained in the spent regenerant was immobilized by dosing ferric chloride solutions. The resulting gelatinous sludge was then dehydrated by vacuum filtration and the dried cake was disposed off in a landfill.

ACKNOWLEDGMENTS

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CHAPTER 15

Field experiences with ArsenX\textsuperscript{np}, a very effective and efficient hybrid media for arsenic removal

Edward Belsten, Francis Boodoo, Joe D’Alessandro, Matteo Garegnani & Dave Larose

15.1 INTRODUCTION

ArsenX\textsuperscript{np} is a regenerable, hybrid media for arsenic (As) removal from aqueous streams, that combines the unique chemistry of hydrous iron oxide nanoparticles with the physical stability of a durable, non-friable, spherical polymeric substrate. ArsenX\textsuperscript{np} in fact consists of nanoparticles of iron impregnated into the matrix of a special, macroporous strong base anion exchanger. This ideal combination of selectivity and substrate durability makes ArsenX\textsuperscript{np} an ideal As removal media for municipal water treatment plants as well as point-of-entry (POE) and point-of-use (POU) devices.

ArsenX\textsuperscript{np} has been invented and patented by Prof. Arup K. Sengupta and his team at Lehigh University, Bethlehem, PA, USA and is manufactured upon licence by The Purolite Company, Bala Cynwyd, PA, USA (Cumbal and Sengupta 2005, Demarco et al. 2003).

Water treatment systems incorporating ArsenX\textsuperscript{np}, preferably with a lead-lag configuration, are designed and operated using the same engineering guidelines as conventional ion exchange resins. Superior bead strength means fines will not be generated nor will pressure drop be a concern during long-term performance, even at well head pressures up to 8 bar. Bead sphericity also ensures plug flow of the raw water through the bed thereby maximizing the As loading per vessel and ensuring complete capacity utilization.

ArsenX\textsuperscript{np} is an ANSI/NSF 61 certified media with exceptional affinity and high capacity for As, both arsenate and arsenite.

15.2 THE GREEN VALLEY DOMESTIC WATER DISTRICT ARSENIC TREATMENT SYSTEM

The Green Valley Domestic Water District (GVDWD) is a government owned community water system that supplies drinking water to approximately 8000 residents, businesses, and four golf courses. Green Valley, Pima County, AZ, USA is located 32 km south of Tucson, AZ, USA and 64 km north of Nogales, Sonora, Mexico. Well No. 1 has been a source of public water since 1977.

Well No. 1 has a maximum design flow rate of 320 m\textsuperscript{3} h\textsuperscript{-1}. However, the GVDWD replaced the 320 m\textsuperscript{3} h\textsuperscript{-1} pump with a 170 m\textsuperscript{3} h\textsuperscript{-1} pump in June 2006 since As levels of 13–15 µg L\textsuperscript{-1} have historically been reported for untreated drinking water from this well.

An As treatment system using ArsenX\textsuperscript{np} media was commissioned on 15 June 2006 at Well No. 1. When properly maintained and monitored, the ArsenX\textsuperscript{np} treatment system safely removes the naturally occurring As from the drinking water and maintains compliance with the new federal As drinking water standard of 10 µg L\textsuperscript{-1} effective 23 January 2006.
15.2.1 Arsenic monitoring procedure

The As monitoring procedure is designed to comply with federal compliance policies. Compliance sampling policy for the GVDWD is based on monitoring the well for one year and includes the following:

- compliance samples for As must be collected at the point of entry into the distribution system,
- submit a complete sampling report for a 12 month period,
- if the analytical results are less than or equal to 10 µg L⁻¹ As, the system will not have to be monitored using the compliance sampling protocol for 3 years, after which a compliance period of 1 year will begin again,
- if the analytical results are greater than 10 µg L⁻¹ As, GVDWD will be required to begin compliance quarterly sampling during the first quarter immediately following routine sampling. The system will be considered in compliance when the running annual average As concentration for four consecutive quarters is less than 10 µg L⁻¹.

GVDWD has passed the As sampling protocol as required by local regulators.

15.2.2 General setting

The ArsenX™ treatment system is constructed inside a walled compound for water supply Well No. 1 on an 800 m² site. The site, at West Placita de la Cotonia, is at an elevation of 893 m above sea level.

15.2.3 System overview

The ArsenX™ treatment system consists of a common manifold, three As treatment trains in parallel, an untreated bypass, and two chlorinators, one at the well head and one on the bypass pipeline. Each As treatment train consists of one mechanical filter for suspended solids removal and two As removal media vessels—lead and lag. The two adsorptive media vessels in each train are plumbed so that either vessel can be placed in a lead or lag position.

The As removal section layout is quite simple as adsorptive media regeneration is done off-site and the vessels only need to be equipped with two sluicing ports to load the fresh or regenerated media and discharge the As loaded media. Each vessel holds 3450 L of ArsenX™, manufactured by The Purolite Company.

15.2.4 Treatment process description

The water pumped from Well No. 1 flows into a common manifold. Automatic flow control valves proportion the flow among the three As treatment trains and the blending bypass. The flow control valves on the blending bypass and on each of the three As treatment trains, are set to direct approximately 33% of the total flow (50 m³ h⁻¹) to the blending bypass, with the remaining 67% of the flow (102 m³ h⁻¹) split evenly across the three As treatment trains (34 m³ h⁻¹ on each train). Bypass water is not treated for As removal, and is blended with treated water downstream from the treatment trains in the treated water manifold.

