Water treatment using cryogel-based adsorbents - Targeting environmental pollutants at low concentrations

Önnby, Linda

2013

Citation for published version (APA):
Önnby, L. (2013). *Water treatment using cryogel-based adsorbents - Targeting environmental pollutants at low concentrations*. [Doctoral Thesis (monograph)]. Department of Biotechnology, Lund University.

Total number of authors:
1

Photo: Rasmus Lindblad

I obtained my Diploma in Biotechnology Engineering towards the end of 2007 and I was enrolled as a PhD student in early 2009 at Department of Biotechnology, Lund University. Before and during my studies at Lund University, I was a volounteer for two NGOs, dealing with environmentally and socially releated projects, in Uganda, Kenya and India. I continued working with environmental issues; parts of my Master thesis project was carried out in India, which dealt with treatment of textile dye wastewaters. To continue studying water treatment as a topic for my PhD thesis was hence an obvious choice.

Finding sustainable solutions is something I am passionate about. This is partly what motivates me in my research. Developing new treatment technology for polluted water is very challenging. Besides testing implementation of our ideas, certain underlying phenomenon need to be investigated in depth. This combination of fundamental and applicable research is what I enjoy the most. I live in a small farm house in the countryside with my partner and my two years old daughter. Here, we try to integrate and implement our environmental passion together. It is an interesting project with infinite possibilities, and keeps me going.

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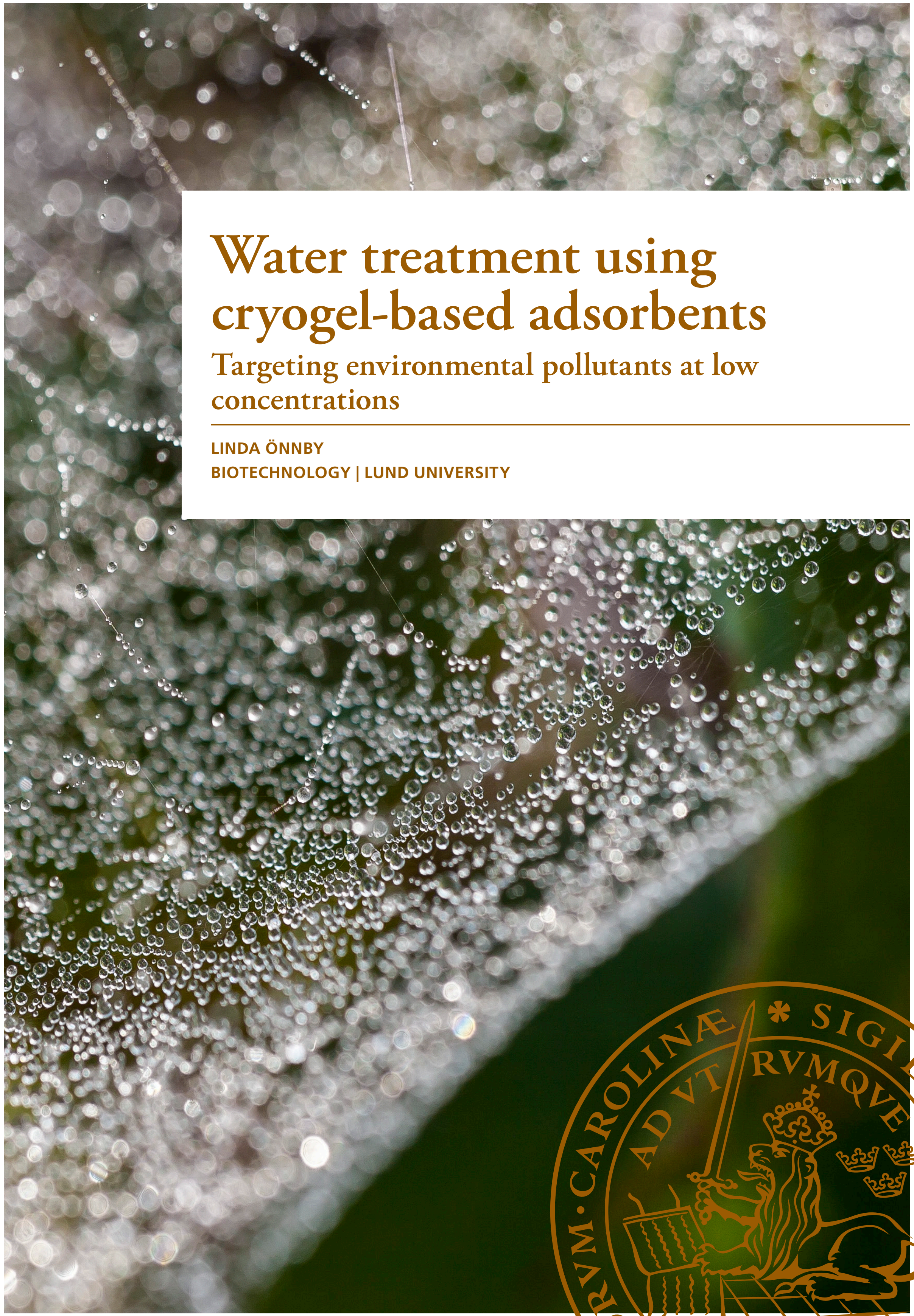
Biotechnology, Lund University

ISBN 978-91-89627-99-4
ISRN LUTKDH/TKBT--13/1153--SE

Printed by Media-Tryck, Lund University, Sweden

LINDA ÖNNBY Water treatment using cryogel-based adsorbents 2013



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Targeting environmental pollutants at low concentrations

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BIOTECHNOLOGY | LUND UNIVERSITY

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Targeting environmental pollutants at low concentrations

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DOCTORAL DISSERTATION
December 2013

Akademisk avhandling för avläggande av teknologie doktorsexamen vid tekniska fakulteten vid Lunds Universitet. Avhandlingen kommer att offentligen försvaras torsdagen den 12 december 2013, kl 13.30 i hörsal B på Kemicentrum, Sölvegatan 39, Lund.

Academic thesis which, by due permission of the Faculty of Engineering at Lund University, will be publicly defended on Thursday 12th December, 2013 at 1.30 p.m. in lecture hall B, at the Centre of Chemistry and Chemical Engineering, Sölvegatan 39, Lund, for the degree of Doctor of Philosophy in Engineering.

Faculty opponent

Professor Jon Petter Gustafsson, Royal Institute of Technology,
Stockholm, Sweden

Cover photo: Water droplets in spider web, by Christer Bergendorff.

Figure 1, 4, 7, 11 and 18, illustrated by Fia Persson
Figure 3, illustrated by Mira Liungman
Structures in Figure 12 and 13 and in Table 2, by Dmitry Berillo

Department of Biotechnology
ISBN 978-91-89627-99-4
ISRN LUTKDH/TKBT--13/1153--SE

Printed in Sweden by Media-Tryck, Lund University, Sweden, 2013

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LUND UNIVERSITY
Department of Biotechnology
P.O. Box 124
SE-221 00 Lund, Sweden

Document name
DOCTORAL THESIS

Date of issue
18 Nov 2013

Author(s)
Linda Önnby

Sponsoring organization
Swedish Research Council

Title and subtitle
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Targeting environmental pollutants at low concentrations

Abstract

The lack of safe, clean water is strongly linked to poverty, underdevelopment and poor health. Water is needed not only to sustain life, but to produce food and in industrial processes. Anthropogenic pollution and natural events can jeopardize access to safe water. Inorganic pollutants or toxic metal ions such as arsenic and cadmium are of special concern since these are persistent and accumulate in nature. Contaminated water used for direct consumption or for irrigation of crops can thus lead to direct and indirect exposure to humans to these metals.

To improve access to safe water, treatment must be developed to remove even low concentrations of toxic metal ions. Adsorption is a suitable technique. In this work, adsorbents were developed for various kinds of water sources; dinking water, wastewater, industrial water and leachate from a biogas process, all of which contained metal ions, such as As or Cd, at low concentrations. The adsorbents developed were based on a polymer cryogels, produced via cryoconcentration. Cryogels have a highly interconnected and porous structure, making them suitable for water treatment. The cryogels evaluated in this thesis were all based on the polymer polyacrylamide (pAAm).

In the first study, a pAAm cryogel was chemically modified with chelating functionalities suitable for the removal of heavy metals (i.e. Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2}). A rational design was suggested, involving preparation of the polymer inside plastic carriers to increase the mechanical stability of the material. Another strategy using particles was explored by embedding either nanoparticles (NPs) or molecularly imprinted polymers (MIPs) in pAAm-cryogels. The ability of Al_2O_3 NPs or MIPs in cryogels (called Alu-cryo and MIP-cryo, respectively), to remove As(V) was investigated. Both Alu-cryo and MIP-cryo exhibited adsorption capacities similar to those when the respective particles were applied in suspension. MIP-cryo showed higher selectivity but lower adsorption capacity than Alu-cryo.

To improve the removal of As(III) without any pretreatment, co-precipitated Fe-Al hydrous oxides were prepared and embedded in cryogels. As(III) could be removed from smelting wastewater in flow-through mode, reducing the concentration to European industrial emission standards. The removal of Cd^{2+} from leachate resulting from the anaerobic digestion of seaweed was studied using hydrothermally modified TiO_2 embedded in cryogels. This cryogel was shown to be successful in removing Cd^{2+} when tested in flow-through mode, and high adsorption capacities were obtained. Toxicity and particle leakage were studied in NP-embedded cryogels. Although no evidence of particle leaking was found, toxicity resulted from the leakage of the monomer acrylamide from the cryogel.

The findings of this work show that cryogel-based have potential in water treatment, due to their broad range of applications and the flexibility of the material. New and improved methods of particle immobilization in cryogels should be investigated, and pAAm should be replaced by non-toxic alternatives. Making cryogel materials with high adsorption capacities, which can be regenerated, can reduce the cost of water treatment. It is also important that novel technology meets environmental safety requirements to ensure the supply of safe water.

Key words
Adsorption, cryogels, nanoparticles, arsenic, cadmium, water treatment, composites

Classification system and/or index terms (if any)

Supplementary bibliographical information

Language English

ISSN and key title

ISBN 978-91-89627-99-4

Recipient's notes

Number of pages: 174

Price

Security classification

Signature

Date 4 Nov 2013

Populärvetenskaplig sammanfattning

Tillgången till rent vatten är avgörande för människans överlevnad, tillgång till vatten kan förbättra den allmänna hälsan och därmed också vår fortsatta existens på jorden. Naturkatastrofer eller mänsklig påverkan genom t.ex. industrin kan dock resultera i att vattenkällor, tidvis eller permanent, blir förorenade med miljögifter som hindrar människans konsumtion av rent vatten. Detta är en verklighet i många delar av världen. Merparten av de människor som saknar tillgång till rent vatten lever också i utvecklingsländer. Det finns tveklöst starka samband mellan fattigdom, god hälsa och tillgång till rent vatten. Även i de ekonomiskt starka länderna finns det dock liknande vattenproblematik. I takt med att det utvecklas nya produkter och att vi ändrar vår livsstil, påverkas till exempel utsläpp och därmed vattenkvalitén. Utöver dricksvatten, behövs vatten också inom industrin och jordbruk.

Kännedomen om att arsenik är giftigt har vi bland annat fått läsa om i Agatha Cristies deckare, där ämnet ofta används som mordvapen. Arsenik och kadmium är båda toxiska metaller redan vid låga koncentrationer (arsenik är egentligen en metalloid, men för enkelhetens skull kommer den att nämnas tillsammans med gruppen metaller). I Bangladesh är arsenik ett utbrett hälsoproblem, då det finns i grundvattnet som används som dricksvatten. Arsenik förekommer naturligt i vattnet, då det frisläpps från berggrunden, en process som gynnas vid bland annat syrefattiga förhållanden. Med tanke på grundvatten utnyttjas som dricksvattenkälla för en stor del människor runt omkring i världen, kan förorenat grundvatten ge drastiska hälsoeffekter.

Exponeringen för arsenik och kadmium kan också ske via livsmedel. Både arsenik och kadmium har detekterats i matprodukter däribland i ris och vete. Detta kan vara en konsekvens från att handelsgödsel innehållande kadmium används eller att jordbruksfält bevattnas med kontaminerat vatten. Om kadmiumproblemet har vi läst i svenska media. Särskilt i norra Europa är sannolikheten för kadmiumanrikning i mat stor, en effekt av att kadmiumanrikning i odlade produkter gynnas i sura jordar likt de jordar som påträffas i Sverige. Arsenik finns även i Sverige, bland annat vid småländska glasbruk, där man nyligen upptäckte tonvis arsenik i gamla glasdeponier från flera decennier tillbaka i tiden. Konsekvensen eller påföljden efter en lång tids exponering av arsenik och/eller kadmium är bland annat cancer, även när ämnena finns vid låga koncentrationer. Gränsvärdet för arsenik i samband med dricksvattenkonsumtion är 10 µg/l, medan det för kadmium är 3 µg/l, industrins gränsvärden är cirka 10 gånger högre.

För att slippa en rad av ovan beskrivna konsekvenser behövs åtgärder. Ämnena behöver separeras, elimineras eller reduceras från miljön, från till exempel vatten som annars sprider ämnena till flera platser. Vattenreningstekniker som avser dessa farliga ämnen är betydande och också utmanande. En reningsmetod som skall fungera i naturliga eller industriella vatten, vid aktuella koncentrationer, ställer höga krav på teknikens effektivitet. Inom industrin utnyttjas främst fällning för att avskilja metaller från utgående vatten. Fällning är effektivt när metaller finns vid höga koncentrationer såsom 100-1000 mg/l, någon fullständig avskiljning av metaller är dock svår att uppnå med hjälp av denna teknik. Andra reningsmetoder som är lämpliga för metaller vid låga koncentrationer är dock adsorption. Med adsorption menas att metalljonen fastnar på en fast yta av ett material. Material som utnyttjas för adsorption kallas adsorbenter.

Vi har utvecklat och designat adsorptionsmaterial som baseras på en gel. Gelen kan fungera som en bärare för ytterst effektiva absorbenter. Vi har därefter skräddarsytt adsorbenterna med avseende på vilken metalljon som skall avlägsnas och i vilken typ av vatten den befinner sig i. En effektiv adsorbent är ett material som kan erbjuda en stor yta för metalljonerna att fastna på. Idag hittar man dessa möjligheter inom nanotekniken. Generellt sätt erbjuder små partiklar en större yta uttryckt per volymenhet jämfört med större partiklar.

Gelen kan liknas vid en tvättsvamp: den har god absorptionsförmåga och kan därför suga upp vatten och svälla. Den har också ett nätverk med porer som liknar tvättsvampen. Skillnaden är att porerna i gelen är av mindre storlek, mellan 1 till 100 µm. Denna gel får vi genom att tillverka den på ett sätt som sedan länge är känt inom livsmedelsindustrin, genom så kallad kryo-koncentrering. I praktiska termer utgår vi från en vattenlösning innehållande gelens monomerer (byggstenar) som fryses vid -12 grader Celsius. Vi kallar dessa typer av geler för kryogeler och de har en porös struktur som liknar ett nätverk av kanaler, likt de vi ser i tvättsvampen. Porösa material kan vara särskilt lämpliga för vattenrening i form av t.ex. filter, då vatten lätt kan passera igenom.

I vår första studie ville vi testa om det var möjligt att kemiskt förändra kryogelen för att fånga en rad olika tungmetaller från vattenlösningar. Detta var möjligt och vi kunde också bestämma vilka de optimala förhållanden var för att adsorptionen skulle fungera som bäst. För att öka adsorbentens kapacitet, valde vi att undersöka en ny strategi. Vi använde oss av partiklar, främst av metalloxider som naturligt binder både arsenik och kadmium i jorden. Dessa partiklar bäddade vi in i kryogelen när vi bildade den. Kryogelen fick på så sätt fungera som en bärare för dessa partiklar. De partiklar vi har studerat har varit av varierande storlek, från tusendels millimeter till nano-storlek, det vill säga en miljondels millimeter.

I en studie visade vi att arsenik kunde adsorberas från vatten i närvaro av andra konkurrerande joner som påträffas i vattenreningsverk. Denna kryogel innehöll en adsorbent som var skräddarsydd till att vara mer selektiv jämfört med den andra arsenik-adsorbenten i samma studie. En selektiv adsorption kan vara en fördel då man vill avlägsna något giftigt eller värdefullt från t.ex. ett processvatten. Ett praktiskt exempel är gruvindustrins processvatten som innehåller en rad olika metaller. Vi testade vår metod på detta industrivatten och klarade att reducera arsenik till det tillåtna gränsvärdet enligt EU:s regler för industriutsläpp.

Inom ramen för denna avhandling tillverkade vi även en kryogel som var särskilt lämpad för kadmium. Vi undersökte dess förmåga att avlägsna kadmium från ett lakvatten från en biogasprocess där tång rötats. Trots att lakvattnet innehöll en del slam klarade kryogelen enkelt att minska kadmiumkoncentrationen i lakvattnet till låga halter. Andra komponenter i lakvattnet såsom ammonium, kalium och magnesium, tilläts vara kvar i lakvattnet. Alla dessa tre ämnen är dessutom viktiga komponenter för jordbruket och det behandlade lakvattnet kunde därför föreslås vara ett bra gödselalternativ.

Att använda kryogeler för vattenrening har visat sig vara en lyckad metod. Innan vi kan säga att metoden kan tillämpas ute i industrin eller vara en tillgång för allmänheten återstår det dock många steg. En stor utmaning berör produktionen av materialet i större skala samt den miljömässiga konsekvensen från det under applikationen. Vinster i form av rent vatten får till exempel inte ge nya miljöproblem. För att få fler svar på denna frågeställning valde vi att undersöka huruvida vår kryogel tappade några nanopartiklar när det var i bruk. Vi utsatte materialet för påfrestningar, bland annat genom att låta stora volymer vatten flöda genom det. Vi kunde under dessa förhållanden inte påträffa några partiklar i det filtrerade vattnet. Däremot upptäckte vi att kryogelen läckte monomerer vid början av användandet. Denna upptäckt visade sig också ge effekter i våra toxiska undersökningar. Studien visade hur viktigt det är att kontrollera nya tekniker för att i ett senare led kunna förbättra dem.

De erhållna resultaten i labbskala presenterade i denna avhandling visar att kryogeler som material för adsorbenter har en bred potential. De preliminära kostnadsanalyserna som gjorts på materialet visar att kostnaden för den bästa adsorbenten är ca trettio gånger dyrare jämfört med kostnaden för adsorbenter tillverkade för svenska hushåll avseende dricksvattenrening. Priset för tekniken påverkas dessutom av adsorbentens livslängd. Kan den regenereras och på så sätt användas på nytt, minskar dock priset drastiskt. En viktig poäng för all den teknik som utvecklas, utvärderas och slutligen tillämpas är att den inte ska tillföra nya miljöproblem för framtida generationer.

Abstract

The lack of safe, clean water is strongly linked to poverty, underdevelopment and poor health. Water is needed not only to sustain life, but to produce food and in industrial processes. Anthropogenic pollution and natural events can jeopardize access to safe water. Inorganic pollutants or toxic metal ions such as arsenic and cadmium are of special concern since these are persistent and accumulate in nature. Contaminated water used for direct consumption or for irrigation of crops can thus lead to direct and indirect exposure to humans to these metals.

To improve access to safe water, treatment must be developed to remove even low concentrations of toxic metal ions. Adsorption is a suitable technique. In this work, adsorbents were developed for various kinds of water sources; dinking water, wastewater, industrial water and leachate from a biogas process, all of which contained metal ions, such as As or Cd, at low concentrations. The adsorbents developed were based on a polymer cryogels, produced via cryoconcentration. Cryogels have a highly interconnected and porous structure, making them suitable for water treatment. The cryogels evaluated in this thesis were all based on the polymer polyacrylamide (pAAm).

In the first study, a pAAm cryogel was chemically modified with chelating functionalities suitable for the removal of heavy metals (i.e. Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2}). A rational design was suggested, involving preparation of the polymer inside plastic carriers to increase the mechanical stability of the material. Another strategy using particles was explored by embedding either nanoparticles (NPs) or molecularly imprinted polymers (MIPs) in pAAm-cryogels. The ability of Al_2O_3 NPs or MIPs in cryogels (called Alu-cryo and MIP-cryo, respectively), to remove As(V) was investigated. Both Alu-cryo and MIP-cryo exhibited adsorption capacities similar to those when the respective particles were applied in suspension. MIP-cryo showed higher selectivity but lower adsorption capacity than Alu-cryo.

To improve the removal of As(III) without any pretreatment, co-precipitated Fe-Al hydrous oxides were prepared and embedded in cryogels. As(III) could be removed from smelting wastewater in flow-through mode, reducing the concentration to European industrial emission standards. The removal of Cd^{2+} from leachate resulting from the anaerobic digestion of seaweed was studied using hydrothermally modified TiO_2 embedded in cryogels. This cryogel was shown to be successful in removing Cd^{2+} when tested in flow-through mode, and high adsorption capacities were

obtained. Toxicity and particle leakage were studied in NP-embedded cryogels. Although no evidence of particle leaking was found, toxicity resulted from the leakage of the monomer acrylamide from the cryogel.

The findings of this work show that cryogel-based adsorbents have potential in water treatment, due to their broad range of applications and the flexibility of the material. New and improved methods of particle immobilization in cryogels should be investigated, and pAAm should be replaced by non-toxic alternatives. Making cryogel materials with high adsorption capacities, which can be regenerated, can reduce the cost of water treatment. It is also important that novel technology meets environmental safety requirements to ensure the supply of safe water.

