EVALUATION AND OPTIMIZATION OF ADVANCED OXIDATION COAGULATION FILTRATION (AOCF) TO PRODUCE DRINKING WATER WITH LESS THAN 1 µg/L OF ARSENIC

BENCH AND PILOT SCALE INVESTIGATION

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DEDIATION

I dedicate this research work to my father, Mr. Mushtaq Ahmad, who has given me the gift of life, a kidney. He is and has always been a source of inspiration for me. Mr. Mushtaq had studied Mechanical Engineering and then became associated with international paper manufacturing industry. Now a days, he works as an engineering consultant in Pakistan.
Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic

SUMMARY IN ENGLISH

Arsenic (As) is an extremely poisonous element. It has been reported to cause contamination of drinking water sources in many parts of the world. The current drinking water permissible limit for As in the European Union (EU), United States of America (US), Japan and many other high income countries is 10 µg/L. The World Health Organization (WHO) has a general rule that no substance may have a higher lifetime risk of more than 1 in 100,000. However, several studies on toxicity of As suggest that purely based on health effects the drinking water As limit of 10 µg/L is not sufficient. Looking back at the history of WHO’s recommendations for maximum permissible levels, a gradual lowering of maximum allowable As concentration in drinking water can be observed since 1958, when maximum As concentration of 200 µg/L was suggested, till 1993, when the Guidelines for Drinking water Quality (GDWQ) recommended 10 µg/L in a provisional definition. Since 1993, the drinking water As guideline of WHO has remained unchanged. Today there exists a general consensus that, if possible, it is necessary to remove As as far as possible below 10 µg/L, not only for the safety of human health from the toxicity of As but also for avoiding future non-compliance issues when the national standards will be lowered further. The US Environmental Protection Agency (USEPA) and the US Natural Resources Defense Council (NRDC) have already recommended As guidelines below 1 µg/L to attain an acceptable lifetime cancer risk.

In the Netherlands, groundwater is the principle source of drinking water. Water treatment plant of Dorst (WTP Dorst) is one of the drinking water production plants in the Netherlands which make use of the groundwater with elevated As levels. The average As concentration in the source water of WTP Dorst is 12 µg/L. After the treatment, the effluent contains, at an average, 6 µg/L of As. The main goal of this research project was to develop an efficient As removal technology that could be able to produce drinking water with an As concentration of less than 1 µg/L when implemented at WTP Dorst. For this purpose, an innovative three step technique, Advanced Oxidation - Coagulation - Filtration (AOCF), has been investigated in this research through bench-scale and pilot scale experiments. AOCF is an innovative As removal technique, comprising of an advanced oxidation step to convert As(III) to As(V) with potassium permanganate (KMnO₄), followed by the sorption of As(V) onto/into the precipitating coagulations (flocs) formed after a suitable coagulant is added to the aqueous system and finally the removal of the floc-As matrix through granular media filtration.

Firstly, prior to the investigations on AOCF, the existing As removal at WTP Dorst was investigated. Secondly, through a series of bench-scale experiments, the optimum type of coagulant, its combination dose with the selected chemical oxidant (KMnO₄) and optimum process pH were determined. Eventually, the partially optimized technique from the bench-scale was implemented at the pilot scale physical model of WTP Dorst where AOCF was evaluated for As removal and its influence on the removal of other common undesirable groundwater constituents. The study has demonstrated that the existing mechanism of As removal at WTP Dorst is co-precipitation and adsorption with iron oxyhydroxides which are formed after the dissolved iron in raw water comes in contact with the atmospheric oxygen. Most of the As in the source water of WTP Dorst remains in reduced As(III) form after the cascade aeration treatment. However, after the water passes through the filter bed the entire fraction of As in the plant effluent becomes As(V). This rapid
oxidation of As(III) in the full scale filter bed may be due to the oxides of Fe and Mn, deposited over time on the filtration media grains. Iron chloride (FeCl₃) was the most appropriate coagulant for use in As removal from the source water of Dorst according to the bench scale tests. It showed an overall improved As removal efficiency than its competitors, i.e., FeSO₄ and alum, at all the pH values between 5 and 8.5. When chemical oxidation with KMnO₄ was combined with the FeCl₃ coagulation treatment i.e., in AOCF, significant increase in As removal was noticed and residual As levels lower than 1 µg/L were achieved. The AOCF technology has been found capable of consistently reducing effluent As concentrations to below 1 µg/L at pilot scale as well. The new technology could be easily implemented at the pilot scale physical model of WTP Dorst requiring only an addition of a chemical dosing setup. The natural pH of the source water of WTP Dorst has been found to be within the optimum range for achieving maximum As removal by AOCF. Two types of filtration media have been tested in this study, i.e., Virgin Sand media (VS media) and Metal Oxide Coated Sand media obtained from the full scale filters of WTP Dorst (MOCS media). Virgin sand media has shown a slight better As removal efficiency than MOCS media. The application of AOCF did not disturb the pre-existing removal efficiencies of common groundwater undesirable constituents e.g. Fe, Mn and NH₄⁺. However, a decrease in filter run times was noticed due to frequent Fe breakthrough problems. Optimisation of filter run times at pilot setup is therefore recommended before the implementation of AOCF at the full scale treatment process of Dorst. The decrease in filter run times is a commonly encountered operational issue in water treatment, especially when FeCl₃ is used for treatment. The double-layer (dual media) filtration with anthracite and fine sand as top and bottom media layers respectively should be evaluated at pilot scale.
Arseen (As) is een uiterst giftig element. Het is bekend dat As besmetting van drinkwaterbronnen in vele delen van de wereld veroorzaakt. De huidige toegestane grenswaarde voor As in drinkwater in de Europese Unie (EU), de Verenigde Staten van Amerika (US), Japan en vele andere hoge inkomenslanden is 10 µg/L. De World Health Organization (WHO) heeft een algemene regel dat geen enkele stof een hogere levensduur risico van meer dan 1 op 100 000 mag hebben. Echter, uit verschillende studies over de toxiciteit van As blijkt dat wanneer alleen wordt uitgegaan van de gezondheidseffecten de drinkwater As limiet van 10 µg/L onvoldoende is. Terugkijkend op de geschiedenis van de WHO aanbevelingen voor de maximaal toelaatbare niveaus, is er een geleidelijke verlaging van de maximaal toegestane As concentratie in drinkwater waargenomen sinds 1958, toen een maximale As concentratie van 200 µg/L werd voorgesteld, tot 1993, toen de Guidelines for Drinking Water Quality (GDWQ) een voorlopige limiet van 10 µg/L voorstelde. Sinds 1993, is de As grenswaarde in drinkwater van de WHO onveranderd gebleven. Tegenwoordig bestaat er een algemene consensus, indien mogelijk, As zo ver mogelijk te verwijderen onder 10 µg/L, niet alleen om de mensen te beschermen tegen de toxiciteit van As, maar ook voor toekomstige non-compliance gevallen wanneer de nationale normen verder verlaagd worden. De Amerikaanse Environmental Protection Agency (USEPA) en de Amerikaanse Natural Resources Defense Council (NRDC) hebben al aanbevolen om As onder 1 µg/L te houden om een aanvaardbare risico op kanker te bereiken.

In Nederland is grondwater in hoofdzaak de bron van drinkwater. Waterproductiebedrijf Dorst (Wpb Dorst) is een van de drinkwater productie-installaties in Nederland die gebruik maakt van grondwater met verhoogd Arseengehalte. De gemiddelde As concentratie in het grondwater van Wpb Dorst is 12 µg/L. Na behandeling bevat het effluent gemiddeld 6 µg/L As. Het belangrijkste doel van dit onderzoek was een efficiënte technologie voor de verwijdering van As te ontwikkelen die in staat is om drinkwater te produceren met een As concentratie minder dan 1 µg/L, na implementatie op Wpb Dorst. Om dit doel te bereiken is een innovatieve drie stappen techniek, Advanced Oxidation – Coagulation – Filtration (AOCF), onderzocht via bench-scale en pilot-scale experimenten. AOCF is een innovatieve As verwijderingstechniek, die een geavanceerde oxidatiestap omvat om As(III) naar As(V) te converteren met behulp van kaliumpermanganaat (KMnO4), gevolgd door sorptie van As(V) in de neerslaande vlokken die gevormd worden na toevoeging van een geschikt vlokmiddel (coagulant) aan het waterige systeem en tenslotte de verwijdering van de vlok - As matrix via granulaire media filtratie.