In each of the three As treatment trains, water flows sequentially through a solids removal filter and two pressure vessels containing ArsenX™. The two adsorption vessels, located in each As treatment train, are plumbed so that either vessel can be placed in a lead or lag position. The flow from the As treatment trains is directed into a common treated water manifold where it blends with the bypass flow, and it is then sent into the potable water distribution main. The empty bed contact time is approximately 6.1 minutes at an average flow rate of 34 m³ h⁻¹ per train.
The ArsenX® treatment system has the advantage of simplicity, in that it is a simple flow through system with only the extraction well pump used to transmit the water through the treatment system. The ArsenX® media is abrasion and crush resistant, and does not require periodic backwashing for the removal of fines as other competing media often do. ArsenX® is effective over a wide pH range, so the ArsenX® treatment system does not require any chemicals dosage to adjust pH.

A slipstream of water from the blending bypass flows through a tablet chlorinating system. The chlorinated solution is injected back into the bypass line before it is combined with flows from the ArsenX® treatment system. The treated/chlorinated water then flows to the water distribution main (Fig. 15.1).

![Diagram of well head treatment system]

Figure 15.1. Layout of well head treatment system at Green Valley Domestic Water District.
15.2.5 Water chemistry

The water of Well No. 1 has a pH of 7.58 and contains 14 $\mu$g L$^{-1}$ of As, 10 $\mu$g L$^{-1}$ of vanadium (V), 150 $\mu$g L$^{-1}$ of phosphate (PO$_4$), 32.20 mg L$^{-1}$ of silica (SiO$_2$) and 5 $\mu$g L$^{-1}$ of other oxyanions (antimony, molybdenum, selenium, uranium, etc.).

Arsenic contained in the water fed to the ArsenX$^{\text{®}}$ vessels is assumed to be all As(V) because of the preceding, in line chlorination. The presence of As(V) and other oxyanions is of interest because they interfere with the As removal process as well as, even if due to other mechanisms, PO$_4$ and SiO$_2$.

15.2.6 ArsenX$^{\text{®}}$ media replacement

The performance of the ArsenX$^{\text{®}}$ in the lead vessel is monitored by periodic sampling and analysis of the water between the lead and lag vessels. Sample ports have been installed on all vessels to plot the media exhaustion levels within the bed. Typically, when the concentration of As at the effluent of the lead vessel reaches 50–65% of the influent As concentration a media change out is scheduled and performed within 30 days. Before the media change out, the lead vessel is isolated, locked out and prepared for media extraction.

ArsenX$^{\text{®}}$ discharge from one vessel containing up to 4250 L of media typically requires 5 hours. This operation includes:

- arrival at site, tailgate meeting job and safety/potable water issues review,
- connection of transfer hoses and media extraction from vessel previously drained by the owner,
- filling of super sacks or drums with As loaded media, their labeling and loading for transport,
- power wash and inspection of internal walls and under drains,
- cleaning site of all debris and wash down, complete paperwork, chain of custody and insure all containers are correctly labeled and secured for transport,
- departure from site.

After exhausted media removal and prior to the installation of the regenerated ArsenX$^{\text{®}}$ all process equipment coming into contact with the treated water is thoroughly disinfected. The installation of up to 4250 L of ArsenX$^{\text{®}}$ in one vessel typically requires another 5 to 6 hours and includes:

- arrival at site, tailgate meeting job and safety/potable water issues review,
- filling the vessel with water up to 150–300 mm above the under drains,
- installing and classifying a NSF/ANSI 61 sub bed (should the system require a sub bed),
- loading of regenerated ArsenX$^{\text{®}}$,
- backwashing and rinsing of regenerated ArsenX$^{\text{®}}$,
- cleaning site of all debris and wash down, complete paperwork,
- departure from site.

Backwashing the regenerated ArsenX$^{\text{®}}$ is necessary to remove fines and turbidity that might have generated during freight and handling. This operation also reduces the probability of channeling while in operation. After the backwash the regenerated ArsenX$^{\text{®}}$ is rinsed for approximately 10 bed volumes. These two steps are performed on all change outs with new or regenerated ArsenX$^{\text{®}}$ to ensure proper bed start up and to obtain optimum performance from the early beginning of the operating cycle.

Once these operations have been completed, the formerly lead vessel now loaded with new or regenerated ArsenX$^{\text{®}}$ is placed back on line in the lag position using the process valves on the manifold.
15.2.7  Regeneration of ArsenX®

The regeneration of the exhausted ArsenX® is performed off site at Purolite’s regeneration facility in Bala Cynwyd, PA. The proprietary regeneration process consists of the following steps:

- exhausted ArsenX® is received and accompanying documentation is reviewed,
- Quality Control personnel performs required analysis on exhausted media, exhausted ArsenX® must pass Quality Assurance/Quality Control established standards prior to regeneration,
- regeneration is performed,
- regenerated ArsenX® is repackaged and relabeled for transport,
- chain of custody documentation is completed, regenerated ArsenX® is released for shipment back to the owner,
- a Toxicity Characteristic Leaching Procedure (TCLP) is performed on the sludge from the regeneration process, the sludge is classified as non-hazardous per the guidelines of the Commonwealth of PA,
- the sludge is sent off-site for disposal by landfilling.