List of papers

I. **Linda Önnby**, Camilla Giorgi, Fatima M. Plieva, Bo Mattiasson
Removal of heavy metals from water effluents using supermacroporous metal chelating cryogels *Biotechnology Progress*, 26, (5), 1295-1302. (2010)

II. **Linda Önnby**, Vusumzi Pakade, Bo Mattiasson, Harald Kirsebom Polymer composite adsorbents using particles of molecularly imprinted polymers or aluminium oxide nanoparticles for treatment of arsenic contaminated waters *Water Research*, 46, (13), 4111-4120. (2012)

III. Prashanth Suresh Kumar, **Linda Önnby**, Harald Kirsebom
Arsenite adsorption on cryogels embedded with iron-aluminium double hydrous oxides: Possible polishing step for smelting wastewater? *Journal of Hazardous Materials*, 250–251, (0), 469-476. (2013)

IV. **Linda Önnby**, Prashanth Suresh Kumar, Kajsa G.V. Sigfridsson, Ola F. Wendt, Stefan Carlson, Harald Kirsebom
Improved arsenic(III) adsorption by aluminium oxide nanoparticles and hydrogen peroxide: Evidence of oxidation to arsenic(V) from X-ray absorption spectroscopy *Submitted*

V. **Linda Önnby**, Christian Svensson, Lubinda Mbundi, Rosa Busquets, Andrew Cundy, Harald Kirsebom
γ-Al_2O_3-based nanocomposite adsorbents for arsenic(V) removal: Assessing performance, toxicity and particle leakage *Submitted*

VI. **Linda Önnby**, Darren Sun Delai, Bo Mattiasson, Harald Kirsebom
Conversion of seaweed digestate from waste to a potent bio-based fertilizer: Selective Cd^{2+} removal using cryogel-supported titanate nanotubes *Manuscript*

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Paper II and III are reproduced by permission of Elsevier

My contribution to the papers

I. I participated in discussions regarding the planning of the experiments, I performed the experimental part regarding one of the evaluated adsorbents, I collected and summarized the data and wrote the manuscript.

II. I planned the major part of the work. I performed the experiments with minor contributions from my co-authors, and I wrote the manuscript.

III. I planned the work regarding arsenic adsorption, I wrote the introduction and I assisted in finalizing the manuscript.

IV. I planned and organized the work together with my co-authors. I performed the experiments regarding arsenic adsorption together with Prashanth Suresh Kumar and I made a major contribution to writing and finalizing the manuscript.

V. I planned and performed the work regarding arsenic adsorption and particle detection. I made a major contribution to writing and finalizing the manuscript.

VI. I planned and performed the work and wrote the manuscript.

Abbreviations

AAm	Acrylamide
pAAm	Polyacrylamide
NPs	Nanoparticles
WHO	World Health Organisation
TREN	Tris(2-aminoethyl)amine
As(III)	Arsenite
As(V)	Arsenate
NOM	Natural organic matter
WWTP	Wastewater treatment plant
POU	Point of use
IMAC	Ion metal affinity chromatography
COOH	Carboxyl
HEMA	2-hydroxyethyl methacrylate
AluNPs	Al_2O_3 nanoparticles
MIP	Molecularly imprinted polymers
APS	Ammonium persulphate
TEMED	N,N,N′,N′-Tetramethylenediamine
IDA	Iminodiacetic acid
TBA	Chelating ligand, evaluated in Paper I
PZC	Point of zero charge
Alu-cryo	Al_2O_3 nanoparticles embedded in cryogels
Fe-Al-cryo	Fe-Al hydrous oxide particles embedded in cryogels
TNTs	Titanate nanotubes
TNT-cryo	TNTs embedded in cryogels
ENMs	Engineered nanomaterials
LCA	Life cycle analysis
USEPA	US Environmental Protection Agency
REACH	Registration, Evaluation, Authorisation and restriction of CHemicals

Contents

Introduction

The supply of clean and safe water in all parts of the world is one of our greatest challenges. Today, over 780 million people do not have access to safe, clean water or adequate sanitation [1]. Every hour, more than 80 children die somewhere in the world as a result of water-related diseases [1,2]. Water is becoming as important a resource as oil. Without water life is impossible.

Environmental pollution poses a threat to the global water supply. Both old and new kinds of pollutants can be found in our water systems, and in the environment in general. Examples of environmental pollutants are polychlorinated biphenyls, polycyclic aromatic hydrocarbons, heavy metals, pesticides, flame-retardants, herbicides, pharmaceutical residues, and endocrine-disrupting compounds. Many new kinds of organic pollutants as well as heavy metals are potentially harmful, even at low concentrations. Environmental pollution may be the result of anthropogenic activities or natural events, and contaminated water can be found everywhere in the world, in both rich and poor countries.

To prevent the contamination of water, or at least to reduce it, sustainable measures must be developed, and implemented. In the developing countries, 90% of all wastewater is not treated at all, and flows directly into rivers, lakes and coastal zones [1]. Apart from the effective implementation of existing water treatment methods, novel methods must be developed. One example of a separation technique that can be applied to treat wastewater is adsorption, the subject of this thesis.

Human exposure to environmental pollutants may be direct or indirect. Groundwater, which serves as drinking water in many parts of the world, is one direct source of exposure. Irrigation of crops for food production is an example of an indirect exposure to environmental pollutants. Toxic substances such as cadmium and arsenic have been detected, for example in rice, threatening sustainable agriculture in many parts of Asia.

New water treatment methods must meet certain requirements. They should be low in cost and have little negative environmental impact over time, to meet the needs for future generations. The aim is to replace potential pollutants with greener alternatives or avoid them altogether.

The scope of this thesis

The aim of this work was to develop novel synthetic adsorbents for the removal of environmental pollutants present at low concentrations. The main focus was on obtaining a high adsorption capacity for specific inorganic pollutants such as cadmium and arsenic (**Papers I, II, III** and **VI**). An important part of this work was the synthesis of novel adsorbents suitable for different kinds of contaminated water sources, e.g. industrial and municipal wastewater (**Papers I, II** and **III**), drinking water (**Papers IV** and **V**) and nutrient leachate from a biogas process (**Paper VI**). The aim was to develop a technology with low environmental impact, which meets the challenges discussed in the introduction. The results presented in **Papers I, II, III** and **VI** demonstrate the efficiency of cryogel-based adsorbents, while suggestions for the further development of these adsorbents are presented in P**apers IV** and V.

Disposition of this thesis

This thesis is divided into seven chapters that deal with environmental separation from different perspectives. First, environmental pollutants will be introduced via heavy metals, with specific emphasis on cadmium and arsenic, two of the pollutants studied in this work. Thereafter, various methods of metal removal and recovery are presented. In the chapter on adsorption, the theory behind adsorption and the various kinds of adsorption, i.e. physisorption, chemisorption and selective adsorption, are discussed. In the following chapter, the cryogels, the polymer adsorbent and the polymer support used for material development are presented. The last two chapters deal with realistic applications of these adsorbents, and present some concluding remarks based on the findings of this research. Six papers are included in this thesis, and they will be discussed and put into perspective throughout this work.

Environmental pollutants

Different toxic substances found in the environment can be considered environmental pollutants. The work described here focuses on pollutants found in water. These are increasing in number, as is our knowledge about them. The list of pollutants found in water is long: ranging from polycyclic aromatic hydrocarbons to organic halogen compounds and inorganic pollutants such as heavy metals. The environmental pollutants of greatest interest in the present work are metals, heavy metals and metalloids. These are found in the environment, as illustrated in Figure 1. Metals and metalloids belong to the group of inorganic pollutants. For the sake of simplicity, metalloids will be considered as metals in this thesis. Metals accumulate in biomass, and persist in nature, as they are nondegradable.

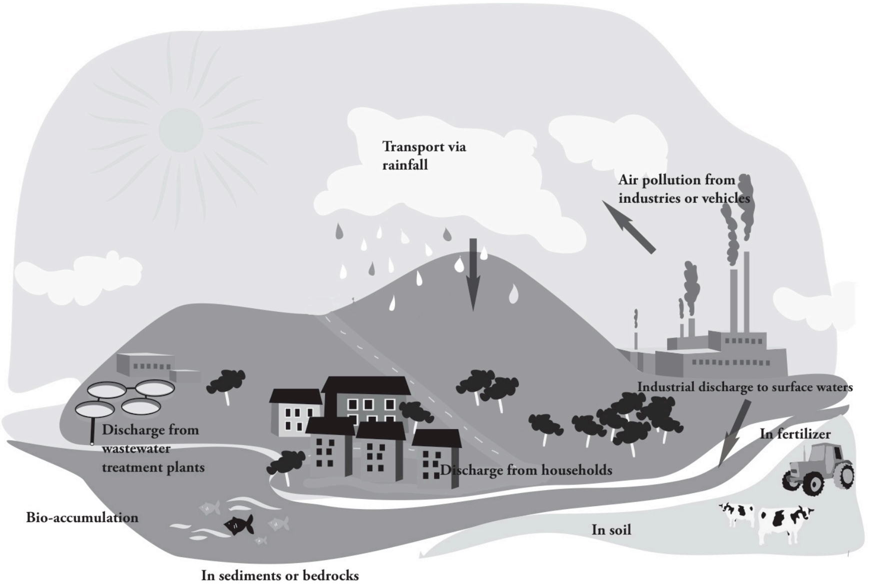


Figure 1. Illustration showing sources of metals in the environment. (Illustrated by Fia Persson).

Heavy metals and cadmium

In chemistry, metals are defined as elements that exhibit good thermal and electrical conductivity and are shiny and hard [3]. There is no commonly accepted definition of heavy metals but they are usually classified according to density or toxicity [4]. Metals, metalloids and transition metals can all be classified as heavy metals. Pollution from heavy metals is known since decades, because metals have been used for more than thousand of years [5]. Metal waste can for instance be attributed to industrial sources, and other metal flows in society can be traced back to urban inputs such as atmospheric deposition, household effluents and traffic-related emissions (Figure 1) [6]. The dominant source of metal waste, or metal-containing wastewater, in Sweden originated from the mining industry. Processes for the extraction of copper or gold are particularly important in this context, especially regarding sources of arsenic [7,8]. Attitudes towards the use of metals have, however, changed over time. The use of lead in petrol was phased out in 1994 in Sweden [9], and Ni/Cd batteries are nowadays carefully recycled, while other cadmium-containing products such as pigments and plastic stabilizers have been replaced [10,11]. The use of amalgam, containing mercury, in dentistry has also ceased in Sweden, and a total ban on mercury was introduced in 2009 [12].

Guidelines for acceptable levels of metals in drinking water and in industrial wastewater are presented in Table 1. The concentration limits vary greatly between different metals, and some are highly toxic at low concentrations. To ensure that water is safe, both for humans and the environment, it is important to ensure that toxic ions are effectively removed, even when they are present at low concentrations. Guidelines should form the basis for decisions by health regulators, policy-makers and advisors to ensure the safety of water.

Table 1. Limits for industrial discharge and guidelines for drinking water. Adapted from [13-18]

Metal	Industrial discharge limit (mg/l)	Guidelines for drinking water (µg/l)	Comments
Cu	0.5	2000	
Zn	1.5	n.a.[a]	Zn is not typically found in drinking water
Pb	0.2	10	
Cd	0.05	3	The Cd:P ratio for mineral fertilizer is set to 35 mg/kg P [19]
Hg[b]	0.03	6	
As[c]	0.15	10	
Cr[d]	0.5	50	
F	n.a.	1500	
Ni	0.5	70	

[a] Zn concentrations > 3-5 mg/l appear opalescent in water [16]
[b] Inorganic Hg
[c] Total As, i.e. As(III) and As(V) [15]
[d] Total Cr, i.e. Cr(III) and Cr(VI) [20]

In Sweden, ore production, mining and smelting plants result in As, Cd, Pb and Hg, at various locations [5,21], usually in the vicinity of a present or a former mining area. Sediments and lakes show especially high metal concentrations (e.g. Hg), affecting the quality of fish for consumption [5]. Regarding toxicity and negative health effects, the metals Cd, Pb, Hg and As are the most commonly studied [10]. In aqueous solutions, heavy metals occur as divalent cations, e.g. Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} etc. Their mobility is dependent on the presence of oxygen and the pH [22]. Heavy metals immobilized in the soil matrix can thus easily end up in aquatic environments if these conditions change. Metals (Me) mobilized as a result of a change in pH follow the reaction in Eq. (1) [3]:

$$\mathrm{Me(s)} + 2\,\mathrm{HCl^{+}} + \frac{1}{2}\,\mathrm{O_2} \leftrightarrow \mathrm{Me^{2+}(aq)} + 2\,\mathrm{Cl^{-}} + \mathrm{H_2O}(l) \qquad \text{Eq. (1)}$$

Cadmium is one of the five most common and harmful toxins found in the food chain [23]. Considerable research has been carried out on cadmium and negative health effects, resulting primarily from cigarette smoking, food intake and the consumption of contaminated water [24]. Cadmium is naturally present in soil and is common in southern Sweden. Mineral fertilizers contain cadmium, which has resulted in increased concentrations of this metal in the soil, and thus further accumulation in crops such as rice or wheat [25-27]. Traces of Cd (and As) found in food such as rice are partly due to the irrigation of crops with contaminated water [28-30]. The intake of Cd-containing rice is estimated to be highest in Asia, where the rice intake per capita is high [28]. High concentrations of cadmium can also be accumulated in biomass cultivated for biogas production, a process that is enhanced by low pH values, i.e. common soil conditions in Sweden [31]. The remaining digestate from a biogas process will thus contain cadmium, rendering this by-product environmentally harmful [32], and preventing its use as a potent, local bio-based fertilizer [33]. It is thus evident that we are facing new challenges in food production and water quality.

Arsenic, arsenate and arsenite

In the 1990s, water contamination by arsenic was detected in Bangladesh [34]. This toxic metalloid was found in groundwater resources and in drilled tube wells providing drinking water for a large proportion of the population [35]. Arsenic is released from sediments and bedrock, and this contamination is still alarming in Bangladesh [8,36]. Arsenic release can also have anthropogenic sources such as herbicides, pesticides, wood preservatives and pigments, some of which have been in use for hundreds of years [7,37]. Arsenic is still being detected in new groundwater sources. Elevated concentrations of arsenic in groundwater have also been found in China, parts of Southeast Asia, countries in southern Europe and South America [38-46]. In August 2013 it was reported that significant amounts of discarded glass containing arsenic (quantities of tonnes) had been deposited close to glassworks in southern Sweden [7,47]. It could therefore be interesting to monitor areas close to glassworks for possible arsenic contamination of groundwater.

In 2003, the European Union decided to reduce the maximum permitted guideline value for arsenic from 50 to 10 µg/l, and the change was thereafter also recommended as the safe level in water by the World Health Organization (WHO) (Table 1) [11,13]. However, this value is exceeded in many countries, especially in Southeast Asia [38,48]. Long-term exposure to arsenic through drinking water results in lung, bladder and skin cancer, as well as gastrointestinal disorders [7,8,37].

Worldwide it has been estimated that about 160 million people are exposed to arsenic through their drinking water [40], and it is therefore important to remove this contaminant. The most common recommendation is to simply not drink contaminated water, once it has been identified. If this is not possible, due to lack of other water sources, the arsenic should be removed [16,45], but this is difficult. In Bangladesh, where more than 50% of the existing tube wells have been screened, and where hydrogeochemical investigations have been carried out since the discovery in the 1990s, more than 10 million people are still exposed to this metal [40]. Providing safe drinking water is thus a challenge.

Arsenic is an oxyanion in water and has similar water chemistry to chromium. Arsenic has two dominating oxidation states in aquatic environments (+3 and +5). The trivalent arsenite (As(III)) has three protonation states: H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{2-}$ with the first acid dissociation constant (pK_a1) of pH 9.2 [49,50]. In Figure 2, the speciation of As(III) and the pentavalent arsenate (As(V)) depending on redox potential (Eh) and pH is shown. As(V) forms the oxyanions H_3AsO_4, $H_2AsO_4^-$ and $HAsO_4^{2-}$ with different redox conditions (Eh) and has a pK_a1 value of pH 2.2 [51]. Therefore, at neutral pH, the two oxyanions of As(III) and As(V) are neutral in the case of As(III) and ionic for As(V). This explains why it is more problematic to remove As(III) from water environments than the divalent heavy metal ions described above. It should also be noted that As(III) is the predominating oxyanion in groundwater (Figure 2) because groundwater is present in reduced environments, and the redox potential is thus low [52]. As(III) is also considered the more toxic anion of the two [36,53]. The mobility of arsenic ions is dependent of the soils, and the presence of Fe, Al, Mn, Ca, natural organic matter (NOM) and clay minerals therefore affects the fate of arsenic in different ecosystems [7,54]. It has recently been suggested that NOM, i.e. humic substances, may play a major role in As(V) adsorption in soils [55].

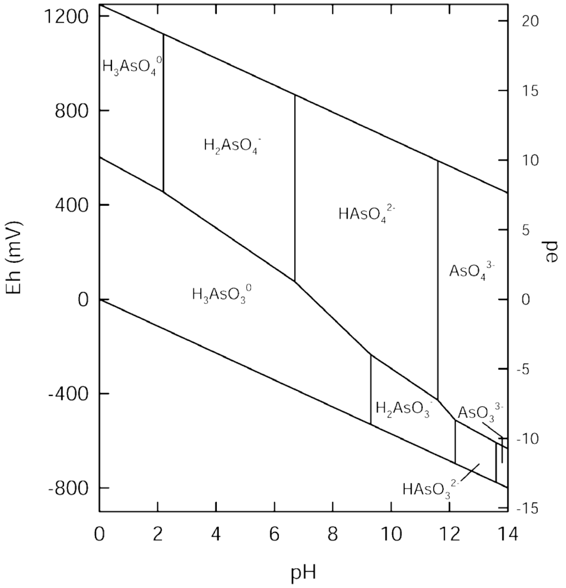


Figure 2. The two arsenic species As(III) and As(V) in the form of oxyanions and their respective prevalence as a function of pH, redox potential (Eh) and relative pressure (pe). (From [36], with permission).

Examples of other ions co-existing with arsenic in groundwater and of toxicological concern are chromium, lithium and boron [56]. However, the work described in this thesis was concentrated mainly on arsenic and cadmium.

Emerging organic pollutants

Emerging pollutants are defined as substances for which there are as yet no recommendations and whose impact on the environment and health are poorly understood. Examples of emerging pollutants today are endocrine-disrupting compounds or pharmaceutically active compounds. Although these substances are present at low concentrations, they may still be potentially harmful. The concentrations of these pollutants in municipal wastewater treatment plants can range from ng/l to µg/l [57-59]. These contaminants are not only difficult to remove because of their low concentrations, but also due to the co-existence with other structurally similar contaminants in wastewater [60]. Other pollutants being discussed in this area today include transformation products and metabolites. These arise when an abiotic or a biotic process transforms a synthetic chemical released to the aquatic environment. Chlorination is one method of treatment in wastewater treatment plants, yielding transformation products [61]. Knowledge concerning synthetic parent chemicals is often greater than that of the environmental impact of transformation products [60]. Transformation products are generally more toxic than their parent compounds.

Water treatment for the removal of metal ions

Different types of treatment methods are used in municipal wastewater treatment plants (WWTPs). A mechanical treatment step to remove unwanted matter is usually followed by chemical treatment and biological treatment. In the biological step, denitrification and nitrification take place. Prior to this step, chemicals can occasionally be added to precipitate phosphate, as too high concentrations of phosphate interfere with the biological step. Occasionally, metals are precipitated here too (or as a final step in the treatment process) if these have entered the treatment plant, but the general design of WWTPs does not include specific metal removal, as this should be removed already at the polluter-site. Before the wastewater is discharged into the environment, sludge is separated from the liquid phase by sedimentation [62]. The WWTP constitute a good example of the different kinds of treatment techniques, which all are possible to use for the removal of metal ions. The following sections provide examples of the treatment methods used for metal removal. Different kinds of waste streams containing metal ions are also discussed.

Metals in industrial wastewater

Precipitation is still a very useful method for the removal of metal ions from industrial wastewater. It is rapid, easy to perform and control, and is less dependent on temperature than biological systems. Precipitation is thus employed in most industrial metal removal processes today [63]. Precipitation of metals is very efficient but not complete, and the efficiency is reduced at lower initial concentrations. Lime or calcium hydroxide are most commonly used chemicals in precipitation, forming a precipitate that can be removed by sedimentation at the end of the process [64]. The chemical precipitation reaction is shown in Eq. (2).

$$\mathrm{Me^{2+}(aq) + Ca(OH)_2(s) \leftrightarrow Me(OH)_2(s) + Ca^{2+}(aq)} \qquad \text{Eq. (2)}$$

Lime precipitation is the most cost-efficient means for metal concentrations above 1000 mg/l [63]. However, the sludge resulting from precipitation may constitute a problem [65,66]. Due to the low efficiency of precipitation with low metal concentrations, levels in the residual wastewater from these processes may exceed regulatory standards. Furthermore, wastewater from mining operations is moreover multi-elemental, and precipitation must be performed stepwise at different pH to recover one metal at a time [64].