Eerst werd, voorafgaand aan het onderzoek naar AOCF, de bestaande As verwijdering op Wpb Dorst onderzocht. Vervolgens werd, door een reeks van bench-scale experimenten, het optimale type vlokmiddel, de dosering ten opzichte van het geselecteerde chemische oxidatiemiddel (KMnO4) en de optimale proces pH bepaald. Uiteindelijk werd de gedeeltelijk geoptimaliseerde techniek uit de bench-scale geïmplementeerd in het pilot-scale fysisch model van Wpb Dorst waar AOCF werd geëvalueerd op het verwijderen van As en de invloed op de verwijdering van andere voorkomende ongewenste grondwater bestanddelen. De studie heeft aangetoond dat het bestaande mechanisme van As verwijdering op Wpb Dorst co-precipitatie en adsorptie met ijzer oxyhydroxides is die worden gevormd nadat het opgeloste ijzer in het
ruwe water in contact komt met de zuurstof in de lucht. Het merendeel van het As in het grondwater van Wpb Dorst blijft in de gereduceerde As(III) vorm na de beluchtingstap in de cascade. Na passage van het filterbed is de gehele fractie As in het effluent dat het wpb verlaat omgezet in As (V). Deze snelle oxidatie van As(III) in full scale filterbed komt waarschijnlijk door de oxiden van Fe en Mn, die zich in de loop van de tijd hebben afgezet op de korrels van het filtermedium. IJzerchloride (FeCl₃) was het meest geschikte vlokmiddel voor het verwijderen van As uit het grondwater van Wpb Dorst volgens de grootschalige proeven. Het toonde een algeheel betere As verwijdering dan de concurrenten, FeSO₄ en alum, bij alle pH-waarden tussen 5 en 8,5. Bij combinatie van chemische oxidatie met KMnO₄ en FeCl₃ coagulatiebehandeling in AOCF, werd een significante toename in As verwijdering waargenomen met als resultaat rest As gehalten lager dan 1 µg/L. Met de AOCF technologie is het mogelijk om in het effluent consequent As concentraties van minder dan 1 µg/L op pilot-scale te bereiken. De nieuwe technologie kan gemakkelijk in het pilot-scale fysisch model van Wpb Dorst geïmplementeerd worden waarbij slechts een chemicaliën doseerinstallatie geïnstalleerd hoeft te worden. De normale pH van het grondwater van Wpb Dorst ligt binnen de optimale range voor het bereiken van maximale As verwijdering door AOCF. Twee soorten van filtratie media zijn in deze studie getest, te weten schoon filterzand (VS media) en filterzand met een laagje metaloxide dat gehaald werd uit de grote schaal filters van Wpb Dorst (MOCS media). Schoon filterzand geeft een iets betere As verwijdering dan MOCS media. De toepassing van AOCF heeft het bestaande verwijderingrendement van andere ongewenste stoffen zoals Fe, Mn en NH₄⁺ niet beïnvloed. Echter, een daling van de filter looptijden trad op als gevolg van frequente ijzerdoorslag. Optimalisatie van filterlooptijden bij proefopstelling wordt daarom aanbevolen vóór de implementatie van AOCF op het full scale behandeling proceess van Wpb Dorst. De daling van de filterlooptijden is een veel voorkomend operationeel probleem in waterbehandeling, in het bijzonder wanneer FeCl₃ wordt gebruikt voor behandeling. De dubbellaag (dual media) filtratie met antraciet en fijn zand als bovenste en onderste laag dient te worden geëvalueerd op pilot-scale.
SUMMARY IN SWEDISH

Arsenik (As) är ett mycket giftig element. Det har rapporterats orsaka förorening av dricksvättern i många delar av världen. Den nuvarande dricksvatten tillåtna gränsen i Europeiska unionen (EU), Förenta staterna (USA), Japan och många andra höginkomstländer är 10 µg/L. Världshälsoorganisationen (WHO) har en allmän regel att inget av ämnet kan ha en högre risk än 1 av 100 000 över en livslängd. Men flera studier om arsenikens toxicitet tyder på att 10 µg/L baserad på hälsoeffekter inte är tillräcklig. Ser man tillbaka på historien om WHO ’s rekommendationer för högsta tillåtna halter, kan en gradvis sänkning av högsta tillåtna koncentration i dricksvatten observeras sedan 1958, när maximal koncentration om 200 µg/L föreslogs, till 1993, då Guide Lines for Drinking Water Quality (GDWQ) rekommenderade 10 µg/L som en provisorisk gräns. Sedan 1993 har denna rekommendation varit oförändrad. Idag finns det en allmän enighet om att, om möjligt, är det nödvändigt att avlägsna As så långt som möjligt under 10 µg/L, inte bara för att undvika hälsorisker för människor, men också för att undvika framtidiga brister i nationella standarder och därmed att sänkas ytterligare. US Environmental Protection Agency (USEPA) och det amerikanska Natural Resources Defense Council (NRDC) har redan rekommenderat riktlinjer under 1 µg/L för att uppnå en acceptabel cancerrisk över en livstid.

I Nederländerna är grundvatten den huvudsakliga källan för dricksvatten. Vattenverket i Dorst (WTP Dorst) är en av de produktionsanläggningar i Nederländerna som utnyttjar ett grundvatten med förhöjda As halter. Den genomsnittliga koncentrationen i råvattnet i WTP Dorst är 12 µg/L. Efter behandlingen innehåller renvattnet en genomsnittlig halt på 6 µg/L As. Det huvudsakliga målet för detta forskningsprojekt har varit att utveckla en effektiv rening som skulle kunna producera ett dricksvatten med en koncentration under 1 µg/L när det införs på WTP Dorst. För detta ändamål har en innovativ trestepsteknik, Advanced Oxidation - Coagulation - Filtration (AOCF), undersökt i bänk och pilotskala. AOCF är en innovativ reningsteknik, som består av ett avancerat oxidationssteg för att konvertera As(III) till As(V) med kaliumpermanganat (KMnO₄), följt av sorption av As(V) på utfällda flockar efter det att ett lämpligt koaguleringsmedel tillsatts till vattnet och slutligen avlägsnandet av flockarna som innehåller As genom filtering. Innan studierna av AOCF undersöks den befintliga reningstekniken på WTP Dorst. Sedan fastställdes, genom en serie bänkskaleexperiment, den optimala typen av koagulant, dess dos kombinerad med det valda oxidationsmedlet (KMnO₄) samt optimalt pH för processen. Så genomfördes den delvis optimerade tekniken i pilotskala vid WTP Dorst då AOCF också utvärderades med avseende på avlägsnandet av andra vanliga oönskade komponenter. Den nuvarande reningstekniken utgörs av medfällning på Fe-oxyhydroxider bildade efter luftning av vattnet. Stordelen av As(III) i råvattnet kvarstod som As(III) trohållandet av As(V) i råvattnet, trots kaskadluftning av vattnet. Men sedan vattnet passerat genom filterbaden hade all As(III) oxidaterats till As(V). Denna snabba oxidation av As (III) i fullskala i filterbaden kan bero på oxiderna av Fe och Mn, som deponerats över tiden på kornen i filtrermediet. Järnchlorid (FeCl₃) var det mest lämpliga koaguleringsmedlet för avlägsnandet av As i råvattnet i Dorst enligt bänkskaleexperimenten. Den visade en genomgående förbättrad reningseffekt än andra tänkbara kemikalier t ex FeSO₄ och alun vid alla pH-värden mellan 5 och 8,5. När kemisk oxidation med KMnO₄ kombinerades med FeCl₃ koagulation i AOCF tekniken observerades en påtaglig ökning av
reningseffekten och halter lägre än 1 µg/L uppnåddes. AOCF tekniken har visat sig kapabel att genomgående minska halten i renvattnet under 1 µg/L även i pilotskala. Den nya tekniken kan lätt införas i pilotskala vid WTP Dorst då den endast kräver införandet av ett doseringssteg. Det naturliga pH-värdet i råvattnet vid WTP Dorst har befunnits vara inom det optimala området för att uppnå maximal rening med AOCF. Två filtermaterial har testats i denna studie, Virgin Sand media (VS media) och Metal Oxide Coated Sand som erhållits från fullskalfilter vid WTP Dorst (MOCS media). Virgin Sand media har visat en något bättre reningseffekt än MOCS media. Införandet av AOCF störde inte den redan existerande avskiljningen av vanliga föroreningar, t.ex. Fe, Mn och NH₄⁺. Dock konstaterades en minskning i filtrens livslängd på grund av genombrott av Fe. Optimering av filtrens livslängd rekommenderas därför innan AOCF införs i fullskala vid Dorst. Minskning av filterlivslängd är vanligt förekommande vid vattenbehandling, särskilt när FeCl₃ används i processen. En dubbel-lager filtrering (dual media) med antracit och fin sand som topp-respektive bottenmedia bör utvärderas i pilotskala.
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The work presented in this document would not have been possible without my close association with many people who were always there when I needed them. I take this opportunity to acknowledge them and extend my sincere gratitude for helping me make this thesis a possibility. Completing this research project was probably the most challenging task of my academic career. It has been a great privilege to spend excellent time in Brabant Water - Netherlands for the sake of this research project. The continuous support from KTH-International Groundwater Arsenic Research Group (GARG) throughout this research was remarkable.

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I express my heart-felt gratitude to Jink Gude for his constant motivation and support during the course of my thesis. I enjoyed the personal discussions with him and the time I spent with him at Dorst and in Breda. I am a fan of his energy during work, critical thinking and innovative nature. I wish him success for his upcoming PhD studies at TU Delft and I know he is going to be a famous arsenic consultant soon. Please don’t forget me then Jink...