The regeneration itself consists of several steps during which ArsenX® is contacted with aqueous solutions of simple chemicals such as sodium chloride (NaCl), sodium hydroxide (NaOH) and carbon dioxide (CO₂) under specific temperature and pressure conditions. The regeneration removes from exhausted ArsenX® all As and collected oxyanions as well as PO₄ and SiO₂ while leaving on place the nanoparticles of iron oxide without damaging their structure, that is crucial to achieve optimum performances in the following runs. After repeated regenerations however, the ArsenX® media will gradually lose capacity to adsorb As. The loss in capacity is dependent on the water chemistry at the specific site as well as changes in the influent concentrations of As and other competing constituents. The regenerability of ArsenX® is a peculiar and interesting characteristic of this As removal media as it allows one to divide the initial purchasing cost of the media over a number of runs. The off-site regeneration of ArsenX® obviously has its cost that is however very competitive if compared to the one-off use of the media. The ArsenX® regeneration cost includes the treatment of the resulting waste waters and the safe disposal of the As containing sludges. At the end of its useful lifetime, the exhausted ArsenX® is safely disposed off by landfilling.

15.2.8  Performance of ArsenX® at GVDWD

As already said, the As removal facility at Well No. 1 of GVDWD was commissioned on 15 June 2006. To date Purolite has changed out the lead beds twice and the lag beds once. The As treatment plant has had a somewhat consistent flow rate of 102 m³ h⁻¹, with intermittent peaks at 115–125 m³ h⁻¹.

Purolite’s initial projections for the GVDWD As treatment plant were 624.5 million cubic meter (mm³) treated before a 9 µg L⁻¹ effluent break at the lead vessels. Each of the three lead vessels holds 3450 L of ArsenX®. This capacity equates to 60,500 m³ of treated water per m³ of virgin media, or 60,500 bed volumes (BV). This production capacity was achieved and exceeded during the first run with fresh ArsenX®.

After the first media change out, with the formerly lag vessel in first position and the regenerated ArsenX® in lag position, the capacity of the lead vessels was 52,000 BV. This represents a 14% reduction in capacity, but this was expected as, during the first run, the lead bed was allowed to overrun approximately 60 days before media extraction for regeneration. This equates an additional production of 147 mm³, which means 23% of design capacity, and this caused an extra As loading on the lag vessel. Accounting for this, the media capacity for
As has actually been the same of the capacity of the initial run, and this has been confirmed by the analytical checks on the exhausted ArsenX<sup>®</sup>. After the second media change out, with the regenerated ArsenX<sup>®</sup> back in first position and freshly regenerated ArsenX<sup>®</sup> in lag position, the capacity of the lead vessels was 53,200 BV. This represents a 12% reduction in capacity versus the initial projection for virgin ArsenX<sup>®</sup>, but only a 7% reduction versus our expectations. We in fact expect a gradual reduction of As capacity after each regeneration. The analyses carried out in the exhausted media showed however a particularly high SiO<sub>2</sub> loading that, unfortunately, affects As removal performances. This, we believe, was the result of a change in the well water composition of which, unfortunately, we have no analytical confirmation. We reacted with a modified, reinforced regeneration procedure, and the analytical checks on the regenerated ArsenX<sup>®</sup> samples have shown all key parameters to be in line with expectations.

The run after the third media change is still ongoing at the present time. In the case of Well no. 1 of GVDWD, initial data suggest that the regenerated ArsenX<sup>®</sup> will operate economically for 8–10 regenerations, unless SiO<sub>2</sub> will build up on the ArsenX<sup>®</sup> at a rate higher than expected. The modified regeneration sequence, already in use at Bala Cynwyd, showed however to be effective in controlling SiO<sub>2</sub> build up and this makes us confident that expectations will be fully met.

### 15.3 THE BORGO VALSUGANA ARSENIC TREATMENT SYSTEM

Borgo Valsugana is a nice, small village with some 6700 inhabitants located within the Province of Trento, in the mountains of the northeast of Italy.

The municipality of Borgo Valsugana was obliged to consider the installation of an As treatment system after the coming in force of the new limit of 10 µg L<sup>−1</sup> of As in drinking water. In fact, the main source of the municipal water distribution system was a spring known to contain a few µg L<sup>−1</sup> of As over the new limit.

The spring is located in the mountains above the village and ArsenX<sup>®</sup> was chosen as the As removal technology because of its efficiency, reliability, ease of installation and reduced maintenance. The spring generates a flow rate of 72 m<sup>3</sup> h<sup>−1</sup>, 54 of which to be treated for distribution as potable water.

The As removal plant was erected by Eurotec WTT, an Italian OEM, after winning a public tender and, since its commissioning, it produces a drinking water fully complying with the current standard of 10 µg L<sup>−1</sup> of As, as required by the regional and national authorities.

#### 15.3.1 System overview and treatment process description

The water treatment system consists of two As removal vessels arranged in such a way that they are normally operated in series to produce the currently required 54 m<sup>3</sup> h<sup>−1</sup> of drinking water, but could also be operated in parallel should the need arise to increase the throughput. While in the series operation mode, either vessel can be placed in the lead or the lag position. Each vessel has a diameter of 1500 mm and a cylindrical height of 2500 mm, and holds 2700 L of ArsenX<sup>®</sup>. The empty bed contact time is 3.0 minutes at the design flow rate of 54 m<sup>3</sup> h<sup>−1</sup>.

The plant design did not include any mechanical filter as the spring water was expected not to contain any suspended solid.

#### 15.3.2 Spring water analysis

The spring water has an electrical conductivity of 100–110 µS cm<sup>−1</sup>, a pH of 7.4 and contains As in an amount variable from 19 to 27 µg L<sup>−1</sup> (22 µg L<sup>−1</sup> used for design purposes). The other parameters of interest are: 31 µg L<sup>−1</sup> of PO<sub>4</sub> and 1.0 mg L<sup>−1</sup> of SiO<sub>2</sub>, no V, while 5 µg L<sup>−1</sup> of
Field experiences with ArsenX™

other oxyanions were taken into account in the design. The picture is completed by a total hardness of 44 mg L\(^{-1}\) as CaCO\(_3\), a total alkalinity of 60 mg L\(^{-1}\) as CaCO\(_3\), 25 mg L\(^{-1}\) of SO\(_4\), 0.3 mg L\(^{-1}\) of NO\(_3\), 3 mg L\(^{-1}\) of Cl, 10 µg L\(^{-1}\) of Fe and no Mn.