Biological treatment

Bioremediation is described as a method in which pollution is removed using biological means, i.e. organisms or plants [67]. Unlike organic contaminants, metals cannot be degraded or broken down into metabolites and by-products because they are elemental. In addition, metals often have inhibitory effects on microorganisms. Bioremediation for the removal of metals is, however, possible, and innovative techniques based on bioremediation have emerged during recent decades [68]. Bioremediation strategies can enable metal precipitation or the microbial reduction of metals from a highly soluble form to a less soluble form [68,69]. An example of bioremediation to remove metals is the use of sulphate-reducing bacteria. These bacteria, or Achaea, utilize sulphate instead of oxygen when oxidizing organic compounds [67]. In this anaerobic process, often suggested for remediation at mining sites, which are highly acidic, biogenic hydrogen sulphide (H_2S) is produced, followed by precipitation of metals as metal sulphides as described in Eq. (3) [70-72].

$$H_2S + Me^{2+} \leftrightarrow Me(S) + 2H^+ \qquad \text{Eq. (3)}$$

Fairly good selectivity can be achieved by adjusting the pH, sulphide concentration and the redox potential of the different metals involved in the precipitation step [70,73]. It is envisaged that the bioremediation industry for bioremediation will have a prosperous future, due to the cost efficiency of such treatment. However, individual design and optimization of each bioremediation process is necessary, as every contaminated site is different [74].

Chemical and physical treatment

Another example of chemical treatment, other than precipitation, is the oxidation of the metal to allow it to be removed in a subsequent step. This has been suggested for the removal of arsenic, and will be discussed in more detail in the next chapter on adsorption. Oxygen (O_2), ozone (O_3) and hydrogen peroxide (H_2O_2), or light- and iron-driven catalysis are possible approaches for the oxidation of As(III) to As(V)) (**Paper IV**) and [75-78].

The use of membranes as filters for metal removal has also been studied [64,79]. However, membrane filtration is often energy demanding, which makes it prohibitively expensive in full-scale applications. Theoretically, it should also be possible to take advantage of the charges on metal ions, by attracting them to a surface with the opposite charge. In the case of drinking water contamination by toxic metal ions, a point of use (POU) filter is a useful approach for household use. This is a frequently used mitigation strategy in many developing countries [80]. However, the removal of toxic ions at low concentrations, is most optimally achieved using adsorption [81-83], as discussed in the next chapter.

Adsorption

Adsorption and absorption appear to be very similar words, however, they describe two completely different phenomena, as illustrated below. Adsorption describes the adhesion of a compound or material (the adsorbate) onto the outer surface of an object (the adsorbent). Absorption, on the other hand, describes the uptake of a compound or material (the absorbate) in the bulk of an object (the absorbent).

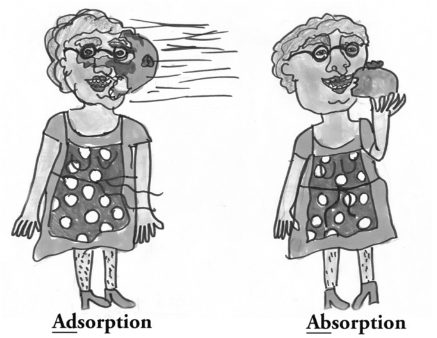


Figure 3. Illustration showing the difference between adsorption and absorption. (Illustration by Mira Liungman).

The work presented in this thesis is concerned with the adsorption of a liquid phase onto the surface of a solid phase. Materials with a high surface area, such as those with pores can adsorb more adsorbate than smooth surfaces as they have greater surface area per unit volume. Before discussing materials in depth, some fundamental and theoretical aspects of adsorption are discussed in the next section.

Theoretical adsorption models

Many theoretical models describing adsorption can be found in the literature. However, none of them describes the whole process of adsorption, as they are only approximations of the physical process. The adsorption models used in the present work are described in this chapter.

The most common model used to describe adsorption is the Langmuir model. The isotherm was developed in 1916 by Langmuir [84], and correlates the amount of gas adsorbed onto a solid surface with the pressure of the gas at constant temperature. The model is based on the following assumptions:

- adsorbates do not interact with other adsorbates,
- the adsorbent surface is uniform,
- one adsorbate molecule is adsorbed per adsorption site,
- adsorption is only one layer thick (monolayer adsorption), and
- a collision with a vacant site results in adsorption.

To better understand the Langmuir isotherm, the equation will be derived using the illustration in Figure 4, which shows the process of adsorption onto a solid surface. The concentration of the adsorbate, S, in the liquid is expressed as C_S(l) (Figure 4). The amount of S adsorbed is defined as the mass of S adsorbed onto the surface of the adsorbent per unit mass of the adsorbent, and is denoted q_S. The total coverage is denoted θ, and consists of vacant sites (s_*) as well as occupied sites (s).

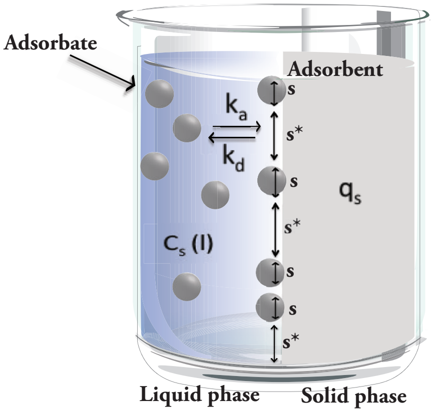


Figure 4. Adsorption at the liquid-solid interface, illustrating the Langmuir isotherm model. (Illustration by Fia Persson).

The sum of θ_S and θ_{S^*} is equal to one. For the occupied sites (s), the fraction of adsorbate on the adsorbent can be expressed as in Eq. (4) [85].

$$\theta_s = \frac{q_s}{Q_s} \qquad \text{Eq. (4)}$$

where Q_s (mg/g) is the saturated adsorbent (e.g. the maximal adsorption capacity). The Langmuir isotherm is an equilibrium expression, implying that the rate of adsorption, k_a, is identical to the rate of desorption, k_d,. At equilibrium, the relation between the amount adsorbed and the amount desorbed can be written:

$$k_a C_s \theta_{s*} = k_d \theta_s \qquad \text{Eq. (5)}$$

and inserting

$$\theta_s + \theta_{s*} = 1 \qquad \text{Eq. (6)}$$

results in:

$$\mathrm{k_a C_s}(1 - \theta_s) = \mathrm{k_d}\theta_s$$

$$= \frac{\mathrm{k_a}}{\mathrm{k_d}}(\mathrm{C_s} - \mathrm{C_s}\theta_s) = \theta_s$$

Replacing k_a/k_d with K_a gives:

$$\theta_s = \frac{K_a C_s}{(1+K_a C_s)} \qquad \text{Eq. (7)}$$

Solving equation Eq. (7) using Eq. (4) finally gives the Langmuir isotherm [84]:

$$q_s = \frac{Q_s K_a C_s}{(1+\mathrm{K}_a C_s)} \qquad \text{Eq. (8)}$$

Another model described in the literature is the Freundlich isotherm. This was presented in 1906, a decade before the Langmuir isotherm. Unlike the Langmuir isotherm, the Freundlich isotherm describes a non-ideal adsorption, implying that multilayer adsorption is possible. The Freundlich isotherm does not predict the adsorption maximum, which is possible using the Langmuir adsorption isotherm. Realistic systems that follow the Freundlich isotherm are sorption processes taking place on natural surfaces such as soil particles. The sorption sites on such particles are often inhomogeneous and can, therefore, have different sorption energies. The Freundlich equation is [86]:

$$q_e = K_F C_e^n \qquad \text{Eq. (9)}$$

The amount adsorbed at the equilibrium phase is here denoted q_e, and K_F is the rate at which the adsorption takes place. C_e is the equilibrium concentration, and n denotes the level and distribution of sorption energies [86]. Typically, n is a number between 0.5 and 1, and the isotherm becomes linear when n is close to 1.

To determine if experimental data correspond well with the Freundlich model, a logarithmic transform of Eq. (9), can be used in linear regression analysis:

$$\log q_e = \log K_F + n \log C_e \qquad \text{Eq. (10)}$$

Adsorption isotherms can be interpreted using linear or nonlinear regressions of the Langmuir or the Freundlich isotherms. Generally, a model fits experimental data well if there is a little difference between the observed and the model's data. The linear model giving the best R^2 is thus regarded as the most optimal fit. Linear regressions have been used in **Papers I, II** and **III**. However, using linear models to nonlinear equations is problematic, as the error variance is altered [87]. Obtained isotherm data was evaluated using nonlinear fitting in the Prism software (**Paper VI**). Obtained adsorption isotherms in this work were moreover all following the Langmuir isotherm.

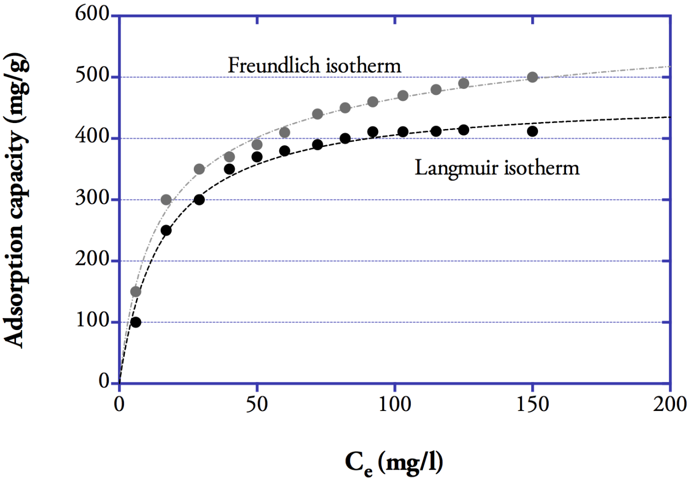


Figure 5. Two typical adsorption isotherms used in this work: the Freundlich and the Langmuir isotherm, showing how adsorption capacity varies for different equilibrium concentrations (C_e).

Adsorption isotherms are valuable tools for the evaluation and the explanation of experimental adsorption data. The maximal adsorption capacity can be derived from the adsorption isotherm, and is used to compare the efficiency of different adsorbents.

Adsorption can be divided into two main groups: physical adsorption commonly called physisorption, and chemical adsorption called chemisorption.

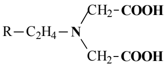
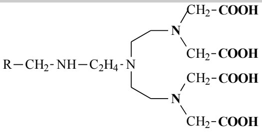
Physisorption

Physisorption takes place due to some kind of attraction, such as an opposite charge between the surface and the adsorbate. These attractions are van der Waal forces, for example a dipolar interaction [3]. These attractions are long-range and weak [85], and the adsorbate retains its identity while adsorbed. Typical values of the enthalpy are about 20 kJ/mol. Because of the low energy involved, this type of attraction does not result in the formation of a chemical bond and, therefore, no bond breaking can take place [85].

Another example of physisorption is chelation, which is the attraction between ligands and a metal ion. A ligand is described as a molecule (a functional group) or an ion that forms a complex with a metal ion. Chelating ligands are formed symmetrically around the metal ion via multiply bound ligands, such that the metal ion occupies the central position [3,88]. Chelating ligands are polar and anionic in nature, i.e. phosphate groups, carboxyl groups, sulph-hydryl and nitrogen-containing (amino) groups [4,89]. The chemical EDTA (ethylenediaminetetraacetic acid) is commonly used as a chelating agent for metal complexation [90]. Chelating ligands can also be found in nature; metals in the soil are often chelated and thereby immobilized in the soil matrix [69]. Chelating agents are also used in biochemistry, for instance, the amino acids glutamic acid and histidine. Chelation therapy provides a means of encapsulating toxic metals, reducing the negative effects resulting from intake in humans [90].

The adsorption of the divalent metal ions Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} was studied using adsorbents with chelating ligands (**Paper I**), similar to the chemical reaction employed in the ionic metal affinity chromatography (IMAC) [91,92]. In IMAC, charged metal ions are used, for example, to target proteins attached to histidine residues (called His-tagged proteins) [93]. Two ligands were studied. The first was a ligand with carboxyl (–COOH) groups derived from the iminodiacetic acid monomer (IDA-ligand). The IDA-ligand contained two –COOH groups per added amine group (Table 2). The second ligand contained (theoretically) twice the number of –COOH groups in the IDA-ligand. This ligand resulted from stepwise attachment reactions, modifying the polyacrylamide (pAAm)-based polymer. In the first reaction, tris(2-aminoethyl)amine (TREN) containing two free amine groups was coupled to an epoxy-group of the pAAm-based polymer. In the second step, bromoacetic acid was added. This resulted in the addition of four –COOH groups (two COOH-groups per amine) for the produced ligand (TBA-ligand). The adsorption capacity of the TBA-ligand was confirmed 4 to 6 times higher than the IDA-ligand, partly due to the higher number of –COOH groups than in the IDA-ligand. It was also observed that the adsorption was pH dependent, resulting from the fact that the carboxyl entities can be protonated (occupied) or deprotonated (available for adsorption), depending on the pH (e.g. pK_a value for the carboxyl group lies between 1.7 and 4.7, whereas the value for acetic acid is 4.7) [3,4]. It was therefore concluded that for the metal ions studied, the optimal pH range for adsorption was between pH 3 and pH 5.

Table 2. Molecular formula, ionic capacity, polymer backbone and protective shell of two chelating ligands attached to a polyacrylamide (pAAm)-based polymer: the IDA-ligand and the TBA-ligand. (From **Paper I**).

Ligand **(resulting sorbent material)**	**Iminodiacetate** **(IDA)**	**Bromoacetate** **(TBA)**
Molecular formula[a]	 $R-C_2H_4-N\begin{matrix}CH_2-COOH\\CH_2-COOH\end{matrix}$	
Ionic capacity (µmol/ml gel)	23	32
Backbone (polymer matrix)	Highly crosslinked pAAm	Highly crosslinked pAAm
Specific ligand attachment reaction	*In situ* incorporation with IDA monomer	Derivatization after polymerization
Protective shell	Plastic carrier from Kaldnes (i.d.[b] = 10 mm)	Plastic carrier from Kaldnes (i.d.= 10 mm)
Monomer concentration (% w/v)	6.8	7.5

[a] $R = CH_2\text{-}O\text{-}CH_2\text{-}CH\text{-}OH$

[b] i.d., inner diameter

Chemisorption

In chemisorption, adsorption to the surface results from a chemical bond, and ions are held on the surface by covalent bonding. Covalent bonding is much stronger than the van der Waal forces responsible for physisorption, and the enthalpy of chemisorption is thus much higher than in physisorption, typically in the region of

200 kJ/mol) [85]. The distance between the adsorbate and the adsorbent is therefore shorter. Moreover, once it has become adsorbed onto the surface, the adsorbate is altered by the release of protons in bond formation.

The use of thiol (SH) groups to improve adsorption affinity is an example of chemisorption. The adsorption of As(V) onto a polymer with added SH functionalities was studied in this work (**Paper II**). However, the density of the -SH groups was very low, resulting in low adsorption capacities. Other materials for the adsorption of As(V) were evaluated, i.e. γ-Al_2O_3 embedded in a pAAm polymer (denoted Alu-cryo). The adsorption of As(III) and As(V) was studied using co-precipitated Fe-Al hydrous oxides [94] embedded in a polymer (denoted Fe-Al-cryo, **Paper III**). The adsorption kinetics for As(III) and As(V) adsorption followed the pseudo-second order kinetics model, indicating that the adsorption is governed by chemisorption and not physisorption (**Paper III**) [95]. The chemisorption process is not usually governed by the difference in charge between the adsorbent and the adsorbate. The sorption processes of the non-ionic As(III) and the ionic As(V) can thus yield (almost) identical adsorption efficiency in a chemisorption process, because it is less dependent on surface charges (Figure 6). The hydroxide from the Fe-Al-hydrous oxide surface is involved in the arsenic adsorption [96].

No significant dependence of adsorption on pH was seen for the metal oxides studied in the chosen pH intervals (the common pH interval was between pH 2 and pH 9) (**Papers II** and **III**). Additional information on As(III) adsorption on the γ-Al_2O_3 nanoparticle (AluNP) surface, obtained from X-ray absorption spectroscopy (**Paper IV**), indicated that As(V) formed a bidentate binuclear complex on the surface, i.e. As-O-Al bonding where two O atoms from an AsO_4 unit individually bind to two Al atoms on the surface of the AluNP, again confirming that adsorption was due to chemisorption in this case.

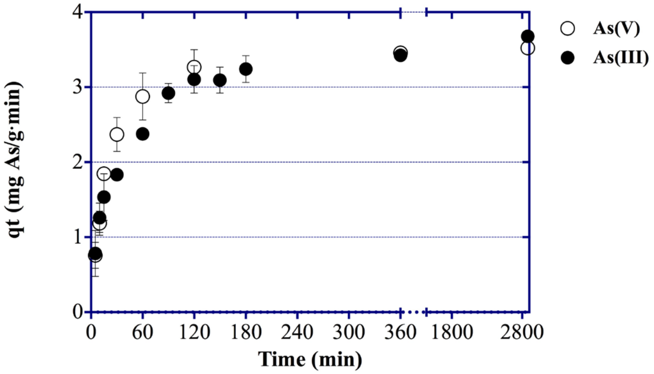


Figure 6. Adsorption kinetics of As(III) and As(V) by Fe-Al-cryo at 5 mg As/l, pH = 7±0.5, T = 22°C. (Adapted from **Paper III**.)

Selectivity and molecularly imprinted polymers

Using molecularly imprinted polymers (MIPs) as adsorbents provides a means of achieving selective adsorption of metal ions and/or organic molecules from water solutions [97-99]. MIPs are synthesized using sophisticated technology involving a template (the print molecule) and a range of different monomers that arrange themselves around the print molecule before the polymer is formed via polymerization [100-102]. When the print molecule is removed from the polymer, the cavity remaining in the polymer exhibits selectivity, able to recognize the print molecule, as illustrated in Figure 7. The interaction between the template and the functional monomers is often noncovalent (i.e. ionic or hydrophobic interactions or hydrogen bonds). Many different kinds of interactions between the template and the functional monomers will increase the binding affinity of the recognition site [103]. Adsorption using this kind of technique is another example of physisorption.

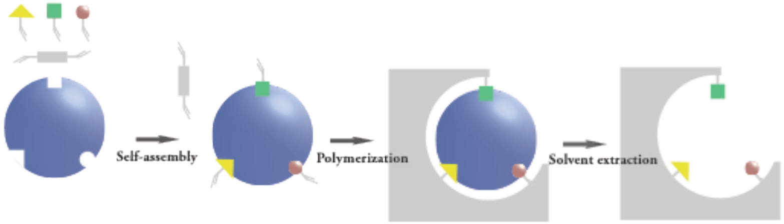


Figure 7. A schematic illustration of the production of a molecularly imprinted polymer (MIP). MIP production starts with self-assembly of the functional monomers around the template, followed by the polymerization, crosslinking and thereafter extraction of the template. (Illustrated by Fia Persson based on a figure in [101].)

MIP technology has been used to make imprints of both organic molecules and metal ions (**Paper II**) and [100,101]. MIPs are frequently compared with synthetic antibodies, which are able to selectively bind a target compound or structural analogues [100-102,104]. MIPs are often commercially available as solid phase extraction cartridges in which the target ion/molecule is enriched. The use of MIPs in water treatment has been mentioned as a growing area of application of these selective polymers [97,105].

The use of MIPs for separations in organic solvents show potential, while their use in aqueous solutions is still limited due to their poor performance [98,105,106]. MIPs are synthesized in organic solvents, which may explain their limitations in aqueous solutions. Another approach is to develop new water-compatible MIPs as discussed in the review by Lei and co-workers [98]. Very efficient sorbent capacities and even removal at low concentrations have been obtained using MIPs in aqueous solutions [107,108]. The use of MIP technology in water treatment combined with cryogels is well studied [107-112]. The main application for MIPs is in the separation of organic molecules, as these have a specific molecular structure that serves as a unique footprint, in contrast to metal ions. Their ability to remove ions relies on the specific size of the atom [97], and some impressive results have been reported in separation of ions using MIPs in aqueous solutions [100] and in solid phase extraction [113]. Selective adsorption can be obtained without using MIPs too and these possibilities are discussed later in this chapter.

The advantage of using MIPs in remediation processes lies in being able to adsorb a specific metal ion from complex solutions, such as those that often make up waste streams. There are three situations in which high selectivity is attractive:

1) removal of a toxic ion to enable the waste stream to be recycled,
2) removal or extraction of a toxic ion present in otherwise valuable solutions, e.g. liquid fertilizer, and
3) recovery of ions or compounds of high added value, e.g. precious metals.

MIP technology was used and evaluated in the present work for As(V) removal from a wastewater stream derived from a municipal wastewater treatment plant (**Paper II**). Since As(V) was present as $H_2AsO_4^-$ and/or $H_2AsO_4^{2-}$ at the pH value used, competing ions (co-ions) naturally present in the wastewater, e.g. NO_3^-, SO_4^{2-}, PO_4^{3-}, were expected to compete for adsorption sites. The synthesized MIP (MIP-cryo) proved to have better selectivity than the Alu-cryo adsorbent, as can be seen in Figure 8.

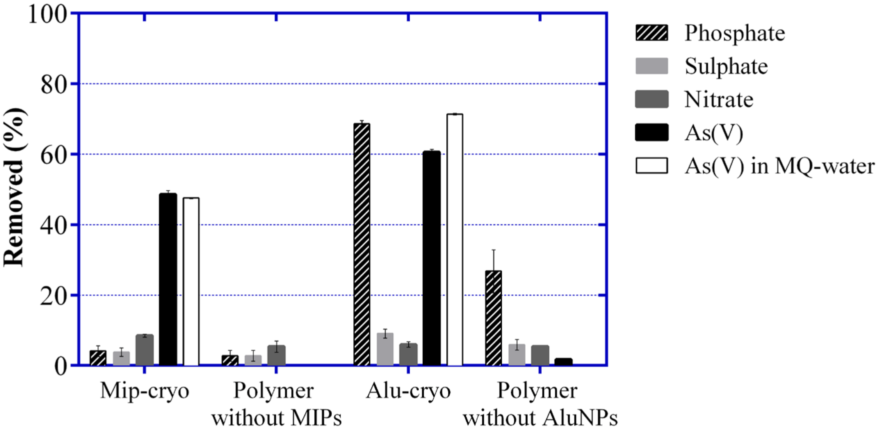


Figure 8. Removal os anions from As(V)-spiked municipal wastewater, (with initial concentrations (mg/l) of 17.7±0.06 (NO_3^-), 56.2±0.15 (SO_4^{2-}), 3.2±0.07 (PO_4^{3-}) and As(V) = 5 mg/l)) using the polymer adsorbents Alu-cryo and MIP-cryo. (Control samples were the polymer support of each adsorbent). Adsorption compared for As(V) present in ultra pure water (As(V) in MQ-water). pH = 7±0.5, T = 22°C. (Adapted from **Paper II**).