My sincere thanks to Tim van Dijk for being with me through out. His scientific inputs, personal helps and friendly nature has always made me feel at ease with him and I could always look back on him for any support during my course of research. I made at least one million phone calls to him asking for help and was always entertained.
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Finally, Jazbah, my wife, thanks for being a part of my life. You have so many good things in you that I would require at least one hundred pages to write about you – so I stop here.
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<tr>
<td>AOCF</td>
<td>Advanced Oxidation Coagulation Filtration</td>
</tr>
<tr>
<td>AF</td>
<td>After-Filtration sampling point</td>
</tr>
<tr>
<td>BW</td>
<td>Brabant Water</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
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<tr>
<td>IARC</td>
<td>International Agency of Research on Cancer</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma - Mass Spectrometry</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma - Atomic Emission Spectroscopy</td>
</tr>
<tr>
<td>IOCS</td>
<td>Iron Oxide Coated Sand</td>
</tr>
<tr>
<td>GDWQ</td>
<td>Guidelines of Drinking Water Quality</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density Poly-Ethylene</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>IN</td>
<td>Inlet sampling point</td>
</tr>
<tr>
<td>ORP</td>
<td>Oxidation Reduction Potential</td>
</tr>
<tr>
<td>PZC</td>
<td>Pint of Zero Charge</td>
</tr>
<tr>
<td>PF</td>
<td>Pre-Filtration sampling point</td>
</tr>
<tr>
<td>MGS</td>
<td>Manganese Green Sand</td>
</tr>
<tr>
<td>MOCS</td>
<td>Metal Oxide Coated Sand</td>
</tr>
<tr>
<td>NF</td>
<td>Nano-Filtration</td>
</tr>
<tr>
<td>S-OH</td>
<td>Neutral Surface Hydroxyl Group</td>
</tr>
<tr>
<td>S-OH&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Positively charged surface hydroxyl group</td>
</tr>
<tr>
<td>S-O&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Negatively charged surface hydroxyl group</td>
</tr>
<tr>
<td>USEPA</td>
<td>Environmental Protection Agency of United States</td>
</tr>
<tr>
<td>UN</td>
<td>United Nations</td>
</tr>
<tr>
<td>UF</td>
<td>Ultra-Filtration</td>
</tr>
<tr>
<td>VS</td>
<td>Virgin Sand</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WTP</td>
<td>Water Treatment Plant</td>
</tr>
</tbody>
</table>
ABSTRACT

Arsenic is an extremely poisonous element. It has been reported to cause contamination of drinking water sources in many parts of the world. The current drinking water permissible limit for arsenic in the European Union is 10 μg/L. The World Health Organization has a general rule that no substance may have a higher lifetime risk of more than 1 in 100,000. However, several studies on toxicity of arsenic suggest that purely based on health effects the arsenic limit of 10 μg/L is not sufficient. The main goal of this research was to develop an efficient arsenic removal technology that could be able to produce drinking water with an arsenic concentration of less than 1 μg/L. For this purpose, an innovative three step technique, Advanced Oxidation - Coagulation - Filtration (AOCF), was investigated through bench-scale and pilot scale experiments in the Netherlands at the water treatment plant of Dorst. Firstly, prior to the investigations on AOCF, the existing arsenic removal at the water treatment plant was investigated. Secondly, through a series of bench-scale experiments, the optimum type of coagulant, its combination dose with the selected chemical oxidant and optimum process pH were determined. Eventually, the partially optimized technique from the bench-scale was implemented at the pilot scale physical model of water treatment plant Dorst where AOCF was evaluated for arsenic removal and its effect on the removal of other common undesirable groundwater constituents. The optimized AOCF technology consistently removed arsenic from groundwater to below 1 μg/L when implemented at pilot scale. The overall effluent quality also remained acceptable. The method is efficient with both types of filtration media tested in this research i.e., virgin sand and metal oxide coated sand, however virgin sand media showed slightly better arsenic removal efficiency.

Key words: Arsenic removal; Coagulation; Drinking water treatment; Iron removal; Potassium permanganate (KMnO₄); Ferric chloride (FeCl₃)

1. INTRODUCTION

1.1 General

Groundwater is the world’s most extracted raw material. Presently approximately 2 billion people rely on groundwater as the only source for drinking water (Buamah, 2009). Groundwater aquifers are generally much less vulnerable to anthropogenic pollution than surface water bodies; however, natural weathering of aquifer matrix may release organic and inorganic substances which in combination with large storage and long residence times can cause persistent contamination of groundwater resources. Arsenic (As) is an extremely poisonous element which occurs ubiquitously in the earth’s crust and has been reported to cause contamination of drinking water sources in many parts of the world, including (but not limited to) Bangladesh, India, Netherlands, China and United States of America (USA). World Health Organization (WHO) estimated in 2001 that about 130 million people worldwide were exposed to elevated As concentrations which were attributed primarily to drinking of As laden water. For a human body As is toxic both in high and low concentrations. Prolonged consumption of trace As concentrations has been reported to cause both carcinogenic and non-carcinogenic health disorders (Tseng et al., 2000; Gosh et al., 2007). For this reason, As levels in drinking water are regulated on a world-wide level and optimizing treatment technologies for As containing source
waters is currently of great urgency and high priority in many countries, including the Netherlands. In the Netherlands, groundwater is the principle source of drinking water; about two-thirds of the country obtains its drinking water supply from groundwater. The groundwater sources used for the production of drinking water contain As concentrations in the range of 0.1-70 µg/L (Stuyfzand et al., 2008). The groundwater treatment processes adequately reduce As to below the European Union’s (EU’s) maximum permissible limit (10 µg/L) and the treatment plant effluents across the country contain As in the range of 0.1 to 7 µg/L (Stuyfzand et al., 2008). Water treatment plant of Dorst (WTP Dorst) is one of the drinking water production plants in the Netherlands which make use of the groundwater with elevated As levels. The average As concentration in the source water of WTP Dorst is 12 µg/L. After the treatment, the effluent contains, at an average, 6 µg/L of As. Although the average effluent As concentration at WTP Dorst is well below the EU’s drinking water As standard and WHO’s currently suggested provisional guideline value, it does not comply with the Brabant Water’s self-established stringent As standard of 5 µg/L. Therefore, the primary motivation for initiating this research project was to optimise the As removal at WTP Dorst so that the effluent As concentration could meet BW’s criteria of drinking water quality.

Arsenic is a very toxic substance. Looking back at the history of WHO’s recommendations for maximum permissible levels, a gradual lowering of maximum allowable As concentration in drinking water can be observed since 1958, when maximum As concentration of 200 µg/L was suggested, till 1993, when the Guidelines for Drinking water Quality (GDWQ) recommended 10 µg/L in a provisional definition. The legislative drop in the maximum permissible drinking water As concentration depends upon technological developments in two principle areas; 1) measurement and quantification and 2) removal processes. In the past decade (after 1993), marked developments in both these areas have been made which strongly indicate that another revision in drinking water As guidelines by WHO in near future may be expected, which will of course affect the world-wide As standards. The WHO has a general rule that no substance may have a higher lifetime risk of more than 1 in 100,000. However, several studies on toxicity of arsenic suggest that purely based on health effects the drinking water arsenic limit of 10 µg/L may not be sufficient. Thus, today there exists a general consensus that, if possible, it is necessary to remove As as far as possible, not only for the safety of human health from the toxicity of As, but also for avoiding future non-compliance issues. The US Environmental Protection Agency (USEPA, 1998) and the US Natural Resources Defense Council (NRDC, 2000) has already recommended arsenic guidelines below 1 µg/L to attain an acceptable lifetime cancer risk. Therefore, in this research achieving residual As concentrations of lower than 1 µg/L was set as a target so that the expected future lowering of drinking water As standard in the Netherlands, even to very low levels, could be accommodated.

Advanced Oxidation - Coagulation - Filtration (AOCF) is an innovative As removal technique, comprising an advanced oxidation step to convert As(III) to As(V) with potassium permanganate (KMnO₄), followed by the sorption of As(V) onto/into the precipitating coagulates (flocs) formed after a suitable coagulant is added to the aqueous system and finally the removal of the floc-As matrix through granular media filtration. In this research AOCF is evaluated for As removal efficiency and optimised for application to the treatment process at WTP Dorst.
KMnO₄ is generally used in water industry to control taste and odors, remove color, control biological growth in treatment plants, and sometimes to remove iron (Fe) and manganese (Mn) when relatively high concentrations of these elements are encountered. Specifically for the oxidation and subsequent removal of As(III), the combination of KMnO₄ and a suitable coagulant has not been evaluated extensively. Recently, KMnO₄ - FeSO₄ and KMnO₄ - FeCl₃ treatment methods have been studied by Guan et al. (2009) and Bordoloi et al. (2013) respectively, however their studies remained confined to laboratory scale or small scale decentralized field systems which did not provide guidance regarding the large scale centralized application of this method and its influence on the removal of other commonly encountered undesirable groundwater constituents.

1.2 Research objectives

The main goal of this research was to develop an efficient As removal technology that could be easily integrated and implemented with the existing treatment process of WTP Dorst so that the new system could be able to produce drinking water with an As concentration of less than 1 µg/L. For this purpose, AOCF technique was investigated through bench-scale and pilot scale experiments. Within the broader scope of evaluating and optimizing the AOCF, certain sub-goals were identified which included the following.

1. To investigate the existing As removal processes at WTP Dorst.
2. To determine at bench-scale the optimum coagulant type for use in Dorst, the optimum Oxidant – Coagulant combination dose and the optimum process pH for AOCF.
3. To investigate at pilot scale:
   - The start-up of As, Fe, Mn and ammonium (NH₄⁺) removal in conventional rapid sand filters.
   - The As removal efficiency of AOCF with Virgin Sand media (VS media) and Metal Oxide Coated Sand media (MOCS media).
   - The effect of AOCF on conventional Fe, Mn and NH₄⁺ removal processes.

2. LITERATURE REVIEW

2.1 Occurrence and global circulation of arsenic

Arsenic, a naturally occurring metalloid, is the 20th most abundant element in earth’s crust. It has an atomic weight of 74.92 g/mol. The average As concentration in the upper crust of earth is estimated at approximately 6 mg per kg of crust material (Sevil, 2005). Arsenic is found in at least 200 different mineral forms including sulfides and sulfosalt, and as minor amounts of arsenides, arsenates, oxides, and silicates (Greenwood and Earnshaw, 1989; Bissen and Frimmel, 2003). Some of the As bearing minerals include arsenopyrite (FeAsS), realgar (As₄S₃), orpiment (As₂S₃), arsenolite (As₂O₃), loelengite (FeAs₂), nicoelite (NiAs), safflorite (CoAs), enargite (Cu₃AsS₄), cobaltitite (CoAsS) and glaucodote ((Co,Fe)₃AsS) (Greenwood and Earnshaw, 1989; Bissen and Frimmel, 2003; Thirunavukkarasu et al., 2005). Typical As concentrations in crustal rocks (Jacks and Bhattacharia, 1998) are presented (Table 2-1). In sea water, the concentration of As varies between 0.09 µg/L and 24 µg/L, and in freshwaters between 0.15 µg/L and 0.45 µg/L, having maximum value of 1 mg/L (Sevil, 2005).