Without any information on the speciation of As, it was assumed in the plant design that As(V) represented the 80% of the As load to the media, even if it was thought that all As contained in the water fed to the ArsenX™ vessels had to be arsenate because of the presence of an appreciable amount of free oxygen in the spring water.

15.3.3 Performance of ArsenX™ at Borgo Valsugana

The As removal facility at Borgo Valsugana was commissioned on 7 January 2008, and this was the first municipal plant with ArsenX™ commissioned in Italy and within all Europe. To date Eurotec WTT, the plant manufacturer who is also in charge for servicing the unit, has regenerated on site the lead bed only once.

Purolite’s initial projections for the As treatment plant of Borgo Valsugana were 388,800 m\(^3\) treated before a 8 µg L\(^{-1}\) effluent break at the lead vessel, and this capacity equates to 144,000 BV or about 300 days of continuous service at the design flow rate of 54 m\(^3\) h\(^{-1}\).

Figure 15.2 shows the influent and residual As content at the outlet of the lead and lag vessels to date. The lead bed was regenerated on site in September 2008. The run was only slightly shorter than anticipated.

During the run the As concentration in the spring water has been up to 21% higher than design and the operating flow rate had quite important excursions. We must also mention a few disruptions in the plant operation caused by the accumulation of suspended solids filtered out by the resin bed that obliged to repeatedly backwash the lead vessel. This was an unexpected problem that might have contributed to the early As breakthrough.

The lead vessel was regenerated onsite at the end of the first run and put back in service again in lead position. This was done to preserve the lag bed from any accumulation of solids, that might disturb the As removal process. The analyses carried out on the regenerated ArsenX™ showed the regeneration had been efficient in removing all As, PO\(_4\) and SiO\(_2\) retained by the media during the previous run. The regenerated ArsenX™ was also subjected to a proprietary As capacity test, that showed the media to be perfectly regenerated and ready for the second operating run.

At the present time the second run is ongoing with fully satisfactory results, and the spring water is being regularly monitored for As, to identify any seasonal variation.

![Figure 15.2](image-url)  
**Figure 15.2.** Influent and residual As content at the outlet of the lead and lag vessels at Borgo Valsugana As removal facility.
15.4 CONCLUSION

The combination of the hydrous iron oxide nanoparticles unique chemistry with the physical stability of a durable, non-friable, macroporous ion exchanger has proved to be an ideal, easy to manage solution to a worldwide problem. ArsenX® has shown to be a very efficient, reliable and cost effective As removal media, capable of providing a safe drinking water with an As concentration never exceeding the 10 µg L⁻¹, even under the worst operating conditions.

Arsenic speciation, V, PO₄, SiO₂, and pH directly influence ArsenX® As removal capacity and seasonal variations of well or spring water composition equally affect its performances, hence, precise information on raw water composition is required for a precise projection.

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REFERENCES


CHAPTER 16

Low-cost solar technologies for arsenic removal in drinking water

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16.1 INTRODUCTION

Groundwaters of the Chacopampean Plain of Argentina (provinces of Córdoba, La Pampa, Santa Fe and Buenos Aires) contain levels of arsenic (As) well above the 10 µg L\(^{-1}\) limit established by the Food Argentine Code (Código Alimentario Argentino 2007), same as recommended by WHO (WHO 2004) (10 µg L\(^{-1}\)). These groundwaters present high salinity, and the As concentrations are generally well correlated with those of other anions (F, V, HCO\(_3\), B, Mo). Waters are predominantly oxic, and have high pH values (7.0–8.7). Hence, As is mainly present as As(V) (Smedley et al. 2002). Metal oxides in the sediments (especially of Fe and Mn) are probably the main source of dissolved As as reported by Smedley et al. (2002), although the dissolution of volcanic glass has also been cited by Nicollì et al. (1989) as a potential source.

In many rural areas of the region, the lack of a drinking water network distribution and the absence of important surface water bodies make necessary to extract water from deep and shallow wells, typically used without any further treatment. In general, water quality is poor, especially in the phreatic zone, because of the bacteriological content and high levels of chemical contaminants and trace elements (Nicollì et al. 1989). This, together with poverty and malnutrition conditions, causes the incidence of water-borne diseases, including chronic endemic regional hydroarsenicism (HACRE in Spanish).

Various methods are known to be useful to remove As from drinking water, including anion exchange, precipitation, ion flotation, and adsorption (Edwards 1994, Hering et al. 1997, Pirnie 2000). Attention has recently focused on advanced oxidation processes (AOPs) such as heterogeneous photocatalysis (HP) (Litter 2009, Yang et al. 1999, Dutta et al. 2005, Ferguson et al. 2005, Yoon et al. 2009) and zerovalent iron (ZVI) (Bang et al. 2005, Su and Puls 2001), considered simple and low-cost technologies to remove As from groundwater that could be applied in poor isolated villages or settlements.

HP is an AOP based on the use of a non-expensive semiconductor, TiO\(_2\), which under the action of UV irradiation (including solar light), promotes the formation of active oxidizing species like hydroxyl or superoxide radicals, able to transform organic and inorganic pollutants into less harmful or more easily removable compounds. This process leads to organic matter mineralization (Litter 2005), bacteria destruction (Ibañez et al. 2003) and transformation of toxic metals or metalloids such as As (Litter 1999, 2009).