The reduction in As(V) adsorption by Alu-cryo in the presence of phosphate is consistent with earlier studies [54,114-116]. Phosphate competes with As(V) for adsorption sites due to its similar physico-chemical structure to phosphate. In nature, this competition can result in the release of arsenic when a phosphate-rich fertilizer is added [117]. The adsorption of arsenic can also be reduced by other components present in the water to be treated when using iron-based adsorbents, e.g. silicates or NOM [118,119]. It is remarkable how the components in complex solutions can alter sorption behaviour, for example, calcium can enhance the adsorption of phosphate to hydrous ferric oxide [120]. From the results presented in **Paper II** it was concluded that the increase in selectivity using MIP technology was obtained at the expense of adsorption, compared with the Alu-cryo adsorbent evaluated in the same study.

The tailoring of MIPs for the adsorption of metal ions is scientifically interesting, but it has yet to be demonstrated that they provide a sustainable means of remediation of arsenic-contaminated sites, partly du to the chemicals required for the production of the polymers and possible leakage of the template [106]. For example, to produce an As-imprinted MIP able to remove certain numbers of moles of As, the same number of moles of As would be needed in the production. Furthermore, to ensure successful imprinting, the template is added in excess (in stoichiometric terms). Thus, MIPs may be useful for the treatment of small-scale waste streams, to remove toxic ions from complex solutions, however, treatment of large-scale streams is not currently feasible.

Another type of material exhibiting selectivity was studied in this work (**Paper VI**) using titanate nanotubes (TNTs) prepared from TiO_2 [121]. These particles have shown high selectivity for Cd^{2+} and Pb^{2+} in the presence of co-ions such as Cu^{2+}, Zn^{2+}, Ni^{2+} or Ca^{2+} [122-124]. The selectivity is furthermore correlated with the hydration energy of the metal ion, i.e. this indicates how easily it separates from the H_2O molecule and replaces Na^+/H^+ on the surface of the TNTs. Thus, the lower the hydration energy, the easier it is to capture the ion on the surface of TNTs [125]. The TNTs were tested in competition experiments, with both co-ions and counter-ions, mimicking the ion content in a leachate similar to that derived from two-step anaerobic digestion (AD) process of marine biomass, i.e. seaweed [126]. Ions such as Na^+, K^+, Mg^{2+} or Ca^{2+} and anions (counter-ions) like NO_3, SO_4^{2-} and/or NH_4^+ were included in the experiments. The results are shown in Figure 9. TNTs were effective in removing Cd^{2+} in the presence of all the co-ions and counter-ions (> 95% removal), and the adsorption of SO_4^{2-}, NO_3^- or NH_4^+ was found to be very low or not detectable (Figure 9a). The divalent light metals Mg^{2+} and Ca^{2+} were also adsorbed at a molar ratio of 5:1, i.e. 5:1 is the molar ratio of Mg:Cd or Ca:Cd. However, the cations Na^+ and K^+ showed less adsorption to TNTs at both molar ratios studied (Figure 9b). Adsorption from TNTs relies also relies on physisorption.

Various kinds of NPs have been reported to be selective adsorbents for ions, such as Fe^{3+} and Hg^{2+} [127-129]. Some of these are useful in solid phase extraction applications where high selectivity is often required. Selectivity can be linked to chemical recognition of certain functional groups to a certain target ion, as in the case between –SH groups and Hg^{2+} [130], as SH groups and Hg^{2+} show high affinity even in biological systems. In Liu et al. (2000), reported that one SH-functionalized silica adsorbent retained its high affinity for Hg^{2+} when in the presence of other metals such as Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+} and when tested in wastewater [129]. Another silica adsorbent with amino functionalities showed a higher adsorption preference for Zn^{2+}, Cr^{3+} and Ni^{2+}. Other co-existing ions (i.e. Cu^{2+} and Hg^{2+}) remained in the solution at high concentrations [129]. Most of these reported selective adsorbents rely on physisorption through electrostatic attraction or chelating complexes.

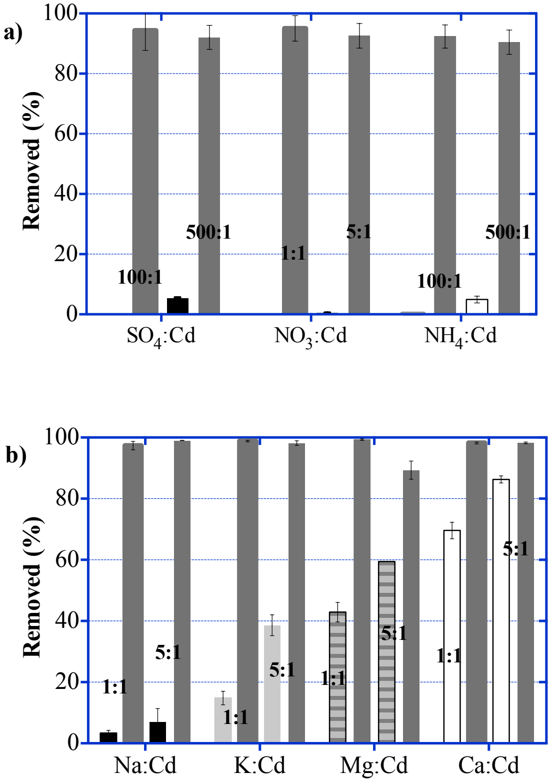


Figure 9. Competition between Cd^{2+} ions at a concentrations of 0.05 mM in a 0.01 M phosphate buffer (pH = 7±0.5, T = 22°C) and a) NO_3^-, SO_4^{2-} or NH_4^+, and b) Na^+, K^+, Mg^{2+} or Ca^{2+}, at various molar ratios given in the figures. (From **Paper VI**).

Adsorption experiments were performed in multi-elemental solutions, indicating preferential adsorption of the divalent cations studied in the order $Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$ (**Paper I**). These results were partly correlated with the electronegative potential of these ions, which followed the order $Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. A similar adsorption trend, as reported in **Paper I**, has been reported when using a polymer containing imidazole groups for adsorption in mixed metal solutions (i.e. $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$) [131]. In both studies, high selectivity for Cu^{2+} was obtained, and Cu^{2+} is a chelating ion, which is exploited in IMAC [132].

Oxidation prior to adsorption

Due to the nature of oxyanion formation of arsenic in water environments, and especially its preferred oxidation state in redox conditions, the removal of non-ionic As(III) is difficult. Pre-oxidation and pH adjustment have been used to increase As(III) removal. It was shown in the present work (**Paper III**) that As(III) could be removed without either of these pre-treatment methods.

Oxidation of As(III) by addition of O_2, O_3 and H_2O_2, has been well studied (**Paper IV**) [133,134]. Oxidation of As(III) in ambient air is very slow: more than two months is required [133]. In addition, oxidation of the non-ionic H_3AsO_3 is slower than for the monoanion $H_2AsO_3^-$ using O_3 [135]. Fe and TiO_2 are also used to speed up oxidation using light or H_2O_2 [75,136,137]. The metal-assisted oxidation using iron or TiO_2 is fast [78,138]. In natural waters, Fe and Mn are possible catalysts in the oxidation of As(III) to As(V) [139]. Dissolved oxygen can for instance react with Fe(II) to generate the active O_2^- ion which is responsible for the oxidation of As(III). Likewise, Mn oxidizes As(III) to As(V). It has been shown to be possible to oxidize As(III) to As(V) in iron-containing water exposed to sunlight [75].

After oxidation, it has been suggested that As(V) be removed using adsorption or coagulation [140,141]. Oxidation and adsorption can, in principle, take place (almost) simultaneously, or as a two-step reaction with two different reaction constants. Typically, the oxidation reaction is fast, while the adsorption process is slower (**Paper IV**) [142]. In the work by Yamani and co-workers, it was confirmed that co-existing NPs of TiO_2 and Al_2O_3 in chitosan beads, accomplished oxidation and adsorption respectively [143]. In the same study, they established that the adsorption of As(V) was faster with Al_2O_3 than with TiO_2, while TiO_2 was faster than Al_2O_3 in the oxidation reaction.

Most of the work presented in this thesis was focused on AluNPs and their use as an adsorbent. The use of iron hydr(oxides), aluminium (hydr)oxides and combinations of these in the removal of arsenic is well documented [48,82,96,144]. Furthermore, these metal oxides are partly responsible for the immobilization of arsenic species in soils, provided that both the pH and the redox potential are fairly constant, or that the other soil components do not alter the mobility of arsenic by competing for adsorption sites in the soil [145]. The removal of As(III) using AluNPs (or Al_2O_3 in general) is, however, poor [146]. Possible ways of improving this adsorption were thus investigated. As(III) adsorption onto AluNPs was enhanced by the addition of H_2O_2. For this specific oxidation reaction, it was also investigated why As(III) oxidation was improved two-fold compared to the system without addition of H_2O_2 (**Paper IV**). When comparing with the adsorption of As(V), there were also significant differences observed between As(III) and As(V), with and without addition of H_2O_2, as seen in Table 3. Interestingly, the decomposition of H_2O_2 did never take place between As(V) and H_2O_2, strengthening the assumption that the role of H_2O_2 was as an oxidizing agent to As(III) in presence with AluNPs. This could also explain why As(III)+ H_2O_2, resulted in similar removal as As(V) (Table 3). Moreover, there was no decomposition of H_2O_2 by the AluNP itself, whereas other metal oxides (e.g. TiO_2) decomposed H_2O_2 both in presence and in absence of As(III). To the best of the author's knowledge, little has been published in the oxidation of inorganic species with AluNPs, or Al_2O_3 particles in general, by addition of H_2O_2. The oxidation of hydrocarbons using Al_2O_3 or Al-based catalysts is, however, well documented in the literature [147].

Table 3. Adsorption of arsenic (As(III) and (As(V)) with and without H_2O_2, and H_2O_2 decomposition. (From **Paper IV**)

	Adsorption of As (%)	**Decomposition of H_2O_2 (µmol)**
As(III)		
Without H_2O_2	51.1±4.8	–
With H_2O_2	95.0±0.9	0.99±0.30
As(V)		
Without H_2O_2	~99%	–
With H_2O_2	~99%	n.d[a]

[a] n.d., not detected

The reason for the improved adsorption of As(III) was investigated using X-ray absorption near-edge spectroscopy (XANES). The X-ray spectra from the three examined samples (As(III), As(V) and As(III)+H_2O_2) indicate the oxidation state of arsenic on the AluNP surface. These measurements confirmed that the spectrum from the As(III)+H_2O_2 sample was identical to that from As(V) suggesting that the As(III)+H_2O_2 sample had been oxidized to As(V), as can be seen in Figure 10. No residual As(V) was found in the suspension, indicating that the oxidation reaction took place on the surface. Surface-promoted oxidation suggests that As(V) is restricted to the surface. The results from **paper IV** were primarily beneficial with regards to prediction of As-speciation in ecosystems, than suggesting a novel treatment system, as other metal-based adsorbents result in oxidation without addition of chemicals.

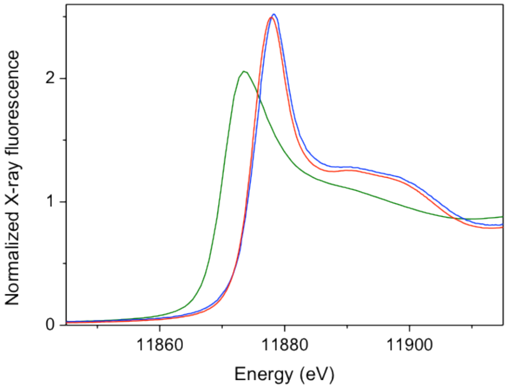


Figure 10. XANES spectra of As/Al_2O_3 adsorption complexes: As(III) (green), As(III) + H_2O_2 (blue) and As(V) (red). (From **Paper IV**).

Adsorbents

Activated carbon is the most common adsorbent for the removal of heavy metal ions from wastewater in full-scale applications [64]. Other carbon materials have shown better efficiency than activated carbon, for example, the recently developed carbon nanotubes (CNTs) [148]. This material is attractive because it has a large surface area per unit volume, and carbon is of biological origin, making it environmentally friendly. Adsorption to carbon is mainly to the result of hydrophobic interactions, ionic interactions or hydrogen bonding, making carbon suitable for the adsorption of organic contaminants as well as heavy metals. Oxidized CNTs have been found to be more efficient adsorbents of heavy metals than activated carbon [149]. These modified CNTs exhibit functional groups such as hydroxyl, phenol and carboxyl on their surface [83].

Metal oxides and waste materials have also been reported to be suitable adsorbents for metal removal [64,148,150,151]. The nature of metal oxides allows them to have a charged surface depending on the pH. At a certain pH value, at the point of zero charge (PZC), the overall net charge of the metal oxide is zero [152]. The surface of metal oxides is usually positively charged (the sum of charges is > 0) when a pH is greater than the PZC. The PZC for the AluNPs used in the present work (**Papers II, IV** and **V**) was determined to be at pH = 7.8±0.1. This explains why AluNPs were more suitable for As(V) removal at pH values close to neutral, i.e. pH < PZC. The PZC of the TNTs derived from the hydrothermal modification TiO_2 was determined to be pH = 3.9±0.2 (**Paper VI**), making them suitable for the removal of divalent metal ions such as Cd^{2+} [125]. Other metal oxides can be used for removal of other toxic metal ions. However, the PZC is not the only factor governing the choice of material for the adsorption of a specific metal ion. For instance, Zr which has a low PZC, making the surface positively charged over a large pH range, is a highly efficient adsorbent for arsenic [153].

Adsorbent particles of different materials and sizes were studied in this work (**Papers II-VI**). NPs offer a high surface area per unit volume and thus exhibit a higher surface reactivity compared to larger particles [154]. AluNPs are described in **Papers II, IV** and **V,** and NPs made from modified TiO_2 (TNTs) are presented in **Paper VI**. Micro-sized particles in the form of Fe-Al hydrous oxides were also evaluated (**Paper III**).

Binary metal oxides have shown good potential as adsorbents in arsenic removal, where oxidation facilitates the removal of arsenic [82,155]. As mentioned above, metal oxides occur naturally in the environment on soil particles, and are responsible for metal immobilization in bedrock and in aquifer sediments. Metal oxides can be produced, e.g. by co-precipitation. The co-precipitation of iron and aluminium, resulting in Fe-Al hydrous oxides has previously been reported to improve material characteristics, for example, increasing the PZC, and surface area and decreasing the rate of solubility of iron from the adsorbent [96].

Most of the data summarized in Table 4 were obtained form adsorption taking place in suspensions [48,115,153]. Various kinds of metal oxides are studied as adsorbents for arsenic removal, but Fe- and Al-based materials are dominating. Combinations of metal oxides often involve a redox active metal oxide that can aid oxidation. Metal oxide combinations commonly studied are Mn/Fe, Cu/Al or Zr/Mn. The Zr-based materials show especially high adsorption capacities: 139 mg/g for As(III) using Zr alone, and 104 mg/g and 80 mg/g for As(III) and As(V), respectively, using the micro-sized binary Zr/Mn hydrous oxide material [153,156]. The results obtained in the present work (**Papers II and III**) are in good agreement with the data presented in Table 4. NPs can thus provide high surface areas and surface energies, making them interesting for applications in adsorption processes [81,154].

Unstable NPs usually aggregate until they are stable [148], which limits the ratio of the active surface area to the volume, at the same time the surface reactivity is lost [154]. To take better advantage of the increased surface areas of NPs they should be dispersed in the medium in which they are required to act. Using supports, forming composite adsorbents, can circumvent this problem. Composite adsorbents may be mobile or static. An example of a mobile composite based on NPs is the addition of a stabilizer or a surface coating to avoid particle aggregation and enhance NP reactivity [157-159]. In static composite adsorbents, NPs are embedded in a supportive material or coated on the surface of a material, as demonstrated in **Papers II, V and VI** and in [160,161]. Nanotechnology and the use of NPs for water treatment, with special focus on the removal of metal ions is addressed in later chapters.

Table 4. Characteristics of some particle-based adsorbents recently developed.

Adsorbent material and dose (g/l)	**Size**	**Specific surface area (m^2/g)**	**Contact time (h)**	**pH**	**Adsorption capacity (mg/g)**
TNTs (1 g/l) (**Paper VI**)	54 nm	258	24	7	Cd = 157
Oxidized CNTs (0.5 g/l) [162]	i.d.[a] = 6-12 mm o.d.[b] = 20-30 mm	n.a.[c]	4	5	Pb = 97.1[d] Cu = 28.5 Cd = 10.9
Zr (0.5 g/l) [163]	60-90 nm	n.a.	48	8	As(III) = 139
Zr/Mn binary hydrous oxide (0.2 g/l) [156]	100 nm	213	24	5	As(III) = 104 As(V) = 80
Nanocrystalline TiO_2 (0.2 g/l) [164]	6 nm	330	22	7.5	As (III) and As(V) > 37.5 (C_{eq} = 44.9 mg/l)
Fe-Al hydrous oxides (2 g/l) (**Paper III**)	< 6 µm[e]	74.3	24	7	As(III)= 24.1
γ-Al_2O_3 (2 g/l) (**Paper II**)	30 nm	40	24	7	As(V)= 20.6
ZVI [f] (0.5 g/l) [165]	n.a.	69	n.a.	7	As(III) = 94 As(V) = 119
Polyaluminium granulate (1 g/l) [48]	1-3 mm	35	40 (As(III)) 20 (As(V))	7.5	As (III) = 18.0 As(V) = 14.8

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[a] i.d., inner diameter, [b] o.d., outer diameter, [c] n.a., not available

[d] C_{eq} in these experiments was 10 mg/l, [e] 90% of the studied particles were less than 6 µm in diameter, [f] Zero-valent-iron encapsulated chitosan nanospheres

Cryogels

Cryogels are polymers with a typical pore range between 1-100 µm [166]. These materials are nowadays defined as supermacroporous polymers (a macroporous polymer has a pore range between 50 nm and 1 µm in diameter) [88]. Cryogels are hydrogels produced using freezing polymerization, or cryoconcentration, which creates a continuous structure of interconnected pores. This is a desirable characteristic, since it makes the material porous, allowing water to flow freely through it. Facilitated diffusion and mass transfer is beneficial in many kinds of (bio)-technological approaches, for example, filters in water purification, for the separation of cells, or as supports for enzymes producing biochemicals in flow-through mode [79,167,168].

Preparation of cryogels

Typically, cryogels are prepared from a solvent (often an aqueous solution) containing either monomers or polymers of about 2-10 wt% [169,170]. The solvent is thereafter allowed to freeze, initiating cryoconcentration. Freezing leads to the formation of two phases: the frozen, or crystalline phase, consisting of ice crystals, and the non-frozen, or polymer phase, containing the precursors of the gel [169,171]. The polymer in the non-frozen phase polymerizes, forming thin walls. After freezing, the gel is allowed to thaw, and the crystalline phase (the solvent) melts leaving behind the open porous three-dimensional polymer structure. Ethanol is often used as the medium for freezing as it has good heat transfer properties. The preparation of cryogels is illustrated in Figure 11, together with a scanning electron microscopy image of the pore system.

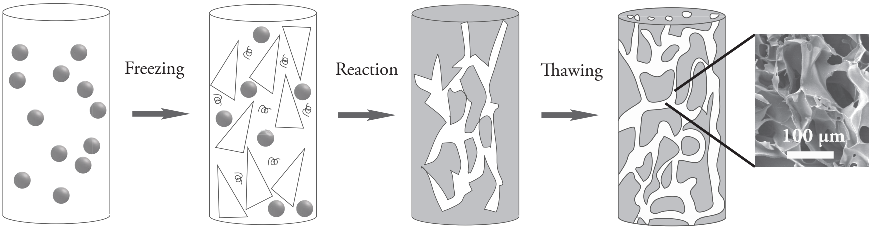

Figure 11. Illustration of the production of cryogels. The scanning electron microscopy image shows the highly porous structure of these cryogels. (Illustrated by Fia Persson with inspiration from [172].)

There are various ways of producing cryogels: one of the more common is free radical polymerization, which was used in the studies described in **Papers I-III, V** and **VI**. Other routes of polymerization are chemical crosslinking and cryogelation by noncovalent structuring of polymers [169]. These routes will, however, not be further discussed in this thesis.