Arsenic is one of the most important mobile elements in the environment. It readily changes its oxidation states through chemical or
biological reactions which are common in the natural environments. From its origin in the bed rock, inorganic As enters into the soil where its average concentration depends upon various factors such as the type of parent rock, anthropogenic activities, local climate, forms or speciation, and redox conditions of the soil and water (Yan Shu, 1994). The principal mechanism of As release from the rocks and soil to the environment is weathering, depending upon the redox environments. Further, the main mode of transport of As in the environment is either by dissolution in rain, river or groundwater or with dust particles through air. Volatile forms of As enter the atmosphere from land and water and then they are returned to soils and sediments by precipitation processes e.g rain and snow. When, somehow, anaerobic and further anoxic conditions develop, the oxidized forms of As are reduced to sulfides in soils and sediments and become immobile again (Pontius et al., 1994).

Apart from the natural processes, anthropogenic activities are also responsible for the release of As to the environment (Nadakavukaren et al., 1984; Hindmarsh & McCurdy, 1986; Bhattachariya et al., 2007). For example, waste streams from metallurgical industry, glass and ceramic industries, dye and pesticide manufacturing industries, petroleum refining, rare earth industry and other organic and inorganic chemical industries have been reported to be the major anthropogenic sources of As (Mudhoo et al., 2011). Other industries which may introduce As to the environment include wood preservative, lead shot manufacturing, phosphate detergent industry and fertilizer manufacturers (Banerjee et al., 1999; Viraraghavan et al., 1999; Smedley, 2006). Mining activities and smelters also discharge As rich wastes into natural environments (Bissen and Frimmel, 2003; Smedley, 2006). Burning of fossil fuels in the household and power plants may also be considered as a source of As pollution. A concept (adopted from Bumbla and Keefer, 1994; Shih, 2005) of As circulation among different elements of the environment i.e., land, air, and water, is presented (Fig. 2-1). It is commonly believed that the toxicity of As(III) is much higher than that of As(V) (Castrode Esparza, 2006). As(III) mainly occurs in reducing environments such as in deep groundwaters or wastewaters devoid of oxygen and As(V) in oxidized systems such as surface waters or aerated groundwater streams.

The molecular structures of common organic and inorganic As compounds are presented (Fig. 2-2).

---

**Figure 2-1: As cycling in the environment (Bumbla and Keefer, 1994).**
The speciation of As is principally controlled by the oxidation state. Within a particular oxidation state pH controls the nature of species (Masscheleyn et al., 1999; Bose and Sharma, 2002). The reactions among different As species with their Log K values are provided (Table 2-2). These reactions can be used to construct an Eh - pH stability diagram (Fig. 2-3) for dissolved As species (Appelo and Postma, 2005). As(V) predominates in oxic water (e.g. surface water) and depending upon the pH value, can exist as H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻ and / or AsO₄³⁻. In the pH range of 6-9, HAsO₄²⁻ and H₂AsO₄⁺ dominate with relatively low concentration of AsO₄³⁻ (Fig. 2-5). Below pH 6, H₂AsO₄⁻ and H₃AsO₄ dominate whiles above pH 9 only AsO₄³⁻ mostly occurs (Fig. 2-5). As(III) is the dominant species under reducing conditions, and therefore it is the principal form of As in groundwater (Fig. 2-3). Depending upon the groundwater pH, the As(III) can exist as H₃AsO₃ and / or H₂AsO₃⁻. Below pH 9, H₂AsO₃⁻ is the dominant species whereas H₃AsO₄ and H₂AsO₄⁻ dominate above pH 9 (Fig. 2-4) (Ferguson and Gavis, 1972; Sracek et al., 2001). It is however noted, both the As(V) and As(III) forms occur in both oxic and reducing conditions due to the slow oxidation and reduction kinetics (Edwards, 1994; AWWARF, 2000; Kim et al., 2000; Stollenwerk, 2003).

**Table 2-1: Natural abundance of As in crustal materials.**

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Arsenic concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Igneous rocks</strong></td>
<td></td>
</tr>
<tr>
<td>Ultrabasic</td>
<td>0.3 - 16</td>
</tr>
<tr>
<td>Basalts</td>
<td>0.06 - 113</td>
</tr>
<tr>
<td>Andesites</td>
<td>0.5 - 5.8</td>
</tr>
<tr>
<td>Granites</td>
<td>0.2 - 13.8</td>
</tr>
<tr>
<td><strong>Sedimentary rock</strong></td>
<td></td>
</tr>
<tr>
<td>Shales and clays</td>
<td>0.3 - 490</td>
</tr>
<tr>
<td>Phosphorites</td>
<td>0.4 - 188</td>
</tr>
<tr>
<td>Sandstones</td>
<td>0.6 - 120</td>
</tr>
<tr>
<td>Limestones</td>
<td>0.1 - 20</td>
</tr>
<tr>
<td><strong>Coal</strong></td>
<td></td>
</tr>
<tr>
<td>Bituminous</td>
<td>9 ± 0.8</td>
</tr>
<tr>
<td>Lignites</td>
<td>7.4 ± 1.4</td>
</tr>
<tr>
<td>Peat</td>
<td>16 - 340</td>
</tr>
</tbody>
</table>

Source: Jacks and Bhattacharya (1998).
<table>
<thead>
<tr>
<th>Arsenic specie</th>
<th>Reaction</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$</td>
<td>-6.76</td>
</tr>
<tr>
<td>As(III)</td>
<td>$H_2AsO_3^- \leftrightarrow H_2AsO_4^- + H^+$</td>
<td>-9.23</td>
</tr>
<tr>
<td>As(V)/As(III)</td>
<td>$H_2AsO_3^- \leftrightarrow H_2AsO_4^- + H^+$</td>
<td>-21.14</td>
</tr>
</tbody>
</table>

Source: Appelo and Postma (2005)

### 2.2 Arsenic contamination of groundwater

Both natural and man-made sources have been identified to be responsible for the introduction of As into groundwater sources. In Poland, Korea and in Brazil, As contamination of groundwater due to anthropogenic mining activities have been reported (Marszalek and Wasik, 2000; Woo and Choi, 2001; Borba et al., 2003). In contrast, in some parts of Turkey elevated As in groundwater is attributed to natural geothermal factors (Gunduz et al., 2009) and in Bangladesh geogenic sources are considered major cause of large scale As contamination. Over the last decade a significant amount of research has been dedicated to understand the underlying mechanisms which are responsible for naturally caused (geogenic) elevated As levels in groundwater. Several theories have been proposed in this context; however, there is still a limited understanding of all the active processes. It is known, that the occurrence of As in groundwater is mainly controlled by iron (Fe) oxide and sulfide dominated minerals. Iron oxides have the ability to bind As onto their surface, whereas sulphide minerals take up As into their structure. Iron oxides are generally formed in oxic conditions and dissolved in an anaerobic environment, while sulfide minerals are generally stable in anaerobic conditions and break down by oxidation (Ravenscroft et al., 2009). As long as Fe-oxides or sulphide minerals are present in the aquifers, As can be immobilized under either oxidizing or reducing conditions, for example, by sub-surface As immobilization technique which will be discussed later in this study. The processes involved in underground As mobilization vary from one place to another depending upon the hydrogeochemical conditions of the soil environment. Based on the wide range of literature focused on As contamination, Ravenscroft et al. (2009) distinguished four principle mechanisms which are believed to control the mobility of As in groundwater. These mechanisms include: reductive dissolution, alkali desorption, sulphide oxidation, and mobilization under the influence of geothermal factors.

### 2.3 Arsenic mobilization processes

#### 2.3.1 Reductive dissolution

Reductive dissolution mobilizes As by the reduction of solid Fe-oxides so that both the aqueous Fe(II) and As(III) are released into the solution. Many Fe-oxide minerals are commonly found in groundwater aquifers, for example, ferrihydrite ($5Fe_2O_3.9H_2O$), goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH) and hematite (Appelo and Postma, 1994). The mobilization process of As takes place due to the gradual depletion of oxygen in an aquifer. Bacterial decomposition of organic matter consumes all the available oxygen which is followed by a well-defined sequence of reactions, going from $O_2$ reduction, $NO_3$ reduction and reduction of manganese oxides to the reduction of Fe-oxides. The overall reductive dissolution of Fe-oxides in an aqueous environment is represented (Eq. 2.1).
After the reduction of Fe-oxides, reaction continuous towards sulphate reduction and methanogenesis. The reduction of As(V) is expected to occur between the reduction of Fe(III) and sulphates (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). Reductive dissolution of As-bearing sediments is supposed to be the primary reason of As contamination of the aquifers in the Bengal Delta Basin, Northern China, Vietnam and Cambodia (Bhattacharya et al., 1997, 2002, 2010; Smedley et al., 2003; Buschmann et al., 2007; Buschmann et al., 2008).

\[
4\text{Fe(OH)}_3(s) + CH_2O + 7\text{H}^+ \leftrightarrow 4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{HCO}_3^- \quad (2.1)
\]

The groundwaters dominated by reductive dissolution are characterised by the presence of As(III) and are always strongly reducing with a near-neutral pH. Other indicators are high concentrations of Fe, Mn and ammonium (NH\textsubscript{4}\textsuperscript{+}), a high alkalinity and possibly a high dissolved organic carbon (DOC). Nitrates and sulphates, however, are nearly absent (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009).