The zerovalent iron technology (ZVI) is based on the use of iron in the elemental form and has been extensively applied to remediation of contaminants such as chlorinated organic chemicals (Bremner et al. 2006) and metals (Rangsivek and Jekel 2005) in groundwater, seeming promising for As remediation (Bang et al. 2005, Su and Puls 2001). The primary advantages of ZVI include low-cost and availability of iron in rural villages, in the form of very cheap materials, and simplicity in handling and scalability. Zerovalent iron nanoparticles increase appreciably the rate of removal of As (Kanel 2006).

This chapter compiles the study of the evaluation of the effectiveness of simple and low-cost solar technologies for As removal from groundwater, based on heterogeneous photocatalysis (HP) and zerovalent iron (ZVI) technologies to remove As from laboratory water
solutions. For HP tests, laboratory prepared and natural samples were placed in bottles internally covered by a TiO$_2$ layer and exposed to solar or artificial UV light. By addition of iron in different forms [iron wool, packing wire or aqueous Fe(III)], simultaneously or after the irradiation, As removal higher than 80% after 6 hours of irradiation was obtained in all cases. ZVI tests with iron wool or packing wire yielded also good removals, although iron wool demonstrated to be a better iron material. Preliminary tests with commercial zerovalent nanoparticles (NZVI) resulted in outstanding results, rendering almost total removal with very low amounts of iron in very short contact times (typically under two hours). Natural waters from two localities of the Chacopampean Plain of Argentina were also tested (Mateu 2007, Morgada et al. 2008, 2009, Morgada de Boggio et al. 2009). UV irradiation improved the results, especially in natural waters. Although both methodologies, HP and ZVI yielded similar results, use of HP could be superior because simultaneous removal of As, natural organic matter, organic pollutants, toxic metals and microbiological contamination can be achieved.

16.2 EXPERIMENTAL

16.2.1 Chemicals

As(V) stock solution (1000 mg L$^{-1}$) was prepared from Na$_2$H$_2$AsO$_4$ · 7H$_2$O (Baker). Humic acids (Aldrich, sodium salts, technical) were used. Fe(III) was added as FeCl$_3$ (Mallinckrodt). Zerovalent iron was introduced in the form of commercial packing wire or iron wool (Virulana®), both non-galvanized. TiO$_2$ (Degussa P-25) was provided by Degussa AG, Germany and used as received. For analytical determinations, (NH$_4$)$_6$Mo$_7$O$_{24}$ · 4H$_2$O (Stanton), potassium and antimonyl tartrate (Baker), L-ascorbic acid (Sigma-Aldrich) and KMnO$_4$ (Riedel-de-Häen) were used. All other chemicals were reagent grade and used without further purification. Water was purified with a Millipore Milli-Q equipment (resistivity = 18 MΩ · cm).

Laboratory samples, 1 mg L$^{-1}$ As(V), were prepared from the stock solution in pure deionized water or in water of controlled ionic composition (CIC) containing 1.3 × 10$^{-4}$ M MgSO$_4$, 2.3 × 10$^{-4}$ M CaCl$_2$, 4.0 × 10$^{-5}$ M NH$_4$Cl, 9.0 × 10$^{-6}$ M FeCl$_3$ and NaOH to adjust pH to 7.8. Natural groundwater samples were obtained from wells of Tucumán and Santiago del Estero, Argentina. Los Pereyra is a small settlement of 1000 inhabitants located 70 km southeast of San Miguel de Tucumán City, and Las Hermanas is a very poor area close to Santiago del Estero City, both located in the northwestern part of Argentina.

16.2.2 Preparation of plastic bottles for use in HP

PET bottles of mineral water or soft drinks (600 mL) were covered internally with a TiO$_2$ layer, according to a procedure developed in our laboratory (Meichtry et al. 2007). Briefly, 10 mL of a 2% w/v TiO$_2$ suspension, pH 2.5 (HClO$_4$), previously ultrasonicated for 30 min, were introduced in the bottle, which was then shaken and rolled long enough to obtain a homogeneous film over the entire wall. The remaining suspension was drained and the bottle was left inverted, taking care that no drops or irregularities were formed on the surface. The bottle was dried at room temperature for 24 h. The impregnation was repeated twice, resulting finally a thin, semitransparent, and homogeneous TiO$_2$ film. To eliminate loose particles, the bottle was half filled with water and vigorously (manually) shaken for 0.5 min. This procedure was repeated twice.

16.2.3 Synthesis and characterization of NanoFe®

NanoFe® was prepared by Nanotek S.A. (Santa Fe, Argentina) according to a proprietary novel methodology of synthesis based on chemical reduction of ferric salts with
borohydride in a stabilized multiphase nanoemulsion (Nanotek 2009). The product was obtained as an aqueous black suspension, and the particles had magnetic properties. The material was characterized by XRD analysis (Siemens D5000 diffractometer), BET specific surface area (Micromeritics Gemini 2360), UV-Vis spectroscopy (Hewlett-Packard diode array UV-visible spectrophotometer, model HP 8453 A), and transmission electronic microscopy (TEM, Philips EM 301) (Nanotek 2009, Morgada et al. 2009). Nanoparticles were stored in 2-propanol until use. Before taking aliquots for any purposes, the 2-propanol suspension was ultrasonicated for 2 min with a Cleanson (25 kHz) ultrasonicator, model CS-1109. The concentration of iron in the suspension, determined by ICP-OES, was 36.6 g L⁻¹.