For free radical polymerization to take place, a system generating a radical is needed. In this work, radicals were generated from the combination of the initiator ammonium persulphate (APS) and the base-dependent activator N,N,N′,N′-tetramethylethylenediamine (TEMED), commonly described as base-dependent redox initiating system [173,174]. In the free radical polymerization process, polymer growth results from the reactions between the radicals generated by the system and the monomers in the unfrozen phase. Polymerization ceases when no more radicals are generated by the system. For the cryogels produced in this work, the polymerization reaction was allowed to continue for about 16-20 h. It is important to keep the solution pH above 8, and to maintain a low temperature, close to the freezing point of the monomers prior to freezing, which is sometimes difficult [175]. If polymerization takes place before the solvent freezes, the resulting polymer will be a hydrogel and not a cryogel. It was necessary to increase the pH of the suspension containing monomers and TNTs in order for polymerization to take place with the APS/TEMED system (**Paper VI**). The cryogels in this work were prepared at -12°C, but lower temperatures can be used for cryogel preparation, as long as the temperature is below the eutectic point. At this point, both the solvent phase and the solute phase (containing the precursors) will freeze [171]. The eutectic point of a sodium chloride solution is -21°C. It has been reported that the rate of freezing determines the pore size of the cryogels [176]. At lower freezing rates, the size of the crystals decerases and the cryogel will have smaller pores [176]. Likewise, if the monomer concentration is increased, the non-frozen phase will increase at the expense of the crystalline phase, resulting in smaller pores with thicker walls [174].

All cryogel materials in the present work were based on pAAm with a monomer concentration between 6 and 7% (w/v). The pAAm cryogels were primarily prepared via co-polymerisation using acrylamide (AAm) and the crosslinker N,N′-methylenebisacrylamide (MBAAm). The structural formulae for these polymers are shown in Figure 12.

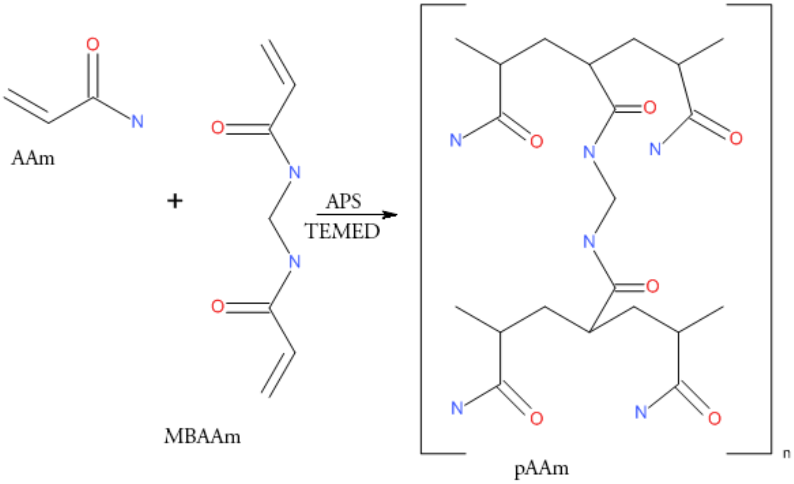

Figure 12. The chemical structures of the monomers AAm and MBAAm and the resulting pAAm using the APS/TEMED system. (By Dmitri Berillo.)

Functionalized cryogels

Functionalized cryogels can be produced by adding functional groups such as –COOH or –SH to a pAAm cryogel (**Papers I-II**) and [131]. Functionalized cryogels were primarily produced (**Papers I** and **II**). In order to chelate heavy metal ions from solution, the pAAm cryogel was modified (**Paper I**). The –COOH functionality was obtained from an *in situ* incorporation with IDA, giving an IDA ligand. The other –COOH functionality was achieved from a two-step attachment reaction. Initially, an epoxy-pAAm cryogel was obtained by polymerization between MBAAm, pAAm and allyl glycidyl ether, as shown in Figure 13. The first reaction took place between the epoxy-pAAm cryogel and TREN, resulting in the addition of the amine functionality to the epoxy-pAAm cryogel. In the second step, -COOH groups were coupled via an attachment reaction using bromoacetic acid. The final ligand was denoted as TBA-pAAm and was used for heavy-metal removal (**Paper I**).

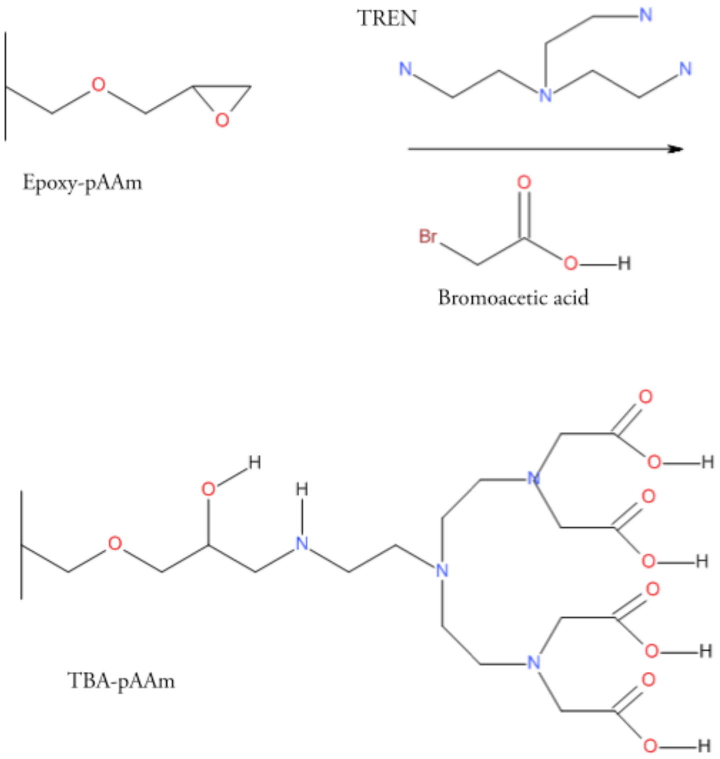

Figure 13. Illustration of the functionalization of the epoxy-pAAm cryogel with TREN and bromoacetic acid, to obtain the TBA-pAAm cryogel with chelating ligands. (Adapted from **Paper I**, by Dmitri Berillo).

A high density of -COOH groups in the TBA-pAAm cryogel is essential for heavy-metal removal. The -COOH density in the TBA-pAAm cryogel was determined to be 32 µmol/ml gel, which is considerably higher than the density of the simple IDA-igand in the IDA-pAAm cryogel (23 µmol/ml gel) (Table 2).

As about 70-93% of cryogels consist of pores, the attachment of ligands will be limited [174,177]. Low adsorption capacity of cryogels may also be due to the size of the target ion/molecule, which determines accessibility to the adsorption site of the polymer. Plieva et al. (2005) reported the adsorption capacity for high-molecular weight molecules, such as the protein lysozyme, was lower than that for Cu^{2+}, suggesting that adsorption was limited by accessibility to the chelating IDA-ligands present in the cryogel [174]. Some of these difficulties can be overcome by using composite cryogels.

Composite cryogels

Making composites can be one way to increase the mechanical strength of cryogels. The prepared functionalized cryogels were protected, as they were prepared inside two kinds of plastic carriers made by Kaldnes (AnoxKaldnes, Sweden): K1 with a diameter of 10 mm and K2 with a diameter of 25 mm (**Paper I**). The carriers containing gel showed better stability after vigorous stirring for 48 h than a gel monolith without protection by Kaldnes carriers, as shown in Figure 14. The mechanical strength of composite cryogels was also investigated using elasticity models (Young's modulus) based on uniaxial compression (**Paper II**). A high value of obtained stress to strain (expressed in pascal) has been found to be correlated with good stability [178]. An increase in mechanical strength with increasing particle loading is a general trend found in composites prepared from metal oxides and cryogels (**Paper II**) and [112].

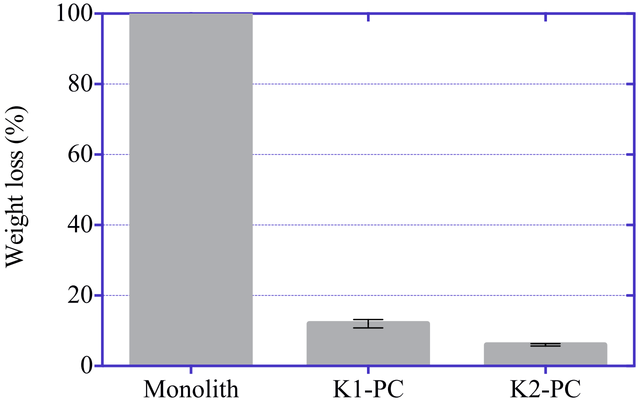

Figure 14. Mechanical stability in terms of weight loss after 48 h rigorous stirring, of IDA-pAAm cryogel composites (K1-PC and K2-PC) and a piece of IDA-pAAm cryogel (Monolith). (Adapted from **Paper I**).

Due to the supermacroporosity of cryogels combined with their thin polymer walls, the surface area of cryogels is low (e.g. 23 m^2/g in **Paper III**), and surface areas of polyvinyl alcohol cryogels have been determined to be about 78 m^2/g [179]. However, the adsorption capacity can be increased by adding particles, which may provide a better way of preparing adsorbents for metal ion removal. In this work, composite cryogels were produced using adsorbent particles of metal oxides or MIPs, embedded in pAAm cryogels.

In contrast to the preparation of functionalized cryogels, the preparation of composite cryogels is simple and can be completed in one step. Different particles were embedded in cryogels and then evaluated with regard to their ability to adsorb metal ions form water (**Papers II-IV** and **VI**). In principle, the cryogels were used as support for highly adsorbent particles, and the adsorption by the support itself was negligible. The adsorption from the support itself was negligible. As with any other material used for immobilization, it should ideally not affect (reduce) the performance of the immobilized adsorbents (e.g. by blocking or decreasing the available surface area of the adsorbent particles). This was confirmed in the present studies (**Papers II-III).** Alu-cryo showed a similar adsorption capacity for As(V) as AluNPs in suspension. Similarly, As(III) removal by Fe-Al-cryo was almost identical to that with Fe-Al hydrous oxide particles in suspension (**Paper III**). However, Savina et al. (2011) reported a reduction in adsorption when using cryogel composites. Only 33% of the adsorption of As(III) achieved with free NPs (α-Fe_2O_3 and α-Fe_3O_4) was exhibited by the respective cryogel composites (the cryogel-support was prepared from polymerization of 2-hydroxyethyl methacrylate (HEMA) [180].

The embedded particles are usually physically entrapped in the cryogel, placing a limit on the particle loading. Also, with this kind of immobilization of NPs, the reactivity of NPs can be compromised. The optimal particle load of the Alu-cryo composite was investigated with 1, 2, 3, 4, 5 and 6% (w/v) of Alu-NPs (**Paper V**). Parameters such as the loss of NPs during the production and use of the composite, and As(V) removal were studied. The optimal mass of AluNPs was determined to be 4% (w/v) for the composite evaluated, as can be seen in Figure 15. At the initial concentration of As(V) of 5 mg/l, the degree of saturation of the adsorbent varied between the Alu-cryogels with various amounts of AluNPs. The uptake of As(V) by the 4-Alu-cryo was similar to that of free AluNPs in suspension. Both these had similar loadings of 2 g AluNPs/l.

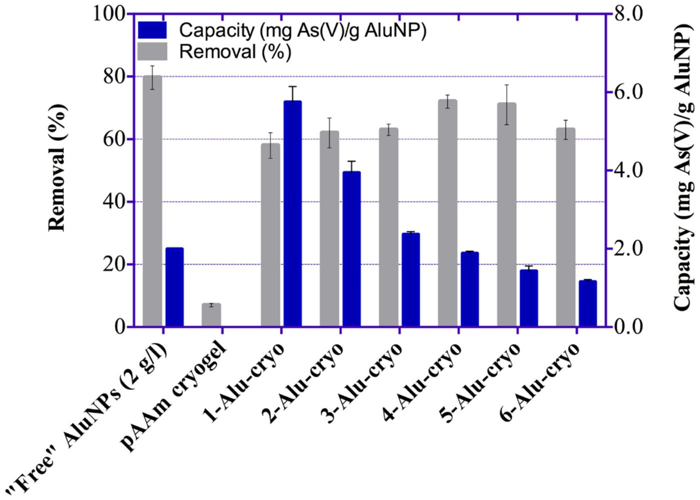

Figure 15. Comparison of As(V) removal and adsorption capacity of free AluNPs in suspension at 2 g/l, unmodified pAAm cryogel, and Alu-cryo composites, containing 1-6& (w/w) AluNPs. The initial As(V) concentration was 5 mg/l, pH = 7±0.5 and T = 22°C. (From **Paper V**).

It was also concluded from the same study that the degree of swelling of the composites decreased by 50% from an initial value of 21.9 g/g (unmodified pAAm cryogel) to 9.7 g/g for the 6-Alu-cryo composite. This is understandable as the dry weight increases with increasing particle mass, and the AluNPs are not able to absorb water like a cryogel.

Particles with higher density, for example, Fe-Al hydrous oxides ($\rho \approx 2.9$ g/cm^3) and TNTs ($\rho \approx 4.6$ g/cm^3), have a tendency to settle fast in the monomer+particle suspension prior to freezing polymerization. The radius of the particles also determines the settling velocity, and is described by Stoke's law [181]. The particles in the resulting monolithic composite are thus heterogeneously distributed; more being found at the bottom of the monolith. Although cryogels can be used to immobilize NPs or other particles, in a stable form, the particles may still agglomerate. This could be avoided with heavier particles by using high-viscosity cryogel suspension, or by changing the charge distribution in the suspension, so as to avoid particle aggregation and sedimentation of the particles.

The actual loading for each composite was determined experimentally using thermogravimetric analysis and compared with the theoretical load. In one of the studies (**Paper III**) the Fe-Al hydrous oxide particle load was 67% of the theoretical amount. For the smaller AluNPs, however ($\rho \approx 4$ g/cm^3), the particle yield was close to 90% of the theoretical (**Paper II**), supporting the theory that particle incorporation is affected by particle density and size. From a production point of view, low incorporation rates will affect the overall cost of these adsorbents, and losses should thus be avoided. In the case of the incorporation of TNTs in the pAAm cryogel (TNT-cryo, **Paper VI**), only 2% (w/v) particle loading could be achieved due to rapid settling of the particles. By measuring the dry weight of the TNT-cryo, it was concluded that 82.5% of the loaded particles remained in the monolith after production, corresponding to 205 mg TNTs/g dry polymer. The tendency of TNTs to form aggregates also affects settling, as the aggregates will have a larger "particle" radius than non-aggregated TNTs.

The particles are incorporated into the thin but dense polymer walls, and their accessibility is key for successful adsorption. Scanning electron microscopy and transmission electron microscopy were used to investigate how the composites in this work were immobilized in the cryogel support. The results are shown in Figure 16.

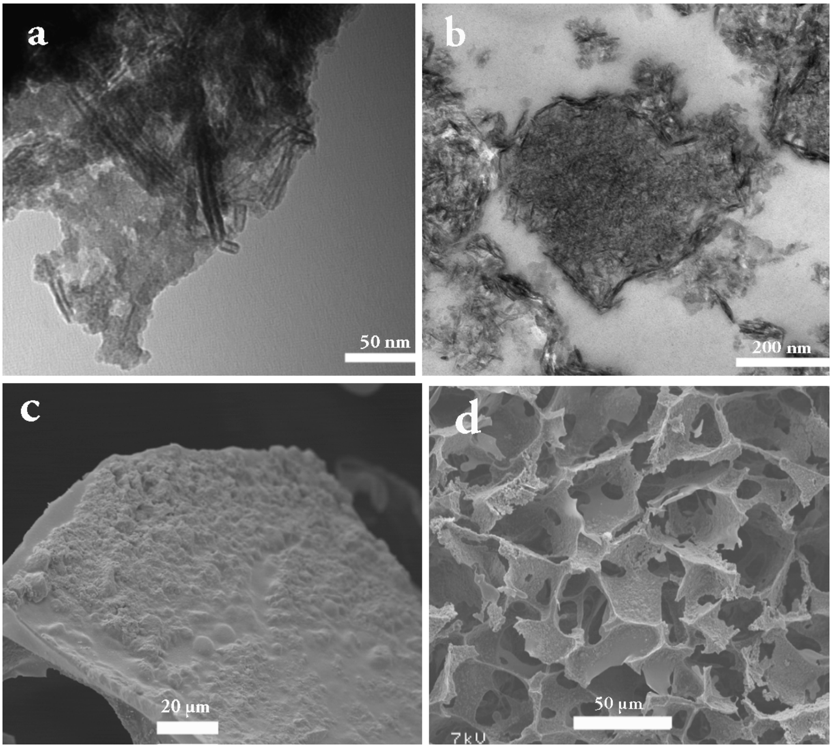

Figure 16. Transmission electron microscopy images (a-b) and scanning electron microscopy images (c-d) of some of the composite cryogels produced in this work. a)TNTs, b) Alu-cryo, c) Fe-Al-Cryo, and d) Alu-cryo.

The continuous interconnected pore system of cryogels provides interesting solutions as supports for NPs and micro-sized particles. Other materials used as static supports for NPs for the removal of arsenic and organic pollutants include chitosan and carbon [143,165,182]. Mobile supports have some disadvantages compared with static supports, as mentioned briefly above. A stabilizing agent must often be added at high ratios in relation to the NPs, and its stability (and thus the reactivity of the NPs) is dependent on the environment in which it is applied [154]. Static supporting materials are, however, expensive. Both static and mobile supports lead to a reduction in reactivity of the NPs. Cryogel composites with NPs provide a simple means of handling NPs, and additional separation steps for the recovery of the NPs can be avoided. Risks associated with NPs in the environment are, however, the subject of debate, and careful risk assessment must be carried out before existing and innovative treatment technologies based on nanotechnology are implemented.

Risk assessment

Nanotechnology, or engineered nanomaterials (ENMs), provide attractive opportunities for the development of novel water treatment methods. The characteristics of ENMs, such as their high specific surface area, anti-microbial activity, photosensitivity, catalytic activity etc. make their use of these materials interesting in many different applications in water treatment [81,183,184]. However, concerns regarding their possible environmental consequences remain. As the surface-to-volume ratio increases with decreasing particle size, ENMs or NPs are of great interest in adsorption-governed separation processes. In addition, both surface energy and surface structure are size dependent, and the nanoscale thus offers highly active adsorption sites [185]. Currently, there is more focus on results of treatment from novel ENM-based technology, and evidence of potential toxicity from the technology during use is often overlooked. Apart from potentially negative health effects on the environment, the cost effectiveness and social acceptability of these treatment technologies must also be investigated [149]. The use of ENMs in water systems will inevitably lead to loss of them. The high production of ENMs has already resulted in these materials being found in water systems in our environment [148,186]. It should be noted that, it is nt always the NPs themselves that are toxic, but the ions dissolved in them [187]. Identifying the possible risks associated with NPs is thus a challenge, as identifying the long-term ecotoxicological effects of NPs freely dispersed in the environment [188].

Possible leakage of NPs from the Alu-cryo composites produced in this work (e.g. 1- to 6-Alu-cryo) was assessed (**Paper V**). In addition to the detection of traces of NPs during the production and use of the Alu-cryo, toxicity and the removal of As(V) were evaluated for the optimal Alu-cryogel (4-Alu-cryo). AluNP leakage into water filtered through the 4-Alu-cryo (0.5 ml cryogel) was measured using particle induced X-ray emission (PIXE) [189]. Traces of AluNPs were investigated in different volumes of filtered water: 1000, 2000 and 4000 ml as well as a control sample (ultra pure water was used, sample denoted 0).

The samples of filtrated water were filtrated through a filter paper and analysed regarding elemental Al using PIXE. A known amount of 30 mg AluNP/l was also included in the analysis (sample denoted "known"). No relative increase of elemental Al was recognized as compared with the known concentration, as can be seen in Figure 17. This indicates that there was no detectable release of AluNPs into the water samples. Toxicity was partly measured as the reduction in the viability of epithelial cells. Based on the results of these measurements, the observed reduction in viability (≈ 40% for the first 20 bed volumes) was determined as being more likely to be the result of leakage of the monomer (AAm) than leakage of AluNPs (**Paper V**). This study shows how important it is to design a reliable toxicity test that includes all the components in the material. These findings suggest that the polymer used in the adsorbents, pAAm, should be replaced in future materials. The monomer AAm is already known to be a potent carcinogen [190].

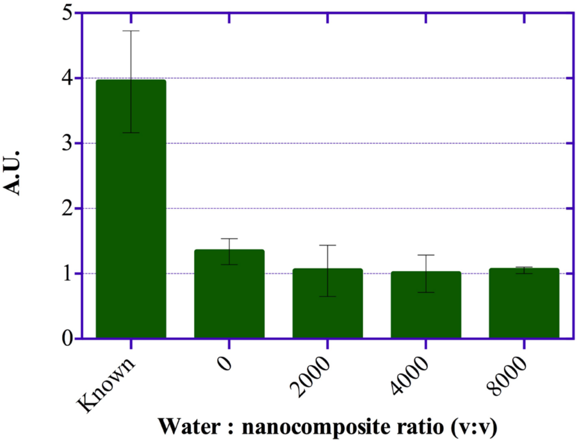

Figure 17. The relative amount (A.U.) of elemental Al in water fractions during leakage studies from the 4-Alu-cryo composite at different water-to-nanocomposite ratios (0, 2000, 4000 and 8000). The known amount of AluNPs was 30 mg/l. (From **Paper V**).

Application of cryogels in water and wastewater treatment

Cryogels have potential for applications in water and wastewater treatment. However, maximum levels of exposure to both NPs and monomers as a result of leakage must be established before cryogel composites can be implemented in the large-scale treatment of water. Other factors, such as cost and reuse, must also be studied for each specific adsorbent. One of the greater advantages of cryogels is the flexibility of their preparation. The material can be prepared as monoliths, discs, beads or particles, to suit specific requirements. Results on laboratory scale may be different from those obtained when treating real water and wastewater due to differences in scale and water chemistry. The social acceptance of the technology and its overall environmental impact must also be assessed. This chapter presents the results obtained from the treatment of water from different sources. The need for system regeneration, the deposition of the pollutant and, finally, the total cost of the treatment are also discussed.