### 2.3.2 Alkaline desorption

In aerobic groundwaters (phreatic aquifers) when conditions are acidic to near-neutral, As(V) is strongly adsorbed by Fe-oxide minerals. However, when the pH increases (≥8) As(V) starts to desorb from the Fe-oxide surfaces and the groundwater becomes contaminated with As. At pH values above 9, significant desorption of As(V) is expected because of the decreased electrostatic attraction between the Fe-oxide surface and the charged As(V) species. Actually, the point of zero charge (PZC) of Fe-oxides occurs below pH 9 and the net surface charge of the oxide becomes negative above the PZC. The uptake of protons by mineral weathering and ion-exchange reactions in combination with evaporation can possibly be the trigger for the rise in pH (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009). If the water produces sulphates or nitrates in the presence of dissolved oxygen, pH may rise as well. Besides a high pH, other indicators of alkaline desorption are an increased salinity and possibly high concentrations of fluorine, uranium, boron, selenium and molybdenum, while concentrations of Fe and Mn remain generally low (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009).
2.3.3 Sulphide oxidation

Arsenic mobilization can also occur when As bearing sulphide minerals, for example pyrite, are exposed to oxygen as a result of a lowered groundwater table due to heavy withdrawal of water. For example, during mining activities large quantities of groundwater are pumped out in order to lower the water table which exposes As-bearing sulphide minerals to aerated conditions. Subsequently, As contamination of groundwater occurs during the post-mining groundwater rebound (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009). The oxidation reactions of Fe-sulphide minerals are presented (Eqs. 2.2 and 2.3). Smedley and Kinniburgh (2002) has listed many cases of As contamination of groundwaters due to mining activities, which include cases from Canada, Germany, Ghana, Greece, Mexico, South Africa, United Kingdom (UK), USA and Zimbabwe. Another situation where sulphide oxidation can generate high concentrations of As is when agricultural nitrate oxidizes a pyritiferous aquifer.

\[
\begin{align*}
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \tag{2.2} \\
4\text{FeAsS} + 11\text{O}_2 + 6\text{H}_2\text{O} & \rightarrow 4\text{Fe}^{2+} + 4\text{H}_3\text{AsO}_3 + 4\text{SO}_4^{2-} \tag{2.3}
\end{align*}
\]

Groundwaters influenced by sulphide oxidation are typically acidic (pH 1-6) and contain high concentrations of sulphates and, but not necessarily, Fe. Other trace metals like copper, nickel, lead, zinc, aluminum, cobalt, and cadmium might also be present (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009).

Figures 2-4 (up) & 2-5 (down): Percentage of As(III) and As(V) species at different pH (Wilson et al., 2003; USEPA, 2005).
Geothermal influence

Groundwater may also get elevated As concentrations when geothermally influenced water streams, for example from active volcanic areas, enter into the groundwater aquifers. It has been reported that the volcanism in the Andes mountain range has lead to the As contamination of groundwater in Chile and Argentina (Smedley and Kinniburgh, 2002). Arsenic associated with geothermal waters has also been reported in many other parts of the world such as in USA, Japan, New Zealand, Chile, Iceland, France etc. (Welch et al 1988; Criaud and Fouillac 1989; Nimick et al., 1998; Wilkie and Hering, 1998). The geothermally influenced waters usually have an increased salinity with high concentrations of chloride and sodium. Other indicators may be high concentrations of boron, lithium, fluorine, silica and a pH higher than 7 (Smedley and Kinniburgh, 2002).

Arsenic exposure and related health effects

Arsenic toxicity strongly depends upon the chemical form in which As is present in water. Inorganic As compounds in which As occurs as As(III) are known to be the most toxic (Castrode Esparza, 2006). According to Pontius et al. (1994), the toxicity scale of As can be presented in the decreasing order from arsine to elemental As (Eq. 2.4):

\[
\text{Arsine} > \text{Inorganic As(III)} > \text{Organic As(III)} > \text{Inorganic As(V)} > \text{Organic As(V)} > \text{Elemental As}
\]

Generally, the toxicity of a compound is measured in terms of its oral LD50 (Lethal Dose 50 %) value, which is the number of milligrams of the compound per kilogram of the body weight that will result within a few days in the death of half of those who ingest that compound in a single dose. Table 2-3 shows the amount of various As compounds per kilogram of body weight required to reach LD50 (Chappell et al., 1999). It is clear that the oral LD50 values for As(III) bearing compounds are significantly less than As(V) compounds and As compounds of organic nature.

Exposure to high levels of As concentrations as shown (Table 2-3) at once is very unlikely, unless deliberated. However, long term exposure to very low As concentrations through drinking of contaminated water may pose serious health related risks. Chronic As ingestion has been found to cause carcinogenic and non-carcinogenic health effects in humans. For example, it has been reported that long-term chronic exposure to As increases health risks related to conjunctivitis (Kapaj et al., 2006; Baydya et al., 2006), skin cancers (Ghosh et al., 2007), internal cancers, diabetes (Tseng et al., 2000), vascular problems (Tseng et al., 1996 & 2003) and reproductive effects (Mukhejee et al., 2003; Tseng, 2003; Buschmann et al., 2008; Florea et al., 2005; Mead, 2005). How rapidly the symptoms develop depends on various factors such as the overall water quality and daily water intake. The As contaminated water, if used for cooking and irrigating crops, can pose a significant health risk as well since crops and foods can take up As from the water. There is no medical treatment of arsenicosis (collective symptoms caused by chronic arsenic poisoning) and the only prevention is to stop ingesting it (Johnston and Heijnen, 2001).

Arsenic poisoning of drinking water – a global issue

Arsenic contamination of drinking water sources is a worldwide problem. Many countries around the world are currently facing this threatening situation. In 2001, WHO estimated that about 130 million
people worldwide were exposed to As concentrations above 50 µg/L. The most serious case of As poisoning through drinking water is currently ongoing in Bangladesh where reductive dissolution of young As-bearing sediments is considered as the major cause for the large-scale As contamination (van Halem, 2011). Countries (and continents) with reported cases of As contamination has been indicated (Table 2-4 and Fig. 2-6).

Before the recent discovery (1990s) of As contamination of groundwater in Bangladesh, As was not routinely analysed when groundwater was used as a drinking water source (Petrusevski et al., 2007). However, with growing international awareness regarding the health effects of drinking As contaminated water, the acceptable As levels in drinking water have become more stringent, therefore As levels from source to effluent are regularly monitored. It is expected that As in drinking water will be an increasing problem in coming years, and that new countries may be identified as having an As problem.

2.6 Worldwide accepted drinking water arsenic levels

2.6.1 The stance of WHO

Drinking water standards in many countries are specified by governmental organizations and legislative documents prepared for ensuring the safety of human health. For example, the European Drinking Water Directive and the USEPA establishes safe drinking water standards. WHO is a specialized agency of the United Nations (UN) which is concerned with international public health. WHO plays a vital role in the international context since the WHO’s recommended drinking water guidelines are sometimes adopted by its member states (194 member states in total). Especially for developing countries with inadequate legislative or administrative framework for such standards, the WHO’s published guidelines on the standards are of much importance. WHO has had a public position on As in drinking water since 1958. In 1958, WHO published the first version of “International Standards for Drinking Water” which included As in the category of toxic substances and an allowable concentration of 200 µg/L was established (WHO, 2011b). In 1963, an updated version of the International Standards for Drinking Water came forward which kept As in the same category of toxic substances, however, a stricter concentration of 50 µg/L was established (WHO, 2011b). In 1971, another updated document of International Standards was published which kept As in the category of toxic substances and reaffirmed the limit of 50 µg/L (WHO, 1971). The permissible limit of 50 µg/L was supported with the observations in Latin American countries where figures higher than 50 µg/L were found, were not known to have caused problems for human health (WHO, 2011b).

Table 2-3: Acute toxicity of different As compounds.

<table>
<thead>
<tr>
<th>Arsenic compound</th>
<th>Oral LD50 (mg/kg body weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Arsenite</td>
<td>15 - 40</td>
</tr>
<tr>
<td>Arsenic Trioxide</td>
<td>34</td>
</tr>
<tr>
<td>Calcium arsenate</td>
<td>20 - 800</td>
</tr>
<tr>
<td>Arsenobetane</td>
<td>&gt;10,000</td>
</tr>
</tbody>
</table>

Source: Chappell et al. (1999).
Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic

Table 2-4: List of As affected countries of the world.

<table>
<thead>
<tr>
<th>Region</th>
<th>Countries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asia</td>
<td>Bangladesh, Pakistan, Comorbia, China, Taiwan, India, Iran, Japan, Myanmar, Nepal, Thailand, Vietnam, Korea</td>
</tr>
<tr>
<td>Americas</td>
<td>Alaska, Argentina, Brazil, Chile, Canada, Dominica, El Salvador, Honduras, Mexico, Peru, United States of America</td>
</tr>
<tr>
<td>Europe</td>
<td>Austria, Croatia, Finland, France, Germany, Greece, Hungary, Italy, Poland, Romania, Russia, Serbia, United Kingdom, Netherlands</td>
</tr>
<tr>
<td>Africa</td>
<td>Ghana, South Africa, Zimbabwe</td>
</tr>
<tr>
<td>Pacific</td>
<td>Australia, New Zealand</td>
</tr>
</tbody>
</table>

Source: Smedley and Kinniburgh (2002); Appleyard et al. (2006); Stuyfzand et al. (2006); Petruvskii et al. (2007); Smedley et al. (2007); Gunduz et al. (2009); Jovanovic et al. (2011).