16.2.4 Experiments of As removal

16.2.4.1 As removal by heterogeneous photocatalysis with TiO₂

As(III) solutions (250 mL, [As(III)]_initial = 1000 µg L⁻¹ in Milli-Q water, pH 7.8) were placed in 600 mL bottles impregnated with TiO₂, and irradiated during 6 h by UV light at a horizontal position. A black-light tubular UV lamp (Philips TLD/08, 15 W, maximum emission at 366 nm) was used, at an irradiance of 800 µW cm⁻². After irradiation, 1.5 g packing wire was added in one or several pieces. In some experiments, packing wire was added at the beginning of the irradiation. Sampling was done always after 24 h in the dark to allow precipitate settlement, and remaining total As in solution was measured spectrophotometrically (see below) after filtration. In some cases, the experiment was repeated reusing the bottle.

Experiments with natural waters from Las Hermanas were performed similarly but under sunlight with addition of Fe₃Cl solution (around 100–200 Fe:As molar ratio) at the end of irradiation. The irradiation of the solar light used in the experiments corresponded to that of the Buenos Aires City in spring (34°38'S, 58°28'W, October 2006) and ranged 1600–2000 µW cm⁻². As concentration was measured by ICP/OES (Mateu 2007, Morgada et al. 2008, Morgada de Boggio et al. 2009).

16.2.4.2 As removal by zerovalent iron (iron wool and packing wire)

CIC waters, containing 1.3 × 10⁻³ M MgSO₄, 2.3 × 10⁻⁴ M CaCl₂, 4.0 × 10⁻⁵ M NH₄Cl, 9.0 × 10⁻⁶ M FeCl₃, and NaOH to adjust pH to 7.8, to make their composition similar to that of Los Pereyra well waters (250 mL) were spiked with 1000 µg L⁻¹ of As(III) or As(V), and placed in 600 mL bottles. Iron was added as packing wire or iron wool. Then, the bottles were exposed to artificial UV light (Philips TLD/08, 15 W, maximum emission at 366 nm) for several hours, followed by 24 h settlement in the dark. The lamp irradiance was 800 µW cm⁻². Similar experiments were performed in the dark. After filtration, As was measured spectrophotometrically (see below) (Morgada et al. 2008, Morgada de Boggio et al. 2009).

16.2.4.3 Nanozerovalent iron particles

Arsenical solutions (150 mL, in CIC water prepared as described in 16.2.4.2) were introduced into a 250 mL glass Erlenmeyer flask (covered by an aluminum foil in reactions performed in the dark) and bubbled with air (1 mL min⁻¹) for 30 min under orbital stirring at 150 rpm in order to reach oxygen saturation. Then, air bubbling was stopped, and a volume of the NanoFe® 2-propanol suspension containing the corresponding amount of Fe(0) (to have final concentrations ranging 0.005–0.1 g L⁻¹) was added, under continuous stirring. The flask was left open to the air with continuous stirring at 150 rpm until the end of the run. In some experiments, humic acids were added at 2 mg L⁻¹.

Irradiations were performed using a reflector UV lamp (Philips HPA 400S, maximum emission at 365 nm). The lamp was started immediately after NanoFe® addition. Irradiance was 5000 µW cm⁻².

Temperature was ambient, without control, and never attained values higher than 30°C. After the runs, samples were analyzed for As by ICP-OES.
16.2.5 Analytical determinations and measurement of irradiances

Spectrophotometric measurements of As(V) were performed through the formation of the arsenomolybdic complex following the method described by Lenoble et al. (2003). Total As was determined similarly but adding 126 mg KMnO₄/mg As (contact time 120 minutes), to previously oxidize As(III). As(III) concentration was calculated by difference. In some experiments, total As was determined by ICP-OES, using a Perkin–Elmer Optima 3100 XL apparatus or by total reflection X-ray fluorescence (TRXRF), using a PANalytical PW3830 X-ray generator. Before analysis, all samples were filtered through a 0.45 µm Millipore membrane.

Irradiances for sunlight and artificial light were measured with a Spectroline DM-365 XA radiometer.

16.3 RESULTS AND DISCUSSION

16.3.1 HP in bottles

In Table 16.1, results of HP experiments with As(III) in bottles coated with TiO₂ and addition of packing wire as described in section 16.2.4.1 under artificial UV light are presented. Results show that there were no relevant differences concerning the way of addition of the packing wire (after or during the irradiation) because similar results were obtained adding the wire in one piece or fragmented; of course, the last procedure would be more complicated (Morgada et al. 2008, Morgada de Boggio et al. 2009).

Although in this case WHO regulation values for the final As content were not attained, it is important to remark that initial As concentrations were rather high, at the highest limit of natural waters, and representative of only a few wells. The guideline values could however be reached by a more prolonged light exposure.

Three consecutive experiments with the same TiO₂-coated bottle in the conditions of Table 16.1 gave 90.5, 89.5 and 96.7% As removal, respectively, indicating that the efficiency was not affected by reuse of the photocatalyst, being even better after reusing.

Experiments in bottles with groundwaters from Las Hermanas (initial As concentrations ranging 900–1800 µg L⁻¹) were performed under sunlight. At the end of the irradiation, Fe(III) as FeCl₃ was added in the indicated Fe/As molar ratio. Results are listed in Table 16.2. In all cases, the final concentrations reached very low values and in one case (W6), the WHO standard was attained. Again, increasing the irradiation time would lead to achieve the guideline values in all cases. It is important to note that the initial Fe:As molar ratio used in the experiments (from 85 to 423) is considerably high; therefore, future work will focus on the optimization of this ratio (Mateu 2007).