Pollutant source determines the adsorbent

An adsorbent material with a rational design was developed, inspired by two earlier studies [191,192]. The TBA- and the IDA-pAAm cryogel were prepared inside a plastic carrier and was able to remove heavy metals in synthetic wastewater with high efficiency. This adsorbent could be used in a stirred reactor or in packed bed configurations (e.g. columns), in a continuous mode, without loss of shape or performance, as can be seen in Figure 18. It was also suggested that the cryogels protected by the plastic carriers could be used in open treatment basins or in rotating reactors.

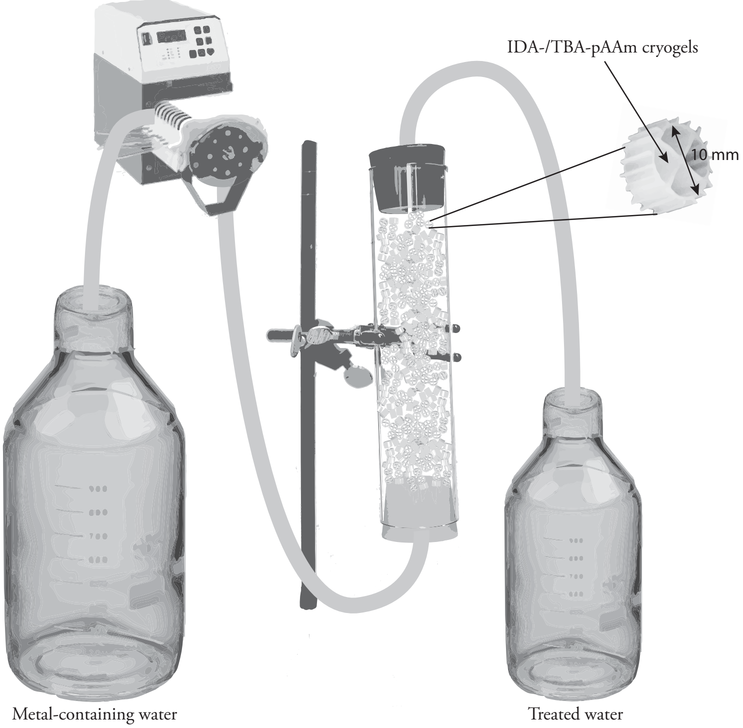

Figure 18. Schematic illustration showing how water contaminated with metal ions can be treated in continous mode. A chelating cryogel was prepared in plastic carriers which were packed in a column.(Ilustrated by Fia Persson.)

Municipal wastewater treatment is primarily designed to remove organic matter, nitrogen and phosphorous using biological systems employing activated sludge. The removal of heavy metals from these systems can therefore be regarded as a further benefit. Occasionally, WWTPs receive water with increased metal ion content. Treatment with adsorbents could be beneficial for these situations. The high inflow of water to WWTPs is a challenge, as it is not yet possible to produce cryogels in sufficiently large quantities. A municipal treatment plant in southern Sweden serving the city of Malmö receives approximately 1.6 m^3/s [193]. In a study by Karvelas et al. (2003), at a WWTP in Greece, over 70% of the Cu and Mn were found in the solid fraction, while roughly 47-63% of the remaining (Pb, Cd, Ni, Zn and Fe) were found in the liquid [6]. Hence, the removal of metals at lower concentrations should be carried out early in the treatment process, before sedimentation has taken place. The use of sewage sludge as a fertilizer is currently the subject of debate, due to its relatively high levels of heavy metals.

Different adsorbents may be required for different kinds of pollutant sources. High levels of phosphate often co-exist with arsenic, and compete for adsorption sites. A more selective adsorbent, such as the MIP-cryo developed in this work (**Paper II**), may provide a useful alternative. The MIP-cryo exhibited higher selectivity, although the overall adsorption capacity was lower that that of Alu-cryo (**Paper II**) and Fe-Al-cryo (**Paper III**).

A possible application of cryogel adsorbents is in a polishing step to remove arsenic, both As(III) and As(V), without the need for pretreatment, from wastewater at a smelting plant. The limit for arsenic release from industrial sources is currently 0.150 mg/l. The use of Fe-Al-cryo on real wastewater from a Swedish smelting plant showed that this limit could be achieved (**Paper III**). Adding adsorption as a polishing step would improve the overall treatment of an existing precipitation process. It would also reduce the amount of arsenic released from the smelting plant, thus improving the quality of the water released to the environment.

The application of composite cryogels as a POU filter is another interesting area. POU filters are necessary in areas where groundwater used for drinking water is contaminated. The challenge in this application, as drilled wells are often located in rural areas with limited communications and waste management, is to avoid hazardous waste generation from exhausted adsorbent materials [194]. Arsenic contamination in groundwater consist predominantly of As(III), and pre-oxidation would be necessary prior to adsorption with certain adsorbent materials. Two-stage treatment of water was shown to be possible by employing oxidation of As(III) to As(V) using H_2O_2 prior to treatment with the Alu-cryo (**Paper IV**). A better choice of POU filter is one using Fe-Al-cryo, as this can remove As(III) in a single step (**Paper III**). Using cryogels as a support in POU filters results in a membrane that can be operated at low pressures. Recent studies on water treatment and on the development of POU filter in general, indicate that cryogels are interesting, as recently demonstrated for disinfection purposes [195]. Ideally, a large range of contaminants should be removed by one single filter, e.g. by adding more than one adsorbent in the supporting material, as this would increase their potential.

It was shown that high volumes of water could be filtered through the Alu-cryo material composite without any detectable loss of NPs, or significant reduction in pollutant removal (demonstrated for As(V), **Paper V**). The use of embedded metal oxides in cryogels to remove inorganic pollutants is an attractive solution. A water volume 8000 times greater than the volume of the Alu-cryo composite itself was able to pass through the filter material without particle leaching. However, the results presented in **Paper V** indicated that AAm leaked out of the polymer support, as has been observed in previous studies [170]. AAm leakage was also seen during the production phase. After washing the composite with 80 bed volumes of water, the concentration of AAm in the filtrate water was significantly less than the permissible limit of 0.5 µg/l [20]. These results show that AAm should not be used in the production of cryogel supports and must be replaced.

Other studies have been published on promising POU filters involving metal oxide (nano) particles, as well as the immobilization of the particles on a support/matrix [80,160,194,196]. The main advantage for most of these published materials, e.g. sand filters with iron matrix or chitosan composites with silver NPs, in comparison to Alu-cryo, is that the technology is simple and can be performed on-site. Sankar et al. (2013) produced a POU filter at ambient temperatures, to be used in India. POU filters should also be low in cost [160]. For example, in the same study, it was shown that filters using AgNPs for water disinfection had a long lifetime, reducing the cost of treatment. Hug et al. (2013) showed that As(III) removal is possible using iron-sand filter (SONO filters) based on locally available iron in Bangladesh [196]. SONO filters have different compartments. One removes iron which prevents clogging due to precipitation of iron hydroxide on the resin used for As(III) removal. These iron-sand filters can also remove Mn and pathogens and in this regard, SONO filters are superior to many other filters developed for application in rural environments [146]. High amounts of NOM and suspended solids would clog a sand filter, which be less likely for a cryogel filter. However, the amount of suspended solids in groundwater treated to provide drinking water is low.

Indirect effects on health arise from the use of contaminated water for irrigation, or fertilizers (solid or liquid) applied to agricultural land. If the Cd^{2+} can be removed from biogas leachate using TNT-cryo (**Paper VI**), the nutrients can be recycled to the soil, and in the long term, better and safer crops can be produced. Not all biomass is of use for the agriculture, for example, high amounts of Cl^- in seaweed, unwanted by most plants, limit its universal use as fertilizers. Studies must be carried out to determine the best stage in the AD process to apply TNT-cryo filters to achieve optimal mobilization of Cd^{2+} and subsequent Cd^{2+} removal. One approach could be to apply the TNT-cryo filter between hydrolysis and the anaerobic step, prior to the precipitation of metal sulphides. The results of the flow-through experiments using real leachate with an initial Cd^{2+} concentration of 5 mg/l, indicated that 500 bed volumes of inflow water could be treated without breakthrough when tested on real leachate (**Paper VI**).

Despite the suspended solids in the bio-leachate (total solids 3.4 wt% and total suspended solids 7.8 mg/l), treatment was possible using TNT-cryo. Further studies are, however, needed for the reduction of Cd^{2+} in marine biomass, and in biomass in general. In addition to removing Cd^{2+} from the liquid phase, it must be shown that Cd^{2+} mobilization can be achieved without jeopardizing potential products such as high-value nutrients and biogas processes with low overall environmental impact. In addition, the goal should optimally be achieved at a reasonable cost.

The application of cryogels has been studied for other environmental purposes, examples being the successful use of adsorbents for oil spills and polycyclic aromatic hydrocarbons from seawater [197,198]. Apart from higher adsorption capacities than the commercially available polypropylene adsorbent, Okay demonstrated higher sorption rates and repetitive removal using butyl rubber as sorbent [197]. Similar successful results were achieved in the removal of organic liquids (e.g. benzene and toluene) as well as crude oils such as diesel oils. However, from an environmental perspective, the use of benzene in the production of the material is questionable [198].

System regeneration

The adsorption of pollutants from contaminated water provides purified water. However, the adsorbent will become saturated or exhausted with time. Regeneration of the adsorbent is preferable to disposal after use, as disposal is associated with higher operational costs and a greater burden on the environment. TNTs and IDA-/TBA-pAAm cryogels have successfully been regenerated using NaOH and HCl/EDTA respectively (**Paper I**) and [125].

With the increased use of metal-based adsorbents, regeneration has recently been shown to be possible by altering the pH [125]. The cost of treatment using an adsorbent that can be regenerated decreases with the number of times the adsorbent can be reused [199,200]. There are some limitations on recycling of the materials based on cryogel supports described in this work. High pH will probably hydrolyse the pAAm backbone, and in the case of TNT-cryo, regeneration of the adsorbent using NaOH is not possible. The recovery of other heavy metals is more interesting than the recovery of arsenic or cadmium, which are both extremely toxic. Some heavy metals can be reused by industry, whereas the use of arsenic and cadmium has practically ceased since many years [7,10].

POU filters with long lifetimes are preferable to POU filters, which need to frequently be replaced. SONO filters have been evaluated over an 8-year period, showing that the iron had been continuously been oxidized [196], and new adsorption sites are generated by iron oxidation and chemical reactions on the surface [146]. Apart from developing efficient POU filters, householders must be encouraged to use these filters, which has proven to be difficult [196].

Deposition

A highly toxic arsenic concentrate is produced from the regeneration of adsorbents used to remove arsenic. Precipitation, for example, with excess iron, can be used to remove the less soluble arsenic [201]. Due to the poor stability of iron arsenates, calcium can be added to ensure safe deposition of these arsenic compounds [201]. The solidified material can thereafter be disposed of in secure landfills [202]. The lab test or procedure for evaluating arsenic waste is called the TCLP (toxicity characteristic leaching procedure), and was developed by the US Environmental Protection Agency (USEPA). This procedure is used to evaluate possible arsenic (or other toxic content) leaching from the solidified product [203]. The concentration of toxic substances being leached out of the solid should not exceed the guidelines for drinking water by more than 100 times. In practice, this means that no more than 1 mg/l can be leached out of the waste deposited in landfills [146]. If this cannot be guaranteed, the waste must be disposed of in a sanitary landfill [202]. Conditions that can lead to the leaching of arsenic, e.g. reducing conditions, should be avoided at the deposition site. A TCLP evaluation should therefore be conducted for all sorbent materials developed [146]. Thus, apart from developing and producing efficient adsorbent materials for arsenic removal, their regeneration and final deposition must also be investigated. The best strategy for deposition would be to mimic the natural immobilization of arsenic in bedrock and sediments. Ensuring the presence of oxygen and controlling the pH at the deposition site will also ensure cleaner environments.

Despite their long lifetimes, cryo-composites will have to be disposed of at some point. For the pAAm cryogel, this is risky in terms of environmental impact and safety. The polymer will probably be hydrolysed at high pH, leading to the leakage of acrylic monomers. AAm is also a chemical on the REACH list. (REACH denotes Registration, Evaluation, Authorization and Restriction of Chemicals, and is used to regulate chemicals in the EU, and was adopted by the European Parliament in June 2007). It contains information on the toxicity of chemicals and their future impact on the environment [204]. The pAAm cryogel should therefore be replaced prior to the implementation of cryogel composites in commercial systems. In this work, AAm has however served as proof of the concept of a cryogel support.

Costs

To estimate the costs of the adsorbents studied in this work, calculations were performed based on price from suppliers offering high bulk volumes of the chemicals required. However, it is difficult to find prices for such large quantities of nanoparticles. The prices of low quantities were consequently reduced by factors between 10 and 30. The costs were estimated for the materials Alu-cryo, Fe-Al-cryo and TNT-cryo. To facilitate comparison, all these materials were considered as POU filters. The prices of the chemicals are given within a certain range, and both the lowest and the highest price were used in the calculations. The results are given in Table 5.

The choice of particles significantly affects the total material cost, depending on how the particles were obtained. Three different routes were considered: i) they were used as received from the supplier (AluNPs for Alu-cryo), ii) they were produced from metal salts (Fe-Al particles for Fe-Al-cryo), or iii) obtained via modification of purchased nanopowder (TiO_2-NPs for TNT-cryo). The loss of particles during production was also taken into account in these costs. It was assumed that the supporting material was pAAm cryogel.

The amount of the pollutant (Cd^{2+} or As(III, V), where all the arsenic species were considered together as As_{tot}) removed by 100 g adsorbent particles supported in pAAm cryogels (volume of cryogel is 25 l (Alu-cryo and Fe-Al-cryo) and 50 l (TNT-cryo)) was estimated using the adsorption capacities obtained in this work (**Papers II, III** and **VI**) (Table 5). This capacity was regarded as being independent of the initial pollutant concentration. For simplicity, an initial pollutant concentration of 0.2 mg/l was considered, and the water was treated until the final concentration of As_{tot} was 10 µg/l and for Cd^{2+} 3 µg/l.

A POU filter containing 100 g adsorbent particles incorporated in cryogel could last almost a year for one family, assuming that a family of five consumes 10 l drinking water per day. The TNT-cryo is superior to all the other materials evaluated due to its high adsorption capacity (Table 5).

The price comparison for Swedish adsorbent materials includes only arsenic filters, as these are sold and used here. Filters for the specific removal of cadmium from water are less available on the Swedish market, as cadmium is primarily a soil contaminant. Filters for heavy metals, however, can be found on the market, but will not be considered here. The market price of Swedish filter devices for the removal of arsenic consists of the cost of the holder/supporting material and the active filter material (consisting of an iron matrix). The market price also contains costs for labour, transport, marketing and a profit [205]. The iron matrix is usually exchanged every second year. The cost of the container was assumed to be 50% of the initial price of the filter device.

To costs of labour and facility rent were estimated and included based on the salary of one laboratory assistant, as start-up production would be of low volumes. It was assumed that the composite material would be held in a container similar to those provided for Swedish filter devices, ans this cost was added to the total cost of the material. The yearly cost for the TNT-cryo was about 30 times higher than the cost of a Swedish filter device for the removal of arsenic in a single household.

Table 5. Estimated costs of Fe-Al-cryo, Alu-cryo and TNT-cryo, for the removal of total arsenic (As_{tot}) and cadmium (Cd^{2+}) from drinking water, assuming 100 g of adsorbent particles in pAAm cryogels. Guideline values, particle costs, capacities, lifetimes (days) and yearly costs are also included.

Adsorbent target ion	**Minimum and maximum cost of particles (%) of total adsorbent cost**	**Capacity (mg/g adsorbent)**	**Guideline (µg/l)**	**Lifetime (days) assuming 10 l/day**	**Minimum and maximum cost (€/year)**
Fe-Al-cryo As_{tot} removal	2 to 4	24.6	10	248	504 to 508
Alu-cryo As_{tot} removal	65 to 83	20.1	10	203	619 to 623
TNT-cryo Cd^{2+} removal	30 to 52	157	5	1577	157

The commercial Swedish filter device is designed for higher flow rates than those evaluated for the cryogel materials studied in this work, and can thus produce higher amounts of pure water per day. Comparison with the cost of commercial arsenic filters on the Swedish market indicates that the cost of any of the cryogel materials is slightly above the normal price range, and further development is required to improve cost-efficiency. The costs of both the arsenic adsorbents developed in this work are much higher than the cost of commercial filters. Increasing the scale of production of these new materials will significantly reduce the cost of the chemicals used, especially the cost of nanoparticles. It should also be noted that the regeneration of the cryogel materials was not considered in these cost estimates. This will reduce the total cost by a factor equal to the number of times the material can be regenerated. Considering the high estimated costs, these materials may be better suited for countries where manpower and transport are available, than in rural areas where material availability and infrastructures are limited.

Conclusions and outlook

Although the use of (nano)particles embedded in cryogels provides interesting solutions for the removal of toxic metal ions from water at low concentrations, the efficiency could be improved by immobilizing the adsorbent particles differently, for example, by anchoring them on the surface or using them as surface coating. This could result in retaining or enhancing NP reactivity. Coating of particles on cryogels is currently being studied using an *in-situ* precipitation flow-through method with the Fe-Al hydrous oxide particles described in **Paper III**. The coating method is flexible, and higher mass loadings can be achieved by increasing the number of cycles or the initial concentrations of the metal salts used in the precipitation step. Using a coating of adsorbent particles on the surface also results in better uptake of As(III), partly due to the improved interaction between the surface of the adsorbent and the As(III) ions in the solution. Moreover, mass transfer and diffusion can be enhanced by applying a flow-through mode is applied to these macroporous materials, further increasing the adsorption efficiency. This could be very beneficial for the removal of As(III) at low concentrations. Similarly, the TNT-cryo described in **Paper VI** would be significantly more efficient if the TNTs could be exposed in the same manner. The conditions for the chemical synthesis of the particles and their immobilization should be mild; hence normal temperatures and the use of more sustainable chemicals in material production are desirable.

Shift towards green chemistry

The polymer used as support for the adsorbent materials was pAAm cryogel. This polymer served as a good proof-of-concept cryogel (**Papers I-III** and **V-VI**), but must be replaced in future applications. The monomer AAm has regulated use, as it is toxic and included in the REACH candidate list of substances of very high concern since 2010. Other polymers used for water treatment today are biopolymers, i.e. degradable polymers that have natural origin. The concept of using available resources or waste material is attractive. However, biopolymers are also degradable polymers and can deteriorate with time, increasing the risk of particle leakage and a decrease in adsorption efficiency. The polymer may also be degraded before the active adsorbent has been exhausted. This is, however, less likely with a synthetic polymer.

All polymers will suffer from bio-fouling when used in wastewater treatment, and the way in which this affects pollutant removal with time must be investigated. Examples of biopolymers that are both natural and cost-efficient (e.g. found in abundance), are chitosan, alginate and cellulose. These polymers can also be used for cryogel preparation, but some of them adsorb heavy metals non-specifically due to their functional hydroxyl groups (e.g. chitosan and cellulose). Studies were performed on different cryogel materials with and without particles to investigate how they were affected during 60 days' exposure to wastewater from a municipal treatment plant ($T = 22°C$, $pH \approx 7$). No difference in weight could be detected between the three different polymer supports (pAAm, cellulose and p(HEMA)-cryogels), regardless of whether they were based on synthetic or bio-polymers. More tests similar to these will be conducted, varying both time and pH.

Final tasks and challenges

Clearly, the choice of adsorbent material affects the overall environmental impact of the adsorbent. Apart from providing a resistant support or suitable immobilization of efficient NPs or adsorbent particles, the overall environmental impact should be kept as low as possible. In a life cycle analysis (LCA), a product is studied from cradle to grave, regarding greenhouse emissions during its production, the environmental benefits it provides and its overall potential impact (positive or negative) on the environment. LCA studies on adsorbent materials used for arsenic removal have shown that the material production and its effect on the environment can be equally important as the benefits obtained from efficient arsenic removal [206]. Understanding these perspectives of green processes is important, and tools such as LCAs can thus be useful.

In summary, we are facing many challenges in ensuring a clean supply of drinking water throughout the world. Many new interesting technologies are being developed, which will hopefully provide intelligent and efficient solutions to the problem. The strategy of using cryogels as supports for NPs is interesting, but the reactivity of incorporated NPs must be improved. In addition, the material should be mechanically strong to allow for high flow rates. On the whole, supported NPs show considerable potential, but important barriers must be overcome before this (nano)technology (and NPs in general) can be commercialized and introduced on a large scale. Cost-efficiency must be improved, for example, by better recovery or regeneration of NPs. Once it has been demonstrated that this technology is safe, it will be important to build up social acceptance so that these devices are actually used in homes. Finally, simple assays must be developed that can demonstrate the environmental safety of this technology. Of the above tasks, the most important, in my opinion, is that we can provide an efficient treatment technology that is environmentally safe, and that will not cause problems for future generations.

Acknowledgements

I have had numerous encounters and met many people during this 4 year long PhD-journey. On the whole, it has been a very interesting period in my life. To start with, it was all made possible thanks to initiative and financial support from Professor Emeritus Bo Mattiasson. I am grateful that you have been able to understand my passion in research.

I owe special thanks to you Dr. Harald Kirsebom, whom I have worked with since spring 2011. I am especially grateful for these past 7 months, when you actively have been supporting me, despite your new job in Denmark and your new family member. I hope we can work (and run) together again!