In 1984, the first edition of WHO’s “Guidelines for Drinking Water Quality” (not standards) was published. In this document WHO categorised As among the inorganic constituents of significance to health (WHO, 2011b), contrary to its previous stance since 1958. WHO recommended 50 µg/L as a guideline value and supported it with the explanation that, based on available human health data, a concentration of 50 µg/L in drinking water was not associated with any adverse health effects. Supporting evidence included the cases in Chile and Taiwan where 50 µg/L was not reported to cause adverse health effects (WHO 1984). In 1993, WHO’s Guidelines for Drinking Water were published which established a new and stricter value of 10 µg/L as a provisional guideline value for As in drinking water (WHO, 1993). The new guideline value was supported by the research of the International Agency for Research on Cancer (IARC) which found sufficient evidence for the carcinogenicity of As in humans (WHO, 2011b). IARC classified As in Group I (carcinogenic to humans). Moreover, estimates from the USEPA were also considered in which a multistage model (both linear and quadratic in dose) was used to estimate the excess lifetime skin cancer risk associated with the ingestion of As in drinking-water. The model based estimates showed that the concentration associated with an excess lifetime skin cancer risk of 10^{-5} (1 in 100,000) was 0.17µg/L (USEPA, 1988; WHO, 1993; WHO, 1996; WHO, 2011b). However, WHO did not establish 0.17 µg/L as its guideline value of As in 1993. There were two principle reasons for not establishing 0.17 µg/L; firstly, it was believed that the results of the model might have overestimated the actual cancer risk and secondly, at that time the practical quantification limit was 10 µg/L for As in water (WHO, 2011b). In the 3rd and 4th edition (2004 and 2011) of WHO Guidelines for Drinking Water Quality, WHO retained 10 µg/L as the provisional guideline. In the background document for As guideline 2011, WHO again provided two main reasons for keeping the level at 10 µg/L. Firstly, the practical quantification limit for As, which is today between 1 and 10 µg/L, and secondly the technological constraint, i.e., difficulty of removing As to concentrations below 10 µg/L. Therefore, presently 10 µg/L is a provisional guideline for As in drinking water established by WHO. It is worth-mentioning that WHO recommends 10 µg/L as a provisional guideline value of As, which means that it is necessary to remove As as far as possible from drinking water. Drinking water with an As concentration below 10 µg/L may not be adequately safe because it was estimated by model based studies that the excess lifetime skin cancer risk associated to exposure of this concentration was 6×10^{-4} (6 in 10,000)(WHO, 1993; WHO, 1996; WHO 2011b).
2.6.2 Worldwide arsenic standards

The WHO provisional guideline of 10 µg/L has been adopted as a national standard by many countries, including Japan, Jordan, Netherland, Mongolia, Namibia, Syria and the USA, and by the European Union (EU) (Petrusivski et al., 2007). The WHO recommendation was adopted by the EU in 2006 and by US in 2001. Implementation of 10 µg/L is not currently feasible for a number of countries including Bangladesh and India which retain the 50 µg/L limit. The most stringent standard currently set for acceptable As concentration in drinking water is by Denmark, which has a national standard of 5 µg/L (Petrusivski et al., 2007). Drinking water As standards of various countries are presented (Table 2-5).

2.7 Detection, quantification and speciation of arsenic

2.7.1 Field test kits for rapid analysis

Detection and quantification of As in drinking water is generally the first step in the assessment of the extent and severity of As contamination. The development strategies for As remediation strongly depends upon the quantification of different species of As. Water samples from groundwater aquifers, treatment trains and storage tanks can be analysed for As using field analysis kits or in the laboratory. Various types of field test kits have been used extensively to measure As in groundwater (Jakariya et al. 2007; Steinmaus et al., 2009). The baseline quantification methodology is same for all of the measurement units. It involves treating the water samples with a reducing agent (eg. zinc) that separates the As by transforming As compounds in the water into As-trihydride (arsine gas AsH₃). Arsenic trihydride diffuses out of the sample where it is exposed to a paper impregnated with mercuric bromide. Reactions between the gas and the paper produce a highly coloured compound. By comparing the colour of the test strip to a colour scale provided with the kit, the amount of As in a sample can be estimated (USEPA, 2004). The accuracy, range and time required for measuring As concentration vary among different test kits. A common problem encountered with As field analysis kits is the under-evaluation of total As concentrations in water samples (Rahman et al., 2002: Erickson, 2003; AusAID, 2004). The expe-
Table 2-5: Drinking water As standards of various countries.

<table>
<thead>
<tr>
<th>Countries/States</th>
<th>As standard (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denmark, New jersey (US)</td>
<td>5</td>
</tr>
<tr>
<td>Australia</td>
<td>7</td>
</tr>
<tr>
<td>WHO, EU, Japan, US, Canada, Taiwan</td>
<td>10</td>
</tr>
<tr>
<td>Mexico</td>
<td>35</td>
</tr>
<tr>
<td>Bahrain, Bangladesh, Bolivia, China, Egypt, India, Indonesia, Pakistan</td>
<td>50</td>
</tr>
</tbody>
</table>


Experiences from the field have indicated that the test kits can detect the presence of As at high concentrations very accurately, however they are generally inaccurate for detecting lower concentrations of As (WHO 2001; Petrusevski et al., 2007). Some commonly used arsenic measurement kits with their measurement range are listed (Table 2-6).

2.7.2 Laboratory analysis methods

Accurate detection and measurement of As in drinking water requires laboratory analysis in well controlled conditions. Several laboratory methods are available for the accurate determination of As in water. The most common of these methods include; inductively coupled plasma mass spectrometry (ICP - MS), inductively coupled plasma atomic emission spectrometry (ICP - AES), atomic adsorption spectroscopy hydride generation (AAS - HG), atomic adsorption spectroscopy graphite furnace (AAS - GF), silver diethyldithiocarbamate method (SDDC) and anodic stripping voltammetry (ASV) (USEPA, 1999; Petrusevski et al., 2007). Presently, ICP - MS is used more frequently because it is a multi-analyte method at lower limits of detection (1 µg/L). In ICP - MS, a sample solution is introduced into a radio frequency (RF) plasma where energy transfer processes cause ionization. The ions are then extracted from the plasma and separated on the basis of their mass-to-charge ratio by means of a mass spectrometer. The ions are then detected by a Faraday detector. The signals are then processed to quantify the concentration of As.

2.7.3 Arsenic speciation analysis

The ICP - MS method coupled with high-performance liquid chromatography (HPLC) (Chana and Smith, 1987; Hakala and Pyy, 1992) is considered as the most efficient laboratory As speciation analysis method available today (Petrusevski et al., 2007; WHO, 2011b). This combination of two processes provides a good separation of As compounds together with an excellent detector sensitivity. Apart from HPLC, various other methods can also separate the As species, such as the selective arsine generation technique (Andreae, 1977; Masscheleyn et al., 1991), ion-exchange chromatography (Grabinski, 1981; Soto et al., 1996), ion-exchange method (Ficklin et al., 1983) and aluminosilicate adsorption (Meng and Wang, 1998). The storage and shipment time for water samples should be considered before As speciation analysis. As(III) may be oxidized to As(V) during sample storage and shipment and hence the results will be deceptive (Borho and Wilderer, 1997; Petrusevski et al., 1997; Fields et al., 2000). There is still a lack of adequate information regarding the sample storage procedures to avoid the oxidation of As species before the analysis. In response to the lack of techniques available for adequately preserving As species, field speciation
protocols have been developed by Ficklin (1982), Clifford et al. (1983), and Edwards et al. (1998). The main idea of the field speciation protocols was to separate As(III) from As(V) by using an anion exchange resin column and then analyse the samples for total As concentration by any of the available methods. Ficklin (1982) used a strong anion exchange resin (Dowex 1 × 8, 100-200 mesh, acetate form) in a 10 cm × 7 mm glass column to separate As(III) from As(V) in water samples that had been filtered through a 0.45-μm membrane filter and acidified with 1% HCl. In contrast, in the protocol by Clifford et al. (1983), a chloride-form strong base anion resin (ASB-2, 30-60 mesh) was used to separate As(III) from As(V) and the sample was not filtered or preserved with an acid. Edwards et al. (1998) made use of Ficklin’s method with some minor modifications.

2.8 Arsenic mitigation strategies

Considering the lethal and irreversible health effects of drinking As contaminated water, effective mitigation measures should be adopted on a global scale as early as possible. USEPA (2005) has identified the following mitigation strategies which can be adopted to control elevated As concentrations in drinking water:

- Abandonment - The total abandonment of the problematic sources and subsequent switch to other sources within the system or purchase from a neighboring system.
- Seasonal use - Switching the problematic sources from full-time use to seasonal or peaking use only with subsequent blending with other full-time sources.
- Blending - The combination of multiple water sources to produce a stream with an As concentration lower than the target level.
- Sidestream treatment - The treatment of a portion of the water with high As concentration and subsequent blending back with the untreated portion of the stream to produce water that meets the target level.
- Treatment – The processing of complete water stream to reduce the As concentration to the target value. The treatment can be at the well head, centralized or point of use level.

2.9 Treatment techniques for arsenic removal

Presence of As in concentration above the acceptable limits in drinking water is a very serious issue. In recent years a pressing need for the optimisation of conventional As removal processes and development of new techniques has been unavoidable, especially after the mass poisoning case of Bangladesh came into highlights (Chen et al., 2006; Mohan and Pittman, 2007). Historically, the most common methods for As removal have been the precipitation processes, for example, coagulation with metal salts, lime softening and Fe/Mn removal by aeration (Litter et al., 2010; Mudhoo et al., 2011). When, in 1993, WHO established 10 μg/L as the new provisional guideline value for As in drinking water, the development of various alternative As removal technologies speeded up. This was because in many circumstances precipitation processes were reported not able to remove As to the desired safe levels (A. Mudhoo et al., 2011). The main focus from the developers of the new technologies has been primarily on adsorption, ion exchange and membrane processes. Many of the removal technologies which have been developed or adapted are capable of removing As very efficiently to trace levels in optimised conditions of laboratory (Johnston and Heijnen, 2001; Mudhoo et al., 2011). However, there are only few processes which have
demonstrated consistently efficient for As removal at pilot scale and full scale treatment systems (Mudhoo et al., 2011). It has been widely reported that most of the processes remove As(V) more efficiently compared to As(III). That is why even presently, precipitative processes, especially coagulation with metals salts and co-removal with Fe and Mn, are considered as most reliable options for efficient removal of As at centralized treatment plants.