It can be concluded that natural waters yielded better results than laboratory waters. Although with groundwater samples FeCl₃ was used, which is more efficient for As removal than wire pieces, and the irradiance was higher, the higher efficiency could be also explained by the presence in natural waters of species that could accelerate Fe(0) oxidation under sunlight (such as natural organic matter) giving rise to photo-Fenton type processes, or that could accelerate As adsorption on the Fe flocs. This was also observed in experiments with zerovalent iron (see sections 16.3.2 and 16.3.3).

Table 16.1. Results of HP experiments of As(III) removal. Conditions: [As(III)]₀ = 1000 µg L⁻¹; pH 7.8; V_solution = 250 mL in 600 mL bottles coated with TiO₂. Addition of 1.5 g packing wire after irradiation. Irradiation time (UV lamp): 6 h. Irradiance: 800 µW cm⁻².

<table>
<thead>
<tr>
<th>Sample</th>
<th>A₅₅₀₀ (µg L⁻¹)</th>
<th>Way of addition</th>
<th>As removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>In one piece, after irradiation</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>In pieces, after irradiation</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>In one piece, during irradiation</td>
<td>80</td>
</tr>
</tbody>
</table>
16.3.2 Zerovalent iron (packing wire and iron wool)

ZVI experiments of As removal in bottles adding packing wire and iron wool as described in 16.2.4.2, were performed. First, iron was added at 6.0 g L\(^{-1}\), the optimized value found in previous tests performed in natural waters from Los Pereyra wells using packing wire (d’Hiriart et al. 2009). The time evolution of As concentration, measured in these experiments immediately after sampling (no settlement in the dark) is plotted in Figure 16.1. As removal was considerably faster with iron wool, reaching a complete removal in 2 h while with packing wire only 30% was obtained in the same time. In addition, after 24 h settlement in the dark (meaning completion of adsorption processes in the formed iron flocs), the As removal was 83 and 100% with packing wire and iron wool, respectively (not shown). The reason for the different results can be attributed to a higher exposed oxidizable surface on the iron wool. However, iron wool was difficult to be removed from the solution because it disintegrated in very fine particles. In these experiments, no significant effect of UV light could be observed (Morgada et al. 2008, Morgada de Boggio et al. 2009).

XRD patterns (not shown) indicated that the initial ZVI samples were composed of only pure metallic iron, with only traces of Al and CaSiO\(_3\) in packing wire. After experiments of As removal, XRD patterns showed signals corresponding to maghemite, lepidocrocite and magnetite. This clearly indicates that ZVI was oxidized during the process.

In a second stage, the effect of the amount of iron wool was studied. Three different iron concentrations, 0.6, 1.0 and 6.0 g L\(^{-1}\) were tested, either under artificial UV light or in dark conditions. Figure 16.2 shows that the initial rate increased with increasing Fe(0) mass, although a complete As removal was obtained for all samples after 24 h settlement in the dark (not shown). In this case, the effect of light could be better analyzed. Although this effect

### Table 16.2. Results of HP experiments of As removal from well waters from Las Hermanas, Santiago del Estero Province. Conditions: \(V_{\text{solution}} = 250\) mL in 600 mL bottles coated with TiO\(_2\). Addition of FeCl\(_3\) after irradiation. Irradiation time: 6 h; range of irradiance: 1600–2000 \(\mu\)W cm\(^{-2}\) (sunlight).

<table>
<thead>
<tr>
<th>Sample</th>
<th>([\text{As}]_{\text{initial}}) (µg L(^{-1}))</th>
<th>([\text{As}]_{\text{final}}) (µg L(^{-1}))</th>
<th>(t_{\text{irr.}}) (h)</th>
<th>([\text{Fe(III)}]:[\text{As}]^*)</th>
<th>As removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>961</td>
<td>31</td>
<td>10**</td>
<td>162</td>
<td>96.8</td>
</tr>
<tr>
<td>W2</td>
<td>1090</td>
<td>13</td>
<td>4.2</td>
<td>214</td>
<td>98.8</td>
</tr>
<tr>
<td>W3</td>
<td>551</td>
<td>30</td>
<td>4.9</td>
<td>423</td>
<td>94.5</td>
</tr>
<tr>
<td>W4</td>
<td>1530</td>
<td>14</td>
<td>3.8</td>
<td>152</td>
<td>99.1</td>
</tr>
<tr>
<td>W5</td>
<td>1830</td>
<td>25</td>
<td>10**</td>
<td>85</td>
<td>98.6</td>
</tr>
<tr>
<td>W6</td>
<td>1630</td>
<td>&lt;10</td>
<td>5.1</td>
<td>143</td>
<td>&gt;99.4</td>
</tr>
</tbody>
</table>

* Molar ratio; ** Partially cloudy (irradiation for two consecutive days).

![Figure 16.1. As(V) removal from laboratory waters of similar composition of Los Pereyra well waters with iron wool or packing wire in 600 mL bottles, \(V_{\text{solution}} = 250\) mL. Conditions: \([\text{As(V)}]_{\text{initial}} = 1000\) µg L\(^{-1}\); pH 7.8; [Fe(0)]\(_{\text{initial}} = 6.0\) g L\(^{-1}\); artificial UV light (800 µW cm\(^{-2}\)) or kept in the dark; no further settlement in the dark.](image-url)
was not so evident at the highest Fe(0) concentrations, it was clearly observed with 0.6 g L⁻¹. This suggests that a more prolonged solar irradiation could provide a good As removal with a less amount of Fe, rendering the process even more economical. No significant differences could be observed starting from As(III) or As(V).