I also want to thank Professor Rajni Hatti-Kaul who was willing to step in as my main supervisor after Bo retired. I am grateful for your support and your constant belief in me.

At the Department of Biotechnology there are some people that need specific acknowledgement. First, there are some staff members that left for other jobs: I am especially thinking of Maria, Lovisa and Marika. I really enjoyed working with you all. Also, I owe special thanks to Prashanth. Thank you for always asking questions - together we developed new skills.

I also need to acknowledge Siv, the secretary of the Department of Biotechnology; thank you for the daily chats and assistance. Mia, thank you for your constant generosity and openness, I very much enjoyed the work we did together on the annual report. Marisa, Rosa and Maryam, three wonderful members of the environmental group. You are one of the reasons why research at the department has been so fun. All the other members of the department, you are all equally important: Johan, Frans-Peder, Eva, Christina, Rawana, Roya, Emmanuel, Ramin, Gustav, Pontus, Maru, Olle, Calle, Amin, Ally, Reza, Ivo, Lesedi, Kosin, Git, Ivo, Tarek, Tim, Hugo, Zubaida, the list goes on!

Thank you Paula for your help and input with the layout and creating PDFs on my Mac. To Alexandra, my best lunch date.

To researchers with whom I have been collaborating or been given help from: Fatima Plieva from Department of Biotechnology, Ola Wendt from Chemical

Analysis and Synthesis, Christian Svensson from Ergonomics and Aerosol Technology, Stefan Carlson and Kajsa Sigfridson from Maxlab, Birgitta Lindén from Chemical Engineering, Rita Wallén from Biological Department, the Brighton team etc.

Thank you Skånska Ingenjörsklubben, Kungliga Fysiografiska Sällskapet in Lund, LTH and Ångpanneföringen for financial support to international conferences.

Outside the department, my dear friends: the Malmö crowd including the Noble-collective (Lina and Nanny) as well as Fia, Linus, Kristina, Maria, Emma, Ludde, Annelie, Åsa-Maja, Tina and Olsson. Thank you for giving me other kinds of inputs in life besides research. In the east Scania area: the family of Hilfon/Liungman, the Malmqvist family in Snogeholm, the honey-makers of Djurröd, Love and Sara, Katja and Jens, Anna E and Anna F. I am so glad to have become friends with all of you.

To the talented photographer Christer: I am so proud to have your photo on my cover. Thanks to Fia and Mira for fantastic illustrations. Thank you Maria for helping with editing skills.

To my external family: Margareth, Thomas, Ellen and Björn with Idris and Rasmus. I am really proud to be part of your loving family.

To mum and dad, for endless support and help and belief in me. I am so happy to be your daughter. To my dear brother Peter, who finally moved back to Sweden, it is so nice to have you close. I look forward to quality time together.

Finally, to my great love in life: Nisse. You keep teaching me important things in life and remind me about my qualities. I am so grateful to have you next to me. Last but not least, to Zäta, my cheerful two year old daughter. It is such an adventure to follow and learn from you. I look forward to all this time we will share together.

References

1. UN. UN Water. 2013 [cited 2013, 17 October]; Available from: http://www.unwater.org/water-cooperation-2013/water-cooperation/facts-and-figures/.
2. UNICEF. Clean Drinking Water. 2013 [cited 2013, 17 October]; Available from: http://www.unicefusa.org/work/water/.
3. Jones, L. and Atkins, P., Chemistry, molecules matter and change. 4th ed, 2000, Michelle Russel Julet, USA.
4. Volesky, B., Biosorption and me. Water Research, 2007. **41**(18): p. 4017-4029.
5. Bindler, R., Yu, R., Hansson, S., et al., Mining, metallurgy and the historical origin of mercury pollution in lakes and watercourses in central Sweden. Environmental Science & Technology, 2012. **46**(15): p. 7984-7991.
6. Karvelas, M., Katsoyiannis, A., and Samara, C., Occurrence and fate of heavy metals in the wastewater treatment process. Chemosphere, 2003. **53**(10): p. 1201-1210.
7. Bissen, M. and Frimmel, F.H., Arsenic — a review. Part I: occurrence, toxicity, speciation, mobility. Acta hydrochimica et hydrobiologica, 2003. **31**(1): p. 9-18.
8. Duker, A.A., Carranza, E.J.M., and Hale, M., Arsenic geochemistry and health. Environment International, 2005. **31**(5): p. 631-641.
9. SCA, Kan ekonomiska styrmedel bidra till en giftfri miljö?, 2007, Swedish Chemicals Agency (KemI): Stockholm, Sweden.
10. Järup, L., Hazards of heavy metal contamination. British Medical Bulletin, 2003. **68**(1): p. 167-182.
11. EU, European Commission Directive, 98/83/EC, related with drinking water quality intended for human consumption, 1998: Brussels, Belgium.
12. SCA, Mercury phase-out - A study of the experiences of Swedish companies, 2011, Swedish Chemicals Agency (KemI): Stockholm, Sweden.
13. WHO, Guidelines for drinking-water quality. Health criteria and other supporting information, 1996, World Health Organization: Geneva, Switzerland. p. 940-9.
14. WHO, Guidelines for drinking-water quality, third edition, volume 1 recommendations, 2004, World Health Organization: Geneva, Switzerland.
15. WHO, Water quality: Guidelines, standards and health, 2001, World Health Organization: Geneva, Switzerland.
16. WHO, Arsenic in drinking-water, Background document for development of WHO guidelines for drinking-water quality, 2011, World Health Organization: Geneva, Switzerland.
17. SEPA, Förslag till gränsvärden för särskilda förorenande ämnen, 2008, Swedish Environmental Protection Agency: Stockholm, Sweden.
18. EU, EU Directive (2010/75/EU) in industrial emissions, 2010, EU Commission.
19. SCA, Kadmiumhalten måste minska - för folkhälsans skull, 2011, Swedish Chemicals Agency (KemI): Stockholm, Sweden. p. 270.
20. WHO, Guidelines for drinking-water quality , 2011, World Health Organization: Geneva, Switzerland.

21. Lindqvist, O., Johansson, K., Aastrup, M., et al., Mercury in the Swedish environment - Recent research on causes, consequences and corrective methods. Water Air and Soil Pollution, 1991. **55**(1-2): p. R11-&.
22. Tyler, G. and Olsson, T., Concentrations of 60 elements in the soil solution as related to the soil acidity. European Journal of Soil Science, 2001. **52**(1): p. 151-165.
23. Thomas, L.D.K., Michaelsson, K., Julin, B., et al., Dietary cadmium exposure and fracture incidence among men: A population-based prospective cohort study. Journal of Bone and Mineral Research, 2011. **26**(7): p. 1601-1608.
24. Jarup, L., Berglund, M., Elinder, C.G., et al., Health effects of cadmium exposure - a review of the literature and a risk estimate. (vol. 24, p. 1, 1998). Scandinavian Journal of Work Environment & Health, 1998. **24**(3): p. 240-240.
25. Akesson, A., Bjellerup, P., Lundh, T., et al., Cadmium-induced effects on bone in a population-based study of women. Environmental Health Perspectives, 2006. **114**(6): p. 830-834.
26. Guttormsen, G., Singh, B.R., and Jeng, A.S., Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil pH. Fertilizer research, 1995. **41**(1): p. 27-32.
27. Mortvedt, J.J., Mays, D.A., and Osborn, G., Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers. J. Environ. Qual., 1981. **10**(2): p. 193-197.
28. Meharg, A.A., Norton, G., Deacon, C., et al., Variation in Rice Cadmium Related to Human Exposure. Environmental Science & Technology, 2013. **47**(11): p. 5613-5618.
29. Naylor, L.M. and Loehr, R.C., Increase in dietary-cadmium as a result of application of sewage sludge to agricultural land. Environmental Science & Technology, 1981. **15**(8): p. 881-886.
30. Arao, T., Kawasaki, A., Baba, K., et al., Effects of water management on cadmium and arsenic accumulation and dimethylarsinic acid concentrations in Japanese rice. Environmental Science & Technology, 2009. **43**(24): p. 9361-9367.
31. SCA, Kadmiumhalten måste minska - för folkhälsans skull, SCA, 2011, Swedish Chemicals Agency (KemI): Stockholm, Sweden.
32. Lehtomäki, A. and Björnsson, L., Two-stage anaerobic digestion of energy crops: methane production, nitrogen mineralisation and heavy metal mobilisation. Environmental Technology, 2006. **27**(2): p. 209-218.
33. SEPA, Hållbar återföring av fosfor - Naturvårdsverkets redovisning av ett uppdrag från regeringen, 2013, Swedish Environmental Protection Agency (Naturvårdsverket): Stockholm, Sweden.
34. Nickson, R., McArthur, J., Burgess, W., et al., Arsenic poisoning of Bangladesh groundwater. Nature, 1998. **395**(6700): p. 338-338.
35. Smith, A.H., Lingas, E.O., and Rahman, M., Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bulletin of the World Health Organization, 2000. **78**(9): p. 1093-1103.
36. Smedley, P.L. and Kinniburgh, D.G., A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 2002. **17**(5): p. 517-568.
37. Matanoski, G.M., Landau, E., Tonascia, J., et al., Cancer mortality in an industrial area of Baltimore. Environmental Research, 1981. **25**(1): p. 8-28.
38. Winkel, L., Berg, M., Amini, M., et al., Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. Nature Geoscience, 2008. **1**(8): p. 536-542.
39. Hug, S.J., Leupin, O.X., and Berg, M., Bangladesh and Vietnam: Different groundwater compositions require different approaches to arsenic mitigation. Environmental Science & Technology, 2008. **42**(17): p. 6318-6323.
40. Michael, H.A., An arsenic forecast for China. Science, 2013. **341**(6148): p. 852-853.

41. Nickson, R.T., McArthur, J.M., Ravenscroft, P., et al., Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Applied Geochemistry, 2000. **15**(4): p. 403-413.
42. Nordstrom, D.K., Public health - Worldwide occurrences of arsenic in ground water. Science, 2002. **296**(5576): p. 2143-2145.
43. Berg, M., Stengel, C., Trang, P.T.K., et al., Magnitude of arsenic pollution in the Mekong and Red River Deltas - Cambodia and Vietnam. Science of The Total Environment, 2007. **372**(2-3): p. 413-425.
44. Berg, M., Tran, H.C., Nguyen, T.C., et al., Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. Environmental Science & Technology, 2001. **35**(13): p. 2621-2626.
45. Rodríguez-Lado, L., Sun, G., Berg, M., et al., Groundwater arsenic contamination throughout China. Science, 2013. **341**(6148): p. 866-868.
46. Katsoyiannis, I.A., Hug, S.J., Ammann, A., et al., Arsenic speciation and uranium concentrations in drinking water supply wells in Northern Greece: Correlations with redox indicative parameters and implications for groundwater treatment. Science of The Total Environment, 2007. **383**(1-3): p. 128-140.
47. Nyheter, S., Småländska glasbruk är miljöbomber, J.Z. Winberg, 2013.
48. Mertens, J., Rose, J., Kägi, R., et al., Adsorption of arsenic on polyaluminum granulate. Environmental Science & Technology, 2012. **46**(13): p. 7310-7317.
49. Sadiq, M., Zaidi, T.H., and Mian, A.A., Environmental behavior of arsenic in soils - theoretical. Water Air and Soil Pollution, 1983. **20**(4): p. 369-377.
50. Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H., Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environmental Science & Technology, 1991. **25**(8): p. 1414-1419.
51. Xu, H., Allard, B., and Grimvall, A., Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water Air and Soil Pollution, 1991. **57-8**: p. 269-278.
52. Smedley, P.L., Zhang, M., Zhang, G., et al., Mobilisation of arsenic and other trace elements in fluviolacustrine aquifers of the Huhhot Basin, Inner Mongolia. Applied Geochemistry, 2003. **18**(9): p. 1453-1477.
53. Lloyd, J.R. and Oremland, R.S., Microbial transformations of arsenic in the environment: From soda lakes to aquifers. Elements, 2006. **2**(2): p. 85-90.
54. Dixit, S. and Hering, J.G., Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environmental Science & Technology, 2003. **37**(18): p. 4182-4189.
55. Gustafsson, J.P., Arsenate adsorption to soils: Modelling the competition from humic substances. Geoderma, 2006. **136**(1–2): p. 320-330.
56. Concha, G., Broberg, K., Grander, M., et al., High-level exposure to lithium, boron, cesium, and arsenic via drinking water in the Andes of northern Argentina. Environmental Science & Technology, 2010. **44**(17): p. 6875-6880.
57. Bendz, D., Paxeus, N.A., Ginn, T.R., et al., Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Hoje River in Sweden. Journal of Hazardous Materials, 2005. **122**(3): p. 195-204.
58. Buser, H.-R., Poiger, T., and Müller, M.D., Occurrence and environmental behavior of the chiral pharmaceutical drug Ibuprofen in surface waters and in wastewater. Environmental Science & Technology, 1999. **33**(15): p. 2529-2535.
59. Ternes, T.A., Occurrence of drugs in German sewage treatment plants and rivers. Water Research, 1998. **32**(11): p. 3245-3260.
60. Schwarzenbach, R.P., Escher, B.I., Fenner, K., et al., The challenge of micropollutants in aquatic systems. Science, 2006. **313**(5790): p. 1072-1077.

61. Sedlak, D.L. and von Gunten, U., The chlorine dilemma. Science, 2011. **331**(6013): p. 42-43.
62. Kemira, About water treatment. A. Lindquist, 2003, Kemira Kemwater, Helsingborg, Sweden.
63. Kurniawan, T.A., Chan, G.Y.S., Lo, W.-H., et al., Physico–chemical treatment techniques for wastewater laden with heavy metals. Chemical Engineering Journal, 2006. **118**(1–2): p. 83-98.
64. Fu, F. and Wang, Q., Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 2011. **92**(3): p. 407-418.
65. Bose, P., Bose, M.A., and Kumar, S., Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. Advances in Environmental Research, 2002. 7(1): p. 179-195.
66. Monser, L. and Adhoum, N., Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. Separation and Purification Technology, 2002. **26**(2–3): p. 137-146.
67. Michael T. Madigan, John M. Martinko, Paul Dunlap, et al., Brock biology of microorganisms. Brock. ed. Vol. 13th. 2009, Pearson International Edition, San Francisco, USA.
68. Williams, K.H., Bargar, J.R., Lloyd, J.R., et al., Bioremediation of uranium-contaminated groundwater: a systems approach to subsurface biogeochemistry. Current Opinion in Biotechnology, 2013. **24**(3): p. 489-497.
69. Leeson, A. and Alleman, B.C., Bioremediation of metals and inorganic pollutants, A. Leeson and B.C. Alleman. 1999, Battelle Press: Ohio, USA.
70. Bijmans, M.F.M., van Helvoort, P.-J., Dar, S.A., et al., Selective recovery of nickel over iron from a nickel–iron solution using microbial sulfate reduction in a gas-lift bioreactor. Water Research, 2009. **43**(3): p. 853-861.
71. Hard, B.C., Friedrich, S., and Babel, W., Bioremediation of acid mine water using facultatively methylotrophic metal-tolerant sulfate-reducing bacteria. Microbiological Research, 1997. **152**(1): p. 65-73.
72. Alvarez, M.T., Crespo, C., and Mattiasson, B., Precipitation of Zn(II), Cu(II) and Pb(II) at bench-scale using biogenic hydrogen sulfide from the utilization of volatile fatty acids. Chemosphere, 2007. **66**(9): p. 1677-1683.
73. Pott, B.M. and Mattiasson, B., Separation of heavy metals from water solutions at the laboratory scale. Biotechnology Letters, 2004. **26**(5): p. 451-456.
74. Caplan, J.A., The worldwide bioremediation industry - prospects for profit. Trends in Biotechnology, 1993. **11**(8): p. 320-323.
75. Hug, S.J., Canonica, L., Wegelin, M., et al., Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. Environ Sci Technol., 2001. **35**(10): p. 2114-21.
76. Hug, S.J. and Leupin, O., Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. Environmental Science & Technology, 2003. **37**(12): p. 2734-2742.
77. Kim, M.J. and Nriagu, J., Oxidation of arsenite in groundwater using ozone and oxygen. Science of The Total Environment, 2000. **247**(1): p. 71-79.
78. Voegelin, A. and Hug, S.J., Catalyzed oxidation of arsenic(III) by hydrogen peroxide on the surface of ferrihydrite: An in situ ATR-FTIR study. Environmental Science & Technology, 2003. **37**(5): p. 972-978.
79. Elcik, H., Cakmakci, M., Sahinkaya, E., et al., Arsenic removal from drinking water using low pressure membranes. Industrial & Engineering Chemistry Research, 2013. **52**(29): p. 9958-9964.

80. Leupin, O.X., Hug, S.J., and Badruzzaman, A.B.M., Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filings and sand. Environmental Science & Technology, 2005. **39**(20): p. 8032-8037.
81. Khin, M.M., Nair, A.S., Babu, V.J., et al., A review on nanomaterials for environmental remediation. Energy & Environmental Science, 2012. **5**(8): p. 8075-8109.
82. Mohan, D. and Pittman, C.U., Jr., Arsenic removal from water/wastewater using adsorbents - A critical review. Journal of Hazardous Materials, 2007. **142**(1-2): p. 1-53.
83. Rao, G.P., Lu, C., and Su, F., Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. Separation and Purification Technology, 2007. **58**(1): p. 224-231.
84. Langmuir, I., The adsorption of gases on place surfaces of glass, mica and platinum. Journal of the American Chemical Society, 1918. **40**(9): p. 1361-1403.
85. Atkins, P. and de Paula, J., Physical chemistry. 7th ed, 2002, Oxford University Press Trento, Italy.
86. Weber, W.J., McGinley, P.M., and Katz, L.E., Distributed reactivity in the sorption of hydrophobic organic contaminants in natural aquatic systems, in Aquatic chemistry - interfacial and interspecies processes. Editor(s): C.P. Huang, C.R. O'Melia, and J.J. Morgan. 1995, American Chemical Society (ACS): San Francisco, USA. p. 363-382.
87. Ho, Y.S., Porter, J.F., and McKay, G., Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. Water Air and Soil Pollution, 2002. **141**(1-4): p. 1-33.
88. IUPAC, Compendium of chemical terminology - the gold book, A.D. McNaught and A. Wilkinson, 1997, Blackwell Scientific Publications: Oxford, UK.
89. Peleka, E.N. and Matis, K.A., Water separation processes and sustainability. Industrial & Engineering Chemistry Research, 2011. **50**(2): p. 421-430.
90. Flora, S.J.S. and Pachauri, V., Chelation in metal intoxication. International Journal of Environmental Research and Public Health, 2010. **7**(7): p. 2745-2788.
91. Porath, J., Immobilized metal-ion affinity-chromatography. Protein Expression and Purification, 1992. **3**(4): p. 263-281.
92. Porath, J., Carlsson, J., Olsson, I., et al., Metal chelate affinity chromatography, a new approach to protein fractionation. Nature, 1975. **258**(5536): p. 598-599.
93. Hermanson GT, K.M.A., Smith PK., Immobilized affinity ligand techniques. 1992, Academic Press Inc., New York, USA.
94. Chubar, N., Kanibolotskyy, V., Strelko, V., et al., Adsorption of anions onto sol-gel generated double hydrous oxides, in Soil and Water Pollution Monitoring, Protection and Remediation. Editor(s): I. Twardowska, et al. 2006, Springer Netherlands. p. 323-338.
95. Ho, Y.S. and McKay, G., Pseudo-second order model for sorption processes. Process Biochemistry, 1999. **34**(5): p. 451-465.
96. Masue, Y., Loeppert, R.H., and Kramer, T.A., Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminum : iron hydroxides. Environmental Science & Technology, 2007. **41**(3): p. 837-842.
97. Mafu, L.D., Msagati, T.A.M., and Mamba, B.B., Ion-imprinted polymers for environmental monitoring of inorganic pollutants: synthesis, characterization, and applications. Environmental Science and Pollution Research, 2013. **20**(2): p. 790-802.
98. Shen, X., Xu, C., and Ye, L., Molecularly imprinted polymers for clean Water: Analysis and purification. Industrial & Engineering Chemistry Research, 2012.
99. Murray, A. and Ormeci, B., Application of molecularly imprinted and non-imprinted polymers for removal of emerging contaminants in water and wastewater treatment: a review. Environmental Science and Pollution Research, 2012. **19**(9): p. 3820-3830.
100. Chen, H., Olmstead, M.M., Albright, R.L., et al., Metal-ion-templated polymers: Synthesis and structure of N-(4-vinylbenzyl)-1,4,7-triazacyclononanezinc(II) complexes,

their copolymerization with divinylbenzene, and metal-ion selectivity studies of the demetalated resins—evidence for a sandwich complex in the polymer matrix. Angewandte Chemie International Edition in English, 1997. **36**(6): p. 642-645.

101. Haupt, K. and Mosbach, K., Molecularly imprinted polymers and their use in biomimetic sensors. Chemical Reviews, 2000. **100**(7): p. 2495-2504.

102. Wulff, G., Molecular imprinting in cross-linked materials with the aid of molecular templates - a way towards artificial antibodies. Angewandte Chemie-International Edition in English, 1995. **34**(17): p. 1812-1832.

103. Mosbach, K. and Ramstrom, O., The emerging technique of molecular imprinting and its future impact on biotechnology. Bio-Technology, 1996. **14**(2): p. 163-170.

104. Benito-Pena, E., Martins, S., Orellana, G., et al., Water-compatible molecularly imprinted polymer for the selective recognition of fluoroquinolone antibiotics in biological samples. Analytical and Bioanalytical Chemistry, 2009. **393**(1): p. 235-245.