In the recent years some innovative (emerging) options for As removal have been investigated at laboratory and pilot scale. These include, for example, coagulation assisted microfiltration (Sevil, 2005), in-situ As immobilization/sub-surface As removal (van Halem, 2011), enhanced coagulation, electrokinetic treatment, iron oxide coated sand (IOCS) adsorption (Petrusevski et al. 2002), manganese oxide coated sand filtration (Bajpai and Chaudhary, 1999), granular ferric hydroxide (GFH) treatment, sulfur modified Fe treatment (USEPA, 2000), permeable reactive barrier, biological treatment and phytoremediation (Feenstra et al., 2007; Petrusevski et al., 2007). Studies are also focused on finding a suitable Fe(II) to As ratio to effectively remove As to less than 5 µg/L by slow sand filtration (Duarte et al., 2009). Most of the As removal methods, either conventional or emerging, rely on a few basic physical-chemical processes. These include oxidation/reduction, precipitation, adsorption and ion exchange, solid/liquid separation and physical exclusion (Johnston and Heijnen, 2001; Duarte et al., 2009). Some biological mechanisms may also play an important role in catalyzing many of the above mentioned chemical processes, however relatively little is known about the potential for biological removal of As from water. Almost all of the As removal technologies possess an added benefit of removing many other undesirable compounds from water. A detailed description of different mechanisms central to most As removal technologies has been provided below.

### 2.9.1 Oxidation/Reduction

Oxidation/Reduction is not a removal technique; however, it plays a vital role in optimising several As removal processes. Most of the As removal technologies are effective at removing As(V) (Hering et al., 1996; Hering et al., 1997). This is because, As(III) is predominantly non-charged below pH 9.2 (Fig. 2-4). On the other hand, As(V) occurs as monovalent or divalent ions in the pH range of natural waters (Fig. 2-5) (Ferguson and Gavis, 1972). The charged nature of As(V) facilitates its removal by adsorption onto the oppositely charged surfaces. The oxidation of As(III) to As(V) may also be important from the perspective of health, since As(III), if remains at trace levels after treatment, is much more toxic than trace levels of As(V) (WHO, 1993; Pontius et al., 1994).

<table>
<thead>
<tr>
<th>Test kit</th>
<th>Manufacturer</th>
<th>Measurement range (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MERCK</td>
<td>Germany</td>
<td>5 – 500</td>
</tr>
<tr>
<td>HACH</td>
<td>USA</td>
<td>10 – 500</td>
</tr>
<tr>
<td>Quick</td>
<td>USA</td>
<td>10 – 1000</td>
</tr>
<tr>
<td>AlI&amp;PH</td>
<td>India</td>
<td>Yes/No</td>
</tr>
<tr>
<td>NIPSOM</td>
<td>Bangladesh</td>
<td>10 – 700</td>
</tr>
<tr>
<td>GPL</td>
<td>GPL</td>
<td>10 – 2500</td>
</tr>
<tr>
<td>Arsenator</td>
<td>UK</td>
<td>&lt;10 - 500</td>
</tr>
</tbody>
</table>

Source: Petrusevski et al. (2007).
Oxidation of As(III) by air is a slow process. Hug et al. (2003) performed laboratory air oxidation experiments with As(III) at pH values typical of groundwaters and found that As(III) oxidation by air occurred on a time scale of tens of minutes. Bissen and Frimmel (2003) studied As(III) oxidation kinetics and reported that only 55% of total As(III) was oxidized in 5 days when the groundwater was purged with air and pure oxygen. For the advanced oxidation of As(III), chemical oxidants are generally required. Some common oxidants which may be used include; gaseous chlorine (Leyte et al., 2005), hypochlorite (Meng et al., 2001), ozone, permanganate (Jekel, 1994; Hug et al., 2003) and hydrogen peroxide (Peyton et al., 2006). Ultraviolet radiations may play a role to catalyze the oxidation of As(III) in the presence of oxygen. In developing countries hypochlorite and permanganate are most commonly applied oxidants (Johnston and Heijnen, 2001). It is worth mentioning that chlorine is a rapid and effective As(III) oxidant, however it may lead to the production of toxic trihalomethanes in the presence of organic matter in water.

Although oxygen assisted oxidation (Eq. 2.5) of As(III) to As(V) is generally slow, solid-liquid interfaces in the presence of dissolved oxygen may catalyze the process. For example, the Fe(III) deposits on the surface of filter sand grains, may facilitate the conversion of As(III) to As(V) by catalytic effects and direct reactions (Sarkar and Rehman, 2000). Hug et al., (2003) studied the Fe-catalyzed oxidation of As(III) and reported that As(III) was not measurably oxidized by only O2, 20−100 μM H2O2, dissolved Fe(II) or Fe(III) hydroxides. In contrast, As(III) was found partially or completely oxidized in parallel to the oxidation of 20−90 μM Fe(II) by oxygen and by 20 μM H2O2 in aerated solutions (Hug et al., 2003). Manganese oxides have also shown a tendency to oxidize As(III) to As(V) (Eq. 2.6). It has been observed that MnO2 leads to a faster oxidation of As(III) in a time scale of few minutes (Sevil, 2005). The oxidation of As(III) to As(V) by MnO2 releases Mn(II) ions which get adsorb onto the MnO2 surfaces and give them a positive charge (Buamah, 2009). As(V) can then readily adsorb to the positive sites and hence removed (Bajpai and Chaudhary, 1999; Buamah et al., 2008; Buamah, 2009).

\[ \text{H}_2\text{AsO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{AsO}_4^- + 2\text{H}^+ \]  
\[ \text{H}_2\text{AsO}_3 + \text{MnO}_2 (\text{s}) \rightarrow \text{HAsO}_4^- + \text{Mn}^{2+} + \text{H}_2\text{O} \]  

Besides physic-chemical processes, biological mechanisms may also play a role in the oxidation of As(III). A wide range of bacteria have been reported for their ability to synthesize and oxidize As(III) enzymatically (Duarte et al., 2009). They include heterotrophic bacteria as well as chemoautotrophic bacteria in which As(III) serves as an electron donor reducing oxygen or nitrate (Duarte et al., 2009; Battaglia-Brunet, 2002). The biological oxidation of As(III) to As(V) by Fe and Mn oxidizing bacteria has been reported as well and it was also reported that As(III) can be efficiently treated without any additional use of chemicals in this bio-process (Casilot et al., 2003). Besides oxidation, bacterial reduction of As(V) to As(III) has also been reported in literature according to Duarte et al. (2009).

**Potassium permanganate (KMnO4): An effective oxidant for As(III)**

Potassium permanganate (KMnO4) can be used to oxidize As(III) to As(V) in AOCF. The As(V) thus produced can be removed to very low concentrations by conventional coagulation/filtration As removal technique (Holm and Wilson, 2006; Bordoloi et al., 2013). Use of KMnO4 for oxidising dissolved Fe(II) and Mn(II) is largely studied and
applied at full scale treatment systems, however its application to specifically oxidize As(III) is relatively a new approach and has not been evaluated extensively. In drinking water treatment KMnO4 is a well established chemical which can oxidize a wide variety of organic and inorganic substances in the pH range of 4 to 9 (EPA, 1999). Most commonly, KMnO4 is used to control taste, odors, color and biological growth in water treatment processes. KMnO4 can be regarded as the most promising chemical oxidant in water treatment industry because it does not produce harmful by-products (as produced in case of Cl2) and is relatively easy to apply (Borho and Weilderer, 1996). The bench-scale investigations conducted by Holm and Wilson (2006) showed that KMnO4 was a better As(III) oxidant compared to NaOCl. The reactions for oxidation of As(III), Fe, Mn and by KMnO4 are provided (Eqs. 2.7, 2.8 and 2.9, respectively).

$$\text{3H}_3\text{AsO}_3 + 2\text{KMnO}_4 \rightarrow 3\text{HAsO}_4^{2-} + 2\text{MnO}_2 (s) + 2\text{K}^+ + 4\text{H}^+ + \text{H}_2\text{O} \quad (2.7)$$

$$\text{3Fe}^{2+} + \text{KMnO}_4 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_3(s) + \text{MnO}_2 (s) + \text{K}^+ + 5\text{H}^+ \quad (2.8)$$

$$\text{3Mn}^{2+} + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(s) + 2\text{K}^+ + 4\text{H}^+ \quad (2.9)$$

According to stoichiometric calculations based on the Eq. 2.8 and 2.9, the KMnO4 doses required for the oxidation are 0.94 mg/mg Fe and 1.92 mg/mg Mn. However, in practice, the actual amount of KMnO4 has been found to be less than that indicated by the stoichiometry (EPA, 1999). This may be due to the catalytic influence of solid MnO2 on the reactions (O’ Connel, 1978). Although KMnO4 is generally considered as a poor disinfectant, it has been proven effective against certain viruses and bacterial species (EPA, 1999). Furthermore, KMnO4 does not interact with other treatment processes (EPA, 1999). While treating water with KMnO4, caution is recommended to prevent overdosing, in that case, excess Mn may pass through the treatment process. Proper dosing is also recommended to maintain in order to ensure that the entire permanganate is reduced and removed upstream of or in the filters. Normally, the overdosing of permanganate is corrected by settling the excess MnO2 solids in the sedimentation basins. However, in systems where flocculation and sedimentation process are not applied, pre-optimisation of dose is strongly advised.