The mechanism of As removal by ZVI involves the formation of complexes of As(III) and As(V) on iron oxides formed in situ as a result of the Fe(0) corrosion reaction. Under irradiation, other processes like photo-Fenton type reactions, etc. are produced that increase removal (Morgada et al. 2009, Lackovic et al. 2000).

Well waters from Los Pereyra were tested with this method. A 250 mL sample was poured in a 600 mL PET bottle containing 1.5 g of packing wire and exposed to solar light for 6 h. A similar experiment was performed in the dark. After 24 h settlement in the dark, both samples were filtered, and remaining As was analyzed by TXRF. Figure 16.3 shows an important As removal efficiency in both cases, but a much better result was obtained under irradiation. This result differs from the one obtained on laboratory samples where for the same Fe(0) concentration almost no differences were observed under irradiation (see Fig. 16.2). The same reasons given for HP experiments can be given in this case: presence of species that could accelerate Fe(0) oxidation under sunlight or As adsorption on the Fe flocs. With more prolonged irradiation and under sunlight irradiation more powerful than that of the Buenos Aires City in spring, the values required by OMS might be reached. Experiments are underway.

### 16.3.3 Nanozerovalent iron particles

XRD patterns of nanoparticles indicated that NanoFe⁰ was composed of metallic iron, maghemite, magnetite and amorphous phases; the particles presented a specific surface area S_{BET} of 55–63 m² g⁻¹ and a particle size (measured by TEM) of 5–15 nm.

Preliminary experiments of As removal with NZVI particles were performed in 250 mL glass Erlenmeyer flasks. In Figure 16.4 are presented the results of dark experiments of As(V) removal with different masses of NanoFe⁰ performed as described in 16.2.4.3. Results indicate that removal was very rapid and increased with [NanoFe⁰]. For [NanoFe⁰] = 0.05 and 0.1 g L⁻¹, removal was higher than 90% after 150 min of contact time. The iron mass was two orders of magnitude lower than when using packing wire or iron wool (see section 16.3.2), indicating that NanoFe⁰ presents an outstanding ability to remove As. This can be explained not only by a higher surface area but also by a high intrinsic activity because this NZVI sample was even more reactive than other tested specimens (Kanel et al. 2006), being effective with a lower optimum NanoFe⁰ mass. It was suggested that the main mechanism for As removal using NZVI is adsorption of As on iron freshly corrosion phases.

![Figure 16.2. Effect of iron mass on As (III or V) removal from CIC waters using iron wool. Conditions: [As]₀ = 1000 µg L⁻¹; pH 7.8; [Fe(0)]₀ = 0.6–6.0 g L⁻¹; artificial UV light (800 µW cm⁻²) or kept in the dark; no further settlement in the dark. V_solution = 250 mL.](image)
Figure 16.5 indicates that UV irradiation enhanced slightly the As removal efficiency. On the other hand, addition of humic acids resulted in removal 50% lower in the dark. However, when the system containing HA was irradiated, although an initial inhibition was seen, removal was higher than without HA. The mechanism under UV light is suggested to be adsorption of As on iron surfaces enhanced by photo-Fenton processes, and it is more complex in the presence of HA, which are UV activators (Morgada et al. 2009).

Results of As removal from Los Pereyra groundwater samples using NanoFe® are reported in Figure 16.6. It can be noticed that removal was also very rapid and good values were obtained after 3 h contact time. However, UV light irradiation resulted in an outstanding removal, with final As content reaching the regulations for drinking waters. Lower [NanoFe®] was needed in comparison with the experiments performed on synthetic waters.

Although low amounts of solid wastes (As-containing iron flocs) are produced by the use of either HP or ZVI that can be handled as usual or easily disposed (Driehaus 2005), the use of NZVI had additional technological advantages: due to the low amount of iron used, the mass of wastes produced in the process is significantly lower. The flocs may be removed by magnetic techniques which is more efficient and faster than centrifugation or filtration. Microbiological contamination could be also abated (not tested yet).
16.4 Conclusions

Economical technologies for As removal have to be investigated urgently to offer solutions in isolated rural or urban localities. Experimental results demonstrate that heterogeneous photocatalysis with TiO$_2$-coated plastic PET bottles, with addition of Fe(III), or only with zerovalent iron are efficient low-cost technologies. In both cases, Fe can be added as very cheap materials as iron wool or packing wire. Even NVZI in the form of the commercial NanoFe® is not expensive because a very low mass is required to achieve a very good As removal. Use of irradiation (artificial UV and sunlight) definitively improves As removal from natural waters. Low amounts of solid are produced in these technologies, that can be handled as usual or easily disposed.

Although both methodologies, HP and ZVI yield similar results, use of HP could be superior because simultaneous removal of As, natural organic matter, organic pollutants, toxic metals and microbiological contamination can be achieved.

However, it is important to remark that for applications, previous analysis of the waters and validation of the method is mandatory because removal technologies are very dependent on the composition of natural waters.

Figure 16.5. As removal with NanoFe®. Effect of UV irradiation and humic acids. Conditions: [As(V)] = 1 mg L$^{-1}$, [HA] = 2 mg L$^{-1}$, [NanoFe®] = 0.025 g L$^{-1}$, $\lambda$ = 365 nm, 5000 $\mu$W cm$^{-2}$.

Figure 16.6. Results with waters from Los Pereyra using nanozerovalent iron. Conditions: [As$_{total}$]$_{initial}$ = 174 $\mu$g L$^{-1}$; [NanoFe®] = 0.025 g L$^{-1}$; reaction time: 3 h, artificial UV light (5000 $\mu$W cm$^{-2}$).
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