105. Piletsky, S.A., Alcock, S., and Turner, A.P.F., Molecular imprinting: at the edge of the third millennium. Trends in Biotechnology, 2001. **19**(1): p. 9-12.

106. Chen, L., Xu, S., and Li, J., Recent advances in molecular imprinting technology: current status, challenges and highlighted applications. Chemical Society Reviews, 2011. **40**(5): p. 2922-2942.

107. Le Noir, M., Plieva, F., Hey, T., et al., Macroporous molecularly imprinted polymer/cryogel composite systems for the removal of endocrine disrupting trace contaminants. Journal of Chromatography A, 2007. **1154**(1-2): p. 158-164.

108. Hajizadeh, S., Xu, C.G., Kirsebom, H., et al., Cryogelation of molecularly imprinted nanoparticles: A macroporous structure as affinity chromatography column for removal of beta-blockers from complex samples. Journal of Chromatography A, 2013. **1274**: p. 6-12.

109. Hajizadeh, S., Kirsebom, H., Galaev, I.Y., et al., Evaluation of selective composite cryogel for bromate removal from drinking water. Journal of Separation Science, 2010. **33**(12): p. 1752-1759.

110. Le Noir, M., Lepeuple, A.S., Guieysse, B., et al., Selective removal of 17 beta-estradiol at trace concentration using a molecularly imprinted polymer. Water Research, 2007. **41**(12): p. 2825-2831.

111. Meng, Z., Chen, W., and Mulchandani, A., Removal of estrogenic pollutants from contaminated water using molecularly imprinted polymers. Environmental Science & Technology, 2005. **39**(22): p. 8958-8962.

112. Koç, İ., Baydemir, G., Bayram, E., et al., Selective removal of 17β-estradiol with molecularly imprinted particle-embedded cryogel systems. Journal of Hazardous Materials, 2011. **192**(3): p. 1819-1826.

113. Ersoz, A., Say, R., and Denizli, A., Ni(II) ion-imprinted solid-phase extraction and preconcentration in aqueous solutions by packed-bed columns. Analytica Chimica Acta, 2004. **502**(1): p. 91-97.

114. Hingston, F.J., Quirk, J.P., and Posner, A.M., Anion adsorption by goethite and gibbsite .1. Role of proton in determining adsorption envelopes. Journal of Soil Science, 1972. **23**(2): p. 177-&.

115. Kanel, S.R., Manning, B., Charlet, L., et al., Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. Environmental Science & Technology, 2005. **39**(5): p. 1291-1298.

116. Jain, A. and Loeppert, R.H., Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J. Environ. Qual., 2000. **29**(5): p. 1422-1430.

117. Davenport, J.R. and Peryea, F.J., Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead arsenate. Water Air and Soil Pollution, 1991. **57-8**: p. 101-110.

118. Su, C.M. and Puls, R.W., Arsenate and arsenite removal by zerovalent iron: Effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. Environmental Science & Technology, 2001. **35**(22): p. 4562-4568.
119. Redman, A.D., Macalady, D.L., and Ahmann, D., Natural organic matter affects arsenic speciation and sorption onto hematite. Environmental Science & Technology, 2002. **36**(13): p. 2889-2896.
120. Wilkie, J.A. and Hering, J.G., Adsorption of arsenic onto hydrous ferric oxide: Effects of adsorbate/adsorbent ratios and co-occurring solutes. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 1996. **107**: p. 97-110.
121. Kasuga, T., Hiramatsu, M., Hoson, A., et al., Formation of titanium oxide nanotube. Langmuir, 1998. **14**(12): p. 3160-3163.
122. Du, A.J., Sun, D.D., and Leckie, J.O., Selective sorption of divalent cations using a high capacity sorbent. Journal of Hazardous Materials, 2011. **187**(1-3): p. 96-100.
123. Liu, W., Wang, T., Borthwick, A.G.L., et al., Adsorption of Pb2+, Cd2+, Cu2+ and Cr3+ onto titanate nanotubes: Competition and effect of inorganic ions. Science of The Total Environment, 2013. **456–457**(0): p. 171-180.
124. Du, A.J., Sun, D.D., and Leckie, J.O., Sequestration of cadmium ions using titanate nanotube. Journal of Hazardous Materials, 2011. **187**(1-3): p. 401-406.
125. Wang, T., Liu, W., Xu, N., et al., Adsorption and desorption of Cd(II) onto titanate nanotubes and efficient regeneration of tubular structures. Journal of Hazardous Materials, 2013. **250**: p. 379-386.
126. Nkemka, V.N. and Murto, M., Exploring strategies for seaweed hydrolysis: Effect on methane potential and heavy metal mobilisation. Process Biochemistry, 2012. **47**(12): p. 2523-2526.
127. Brown, J., Mercier, L., and Pinnavaia, T.J., Selective adsorption of Hg2+ by thiol-functionalized nanoporous silica. Chemical Communications, 1999(1): p. 69-70.
128. Khan, S.B., Rahman, M.M., Marwani, H.M., et al., Selective adsorption and determination of iron(III): Mn3O4/TiO2 composite nanosheets as marker of iron for environmental applications. Applied Surface Science, 2013. **282**: p. 46-51.
129. Liu, A.M., Hidajat, K., Kawi, S., et al., A new class of hybrid mesoporous materials with functionalized organic monolayers for selective adsorption of heavy metal ions. Chemical Communications, 2000(13): p. 1145-1146.
130. Walcarius, A. and Mercier, L., Mesoporous organosilica adsorbents: nanoengineered materials for removal of organic and inorganic pollutants. Journal of Materials Chemistry, 2010. **20**(22): p. 4478-4511.
131. Tekin, K., Uzun, L., Sahin, C.A., et al., Preparation and characterization of composite cryogels containing imidazole group and use in heavy metal removal. Reactive & Functional Polymers, 2011. **71**(10): p. 985-993.
132. Grinstead, R.R., Selective absorption of copper, nickel, cobalt and other transition-metal ions from sulfuric-acid-solutions with the chelating ion-exchange resins XFS 4195. Hydrometallurgy, 1984. **12**(3): p. 387-400.
133. Cherry, J.A., Shaikh, A.U., Tallman, D.E., et al., Arsenic species as an indicator of redox conditions in groundwater. Journal of Hydrology, 1979. **43**(1-4): p. 373-392.
134. Pettine, M., Campanella, L., and Millero, F.J., Arsenite oxidation by H2O2 in aqueous solutions. Geochimica Et Cosmochimica Acta, 1999. **63**(18): p. 2727-2735.
135. Von Gunten, U., Von Sonntag, C., Chemistry of ozone in water and wastewater treatment. 2012, IWA, London, UK.
136. Guan, X.H., Du, J.S., Meng, X.G., et al., Application of titanium dioxide in arsenic removal from water: A review. Journal of Hazardous Materials, 2012. **215**: p. 1-16.

137. Ferguson, M.A., Hoffmann, M.R., and Hering, J.G., TiO2-photocatalyzed As(III) oxidation in aqueous suspensions: Reaction kinetics and effects of adsorption. Environmental Science & Technology, 2005. **39**(6): p. 1880-1886.

138. Lee, H. and Choi, W., Photocatalytic oxidation of arsenite in TiO2 suspension: Kinetics and mechanisms. Environmental Science & Technology, 2002. **36**(17): p. 3872-3878.

139. Oscarson, D.W., Huang, P.M., Defosse, C., et al., Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. Nature, 1981. **291**(5810): p. 50-51.

140. Hering, J.G., Chen, P.Y., Wilkie, J.A., et al., Arsenic removal from drinking water during coagulation. Journal of Environmental Engineering-ASCE, 1997. **123**(8): p. 800-807.

141. Lee, Y., Um, I.-h., and Yoon, J., Arsenic(III) Oxidation by Iron(VI) (Ferrate) and Subsequent Removal of Arsenic(V) by Iron(III) Coagulation. Environmental Science & Technology, 2003. **37**(24): p. 5750-5756.

142. Zhang, F.-S. and Itoh, H., Photocatalytic oxidation and removal of arsenite from water using slag-iron oxide-TiO2 adsorbent. Chemosphere, 2006. **65**(1): p. 125-131.

143. Yamani, J.S., Miller, S.M., Spaulding, M.L., et al., Enhanced arsenic removal using mixed metal oxide impregnated chitosan beads. Water Research, 2012. **46**(14): p. 4427-4434.

144. Giles, D.E., Mohapatra, M., Issa, T.B., et al., Iron and aluminium based adsorption strategies for removing arsenic from water. Journal of Environmental Management, 2011. **92**(12): p. 3011-3022.

145. Goldberg, S., Competitive Adsorption of Arsenate and Arsenite on Oxides and Clay Minerals Contribution from the George E. Brown Jr., Salinity Laboratory. Soil Sci. Soc. Am. J., 2002. **66**(2): p. 413-421.

146. Ahamed, S. and Hussam, A., Groundwater arsenic removal technologies based on sorbents: field applications and sustainability, in Handbook of water purity and quality Editor(s): S. Ahuja. 2009, Academic Press: Amsterdam, Netherlands.

147. Mandelli, D., do Amaral, A.C.N., Kozlov, Y.N., et al., Hydrogen peroxide oxygenation of saturated and unsaturated hydrocarbons catalyzed by montmorillonite or aluminum oxide. Catalysis Letters, 2009. **132**(1-2): p. 235-243.

148. Xu, P., Zeng, G.M., Huang, D.L., et al., Use of iron oxide nanomaterials in wastewater treatment: A review. Science of The Total Environment, 2012. **424**: p. 1-10.

149. Qu, X.L., Brame, J., Li, Q.L., et al., Nanotechnology for a Safe and Sustainable Water Supply: Enabling Integrated Water Treatment and Reuse. Accounts of Chemical Research, 2013. **46**(3): p. 834-843.

150. Sharma, Y.C., Srivastava, V., Singh, V.K., et al., Nano-adsorbents for the removal of metallic pollutants from water and wastewater. Environmental Technology, 2009. **30**(6): p. 583-609.

151. Volesky, B. and Holan, Z.R., Biosorption of heavy metals. Biotechnology Progress, 1995. **11**(3): p. 235-250.

152. Mustafa, S., Dilara, B., Nargis, K., et al., Surface properties of the mixed oxides of iron and silica. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2002. **205**(3): p. 273-282.

153. Zheng, Y.M., Yu, L., Wu, D., et al., Removal of arsenite from aqueous solution by a zirconia nanoparticle. Chemical Engineering Journal, 2012. **188**: p. 15-22.

154. Crane, R.A. and Scott, T.B., Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. Journal of Hazardous Materials, 2012. **211**: p. 112-125.

155. Pillewan, P., Mukherjee, S., Roychowdhury, T., et al., Removal of As(III) and As(V) from water by copper oxide incorporated mesoporous alumina. Journal of Hazardous Materials, 2011. **186**(1): p. 367-375.

156. Zhang, G.S., Khorshed, A., and Chen, J.P., Simultaneous removal of arsenate and arsenite by a nanostructured zirconium-manganese binary hydrous oxide: Behavior and mechanism. Journal of Colloid and Interface Science, 2013. **397**: p. 137-143.
157. Kanel, S.R., Nepal, D., Manning, B., et al., Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation. Journal of Nanoparticle Research, 2007. **9**(5): p. 725-735.
158. Simeonidis, K., Gkinis, T., Tresintsi, S., et al., Magnetic separation of hematite-coated Fe3O4 particles used as arsenic adsorbents. Chemical Engineering Journal, 2011. **168**(3): p. 1008-1015.
159. Raveendran, P., Fu, J., and Wallen, S.L., Completely "green" synthesis and stabilization of metal nanoparticles. Journal of the American Chemical Society, 2003. **125**(46): p. 13940-13941.
160. Sankar, M.U., Aigal, S., Maliyekkal, S.M., et al., Biopolymer-reinforced synthetic granular nanocomposites for affordable point-of-use water purification. Proceedings of the National Academy of Sciences of the United States of America, 2013. **110**(21): p. 8459-8464.
161. Zhang, K., Kemp, K.C., and Chandra, V., Homogeneous anchoring of TiO2 nanoparticles on graphene sheets for waste water treatment. Materials Letters, 2012. **81**: p. 127-130.
162. Li, Y.H., Ding, J., Luan, Z.K., et al., Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes. Carbon, 2003. **41**(14): p. 2787-2792.
163. Zhang, G., Liu, H., Qu, J., et al., Arsenate uptake and arsenite simultaneous sorption and oxidation by Fe-Mn binary oxides: Influence of Mn/Fe ratio, pH, Ca2+, and humic acid. Journal of Colloid and Interface Science, 2012. **366**(1): p. 141-146.
164. Pena, M.E., Korfiatis, G.P., Patel, M., et al., Adsorption of As(V) and As(III) by nanocrystalline titanium dioxide. Water Research, 2005. **39**(11): p. 2327-2337.
165. Gupta, A., Yunus, M., and Sankararamakrishnan, N., Zerovalent iron encapsulated chitosan nanospheres - A novel adsorbent for the removal of total inorganic Arsenic from aqueous systems. Chemosphere, 2012. **86**(2): p. 150-155.
166. Lozinsky, V., Galaev, I.Y., Plieva, F.M., et al., Polymeric cryogels as promising materials of biotechnological interest. Trends in Biotechnology, 2003. **21**(10): p. 445-451.
167. Arvidsson, P., Plieva, F.M., Savina, I.N., et al., Chromatography of microbial cells using continuous supermacroporous affinity and ion-exchange columns. Journal of Chromatography A, 2002. **977**(1): p. 27-38.
168. Aragão Börner, R., Zaushitsyna, O., Berillo, D., et al., Immobilization of Clostridium acetobutylicum DSM 792 as macroporous aggregates through cryogelation for butanol production. Process Biochemistry, (0).
169. Lozinsky, V.I., Cryogels on the basis of natural and synthetic polymers: Preparation, properties and application. Russian Chemical Reviews, 2002. **71**(6): p. 559-585.
170. Plieva, F.M., Andersson, J., Galaev, I.Y., et al., Characterization of polyacrylamide based monolithic columns. Journal of Separation Science, 2004. **27**(10-11): p. 828-836.
171. Kirsebom, H. and Mattiasson, B., Cryostructuration as a tool for preparing highly porous polymer materials. Polymer Chemistry, 2011. **2**(5): p. 1059-1062.
172. Kirsebom, H., Preparation and Characterization of Macroporous Cryostructured Materials, in *Doctoral Thesis*, 2010, Lund University: Lund, Sweden.
173. Lozinsky, V.I., Vainerman, E.S., Titova, E.F., et al., Study of cryostructurization of polymer systems .4. Cryostructurization of the system - solvent vinyl monomer divinyl monomer initiator of polymerization. Colloid and Polymer Science, 1984. **262**(10): p. 769-774.
174. Plieva, F.M., Karlsson, M., Aguilar, M.R., et al., Pore structure in supermacroporous polyacrylamide based cryogels. Soft Matter, 2005. **1**(4): p. 303-309.

175. Carvalho, B.M.A., Da Silva, S.L., Da Silva, L.H.M., et al., Cryogel poly(acrylamide): Synthesis, structure and applications. Separation and Purification Reviews, 2014. **43**(3): p. 241-262.
176. Plieva, F., Xiao, H., Galaev, I.Y., et al., Macroporous elastic polyacrylamide gels prepared at subzero temperatures: control of porous structure. Journal of Materials Chemistry, 2006. **16**(41): p. 4065-4073.
177. Ozmen, M.M. and Okay, O., Formation of macroporous poly(acrylamide) hydrogels in DMSO/water mixture: Transition from cryogelation to phase separation copolymerization. Reactive & Functional Polymers, 2008. **68**(10): p. 1467-1475.
178. Duboeuf, F., Basarab, A., Liebgott, H., et al., Investigation of PVA cryogel Young's modulus stability with time, controlled by a simple reliable technique. Medical Physics, 2009. **36**(2): p. 656-661.
179. Zheng, Y., Gun'ko, V.M., Howell, C.A., et al., Composites with macroporous poly(vinyl alcohol) cryogels with attached activated carbon microparticles with controlled accessibility of a surface. ACS Applied Materials & Interfaces, 2012. **4**(11): p. 5936-5944.
180. Savina, I.N., English, C.J., Whitby, R.L.D., et al., High efficiency removal of dissolved As(III) using iron nanoparticle-embedded macroporous polymer composites. Journal of Hazardous Materials, 2011. **192**(3): p. 1002-1008.
181. McCabe, W., Smith, J., Harriot, P., Unit of operations chemical engineering. 2001, McGraw Hill, Singapore.
182. Mackenzie, K., Bleyl, S., Georgi, A., et al., Carbo-Iron - An Fe/AC composite - As alternative to nano-iron for groundwater treatment. Water Research, 2012. **46**(12): p. 3817-3826.
183. Qu, X., Brame, J., Li, Q., et al., Nanotechnology for a Safe and Sustainable Water Supply: Enabling Integrated Water Treatment and Reuse. Accounts of Chemical Research, 2013. **46**(3): p. 834-843.
184. Hennebel, T., De Gusseme, B., Boon, N., et al., Biogenic metals in advanced water treatment. Trends in Biotechnology, 2009. **27**(2): p. 90-98.
185. Auffan, M., Rose, J., Proux, O., et al., Enhanced adsorption of arsenic onto maghemite nanoparticles: As(III) as a probe of the surface structure and heterogeneity. Langmuir, 2008. **24**(7): p. 3215-3222.
186. Kaegi, R., Voegelin, A., Ort, C., et al., Fate and transformation of silver nanoparticles in urban wastewater systems. Water Research, 2013(0).
187. Franklin, N.M., Rogers, N.J., Apte, S.C., et al., Comparative toxicity of nanoparticulate ZnO, bulk ZnO, and ZnCl2 to a freshwater microalga (*Pseudokirchneriella subcapitata*): The importance of particle solubility. Environmental Science & Technology, 2007. **41**(24): p. 8484-8490.
188. Nel, A., Xia, T., Madler, L., et al., Toxic potential of materials at the nanolevel. Science, 2006. **311**(5761): p. 622-627.
189. Johansson, E.M. and Johansson, S.A.E., PIXE analysis of water at the parts per trillion level. Nuclear instruments & methods in physics research section b-Beam interactions with materials and atoms, 1984. **3**(1-3): p. 154-157.
190. IARC, Monographs on the evaluation of carcinogenic risks to humans: Some industrial chemicals, in *Volume 60*, 1999, World Health Organization: Lyon, France.
191. Plieva, F.M. and Mattiasson, B., Macroporous gel particles as novel sorbent materials: Rational design. Industrial & Engineering Chemistry Research, 2008. **47**(12): p. 4131-4141.
192. Selling, R., Hakansson, T., and Bjornsson, L., Two-stage anaerobic digestion enables heavy metal removal. Water Science and Technology, 2008. **57**(4): p. 553-558.
193. VA-Syd, Sjölunda avloppsreningsverk, 2009: Malmö, Sweden.

194. Leupin, O.X. and Hug, S.J., Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. Water Research, 2005. **39**(9): p. 1729-1740.
195. Loo, S.-L., Fane, A.G., Lim, T.-T., et al., Superabsorbent Cryogels Decorated with Silver Nanoparticles as a Novel Water Technology for Point-of-Use Disinfection. Environmental Science & Technology, 2013. **47**(16): p. 9363-9371.
196. Neumann, A., Kaegi, R., Voegelin, A., et al., Arsenic removal with composite iron matrix filters in Bangladesh: A field and laboratory study. Environmental Science & Technology, 2013. **47**(9): p. 4544-4554.
197. Ceylan, D., Dogu, S., Karacik, B., et al., Evaluation of butyl rubber as sorbent material for the removal of oil and polycyclic aromatic hydrocarbons from seawater. Environmental Science & Technology, 2009. **43**(10): p. 3846-3852.
198. Hu, Y., Liu, X., Zou, J., et al., Graphite/Isobutylene-isoprene rubber highly porous cryogels as new sorbents for oil spills and organic liquids. ACS Applied Materials & Interfaces, 2013. **5**(16): p. 7737-7742.
199. Qu, X., Alvarez, P.J.J., and Li, Q., Applications of nanotechnology in water and wastewater treatment. Water Research, 2013. **47**(12): p. 3931-3946.
200. Lu, C., Chiu, H., and Bai, H., Comparisons of adsorbent cost for the removal of zinc (II) from aqueous solution by carbon nanotubes and activated carbon. Journal of Nanoscience and Nanotechnology, 2007. **7**(4-5): p. 1647-1652.
201. Palfy, P., Vircikova, E., and Molnar, L., Processing of arsenic waste by precipitation and solidification. Waste Management, 1999. **19**(1): p. 55-59.
202. Leist, M., Casey, R.J., and Caridi, D., The management of arsenic wastes: problems and prospects. Journal of Hazardous Materials, 2000. **76**(1): p. 125-138.
203. USEPA, Arsenic treatment technologies for soil, waste, and water, in *EPA-542-R-02-004*, USEPA, 2002: Cincinnati, USA.
204. Pesendorfer, D., EU environmental policy under pressure: Chemicals policy change between antagonistic goals? Environmental Politics, 2006. **15**(1): p. 95-114.
205. Johnsson, K., Manager of Vattenteknik, Sweden, 2013: Personal communication.
206. Dodbiba, G., Nukaya, T., Kamioka, Y., et al., Removal of arsenic from wastewater using iron compound: Comparing two different types of adsorbents in the context of LCA. Resources, Conservation and Recycling, 2009. **53**(12): p. 688-697.