### 2.9.2 Precipitation/Co - precipitation

Arsenic removal techniques based on precipitative or co-precipitative processes have been extensively studied (Moreno-Casillas et al., 2007; Mercer and Tobiason, 2008; Lakshmanan et al., 2008). Most of the times the words “precipitation” and “co-precipitation” are used interchangeably in the context of As removal from water. In reality, inorganic soluble As species cannot be precipitated without the assistance of other precipitating compounds. The precipitation based As removal methods commonly include coagulation/filtration, Fe/Mn removal by aeration or advanced oxidation, coagulation assisted microfiltration, enhanced coagulation, lime softening and enhanced lime softening (USEPA, 2000; Sancha, 2006; Petrusenks et al., 2007; Mudhoo et al., 2011). The frequently applied precipitative techniques have been discussed below in detail.

**Coagulation/ Filtration**

Coagulation followed by rapid sand filtration is a commonly applied water treatment method. For As removal it is one of the most extensively studied techniques (Johnston and Heijnen, 2001). It has traditionally been used to remove solids from drinking water, however, this treatment can effectively remove many dissolved constituents from water such as
As. According to USEPA (2000), coagulation/filtration can successfully achieve As(V) removal efficiency of greater than 90 percent and if optimal operating conditions are adopted, effluent levels of less than 3 µg/L may be obtained. In this method, the major mechanism of As elimination is adsorption onto the charged sites provided by polymerising metal oxy-hydroxide molecules (Sancha, 2006; Mercer and Tobiason, 2008). However, incorporation of soluble As species into growing precipitates (metal hydroxide phase) contributes significantly in As removal as well. This kind of entrapment of As is due to occlusion, inclusion and adsorption, which is sometimes collectively known as co-precipitation. Arsenic removal by direct precipitation i.e, as Al(AsO₄) or Fe(AsO₄), is generally considered less contributing towards the overall removal of As during coagulation (MIT, 2001; Johnston and Heijnen, 2001).

The most commonly used coagulants or precipitants for As removal are aluminum (Al) salts such as alum, and Fe salts such as ferric chloride (FeCl₃) or ferrous sulfate (FeSO₄) (EPA, 2000; Johnston and Heijnen, 2001). As(III) removal during coagulation has been shown to be less efficient than As(V) under comparable conditions (Table 2-7) (Hering et al., 1996; Chwirka et al., 1999; MIT, 2001). In contrast, some studies investigating the adsorption of As(III) and As(V) on various pre-formed Fe-oxides refutes the conventional wisdom that As(III) adsorption to Fe-oxides is less effective than As(V) adsorption (Dixit and Hering, 2003; Grafe et al., 2001; Grafe et al., 2002). The added benefit of coagulation/filtration technique for As removal would be an enhanced removal efficiency for turbidity, natural organic matter (NOM), synthetic organic compounds (SOCs), Fe, Mn, phosphates and fluoride (USEPA, 2000; Johnston and Heijnen, 2001).

The factors affecting the removal of As by coagulation/filtration are widely investigated. Major factors include: coagulant type (Hering et al., 1997), coagulant dose (Hering et al., 1996; Chwirka et al., 2000; Meng et al., 2001; Donmez and Akbal, 2011; Qiao et al., 2012; Bordoloi et al., 2013), pH (Wilkie and Hering, 1996; Scott et al., 1995; Hering et al., 1996; Donmez and Akbal, 2011, Qiao et al, 2012), As speciation (Hering et al., 1996; Qiao et al., 2012), initial As concentration (Wilkie and Hering, 1996; Qiao et al., 2012; Bordoloi et al., 2013), and nature of co-occurring inorganic solutes (Wilkie and Hering, 1996; Mayer and Jarrell, 2000; Bang and Meng, 2004; Qiao et al., 2012; Bordoloi et al., 2013). Many studies have reported Fe(III) based salts as the most appropriate coagulants for As removal (Gupta & Chen, 1978; Cheng et al, 1994; Hering et al., 1997; Donmez and Akbal, 2011). However, the availability, downstream processes carried out at the treatment plant and above all, the raw water quality must be taken into account before the selection of a coagulant for As removal.

A promising modification of the conventional coagulation/filtration technology is the coagulation assisted microfiltration. Microfiltration replaces conventional rapid sand filters and serves as a more effective barrier to small floc sizes. As a result total plant capacity is increased and coagulant dose can be reduced (USEPA, 2000). Membrane fouling because of particulate oxides of Fe and Mn may be a potential disadvantage of coagulation assisted microfiltration (Sevil, 2005). Another effective modification is enhanced coagulation technique. Increased As removal can be achieved by enhanced coagulation which involves either increasing the coagulant dose or decreasing the pH or both (USEPA, 2000).
Table 2-7: As(III) and As(V) removal efficiency of different coagulants.

<table>
<thead>
<tr>
<th>As form</th>
<th>Coagulant</th>
<th>Al₂(SO₄)₃</th>
<th>FeCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>0-20%</td>
<td>40-70%</td>
<td></td>
</tr>
<tr>
<td>As(V)</td>
<td>70-80%</td>
<td>80-100%</td>
<td></td>
</tr>
</tbody>
</table>

Source: Chwirka et al. (1999).

It must be noted that the enhanced coagulation process may become costly due to an increased chemical input and when the post treatment pH adjustment may be required for corrosion control.

Combined removal with iron and manganese

Ground waters which contain high concentrations of dissolved Fe and Mn are generally treated by aeration followed by one or two stage rapid sand filtration. These metals, when oxidized, form solid metallic oxides and hydroxides which can sorb significant amounts of As (USEPA, 2000; Hug et al., 2003; Bissen and Frimmel, 2003). The production of oxidized Fe and Mn species and their subsequent precipitation as hydroxides and oxides is similar to an in situ coagulant addition, with the quantity of Fe or Mn removed translating into a “coagulant dose”.

The Eh-pH diagram of aqueous Fe speciation is provided (Fig. 2-7). The Fe removal in conventional aeration-filtration systems follow two physical-chemical mechanisms which most of the times work simultaneously. One mechanism is the aqueous phase oxidation of Fe(II) to Fe(III) (Eq. 2.10) and immediate hydrolysis to form iron oxyhydroxide (FeOOH or Fe(OH)₃) flocs (Eq. 2.11). For simplicity, this mechanism can be named as flocculative removal mode. The second mechanism is adsorption of Fe(II) on the surface of the filter media, followed by its oxidation to Fe(III) while being adsorbed at the media grains. This mechanism can be regarded as adsorptive removal mode. Arsenic gets removed by both the processes i.e., adsorption onto Fe(OH)₃ flocs and by the dense Fe-oxide coating developed gradually over time on filter media grains.

\[
4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^- \tag{2.10}
\]

\[
4\text{Fe}^{3+} + 4\text{OH}^- + 8\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 8\text{H}^+ \tag{2.11}
\]

\[
4\text{Fe}^{2+} + \text{O}_2(g) + 10\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3(s) + 8\text{H}^+ \tag{2.12}
\]

When source water pH is below 9, the oxidation of influent Mn(II) to solid Mn₃O₄ and/or MnO₂ is generally very slow in the presence of atmospheric oxygen only. Therefore, Mn enters the rapid sand filter beds as dissolved Mn(II) even after the water is aerated in the cascades. Manganese removal occurs therefore only by the adsorptive removal mechanism which is auto-catalytic in nature. It is a physico-chemical removal mechanism during which firstly the adsorption of Mn(II) occurs onto the surface of the filtration media grains, followed by oxidation of the adsorbed Mn(II) to solid Mn₃O₄ and/or MnO₂ (Buamah, 2009). The adsorbed and subsequently oxidized Mn acts as a newly created adsorbent for the incoming Mn(II). In this way, the thickness of the coating keeps on increasing and Mn removal continues. The Mn-oxide coatings formed on the surface of the filter media grains may contribute to the oxidation of As(III).

Lime softening

Ground water softening with lime is very effective in reducing As from drinking water (USEPA, 2000; Fields et al., 2000). Water hardness is primarily due to the presence of calcium and magnesium ions. The lime
is added to provide hydroxide ions which increase the pH of water. At increased pH bicarbonate is converted to carbonate which results in calcium and magnesium removal due to the formation of CaCO$_3$ and Mg(OH)$_2$ precipitates. If insufficient carbonate is present in the water, soda ash is added to remove hardness to the desired levels. Softening for only calcium removal is typically accomplished at pH between 9 and 9.5 (USEPA, 2000). However if magnesium removal is desired, excess lime is added to raise the pH above 10.5 so that magnesium precipitates as Mg(OH)$_2$ (USEPA, 2000). Fields et al., (2000) reported that As removal during lime softening is pH dependent and removal of As(III) and As(V) are low at pH less than 10; however, As(V) removal approaches 100% and As(III) removal approaches to 75% at pH values greater than 10.5. It means that when pH is high enough to precipitate Mg(OH)$_2$, As adsorption and subsequent removal increases. Post treatment pH adjustment may be accomplished by recarbonation with CO$_2$. Softening can also be accomplished by caustic soda (NaOH).

### 2.9.3 Adsorption and ion exchange

Adsorption is a key process in many As removal techniques and may be regarded as the most important As removal mechanism. Adsorption is defined as the separation of a substance from one phase accompanied by its concentration on the surface of another. The adsorbing phase is known as the adsorbent and the material concentrated is called adsorbate. Interactions between adsorbate and adsorbent consist of molecular forces which can be classified into two main categories i.e., short range forces (Chemical forces) and long range forces (Colulombic forces). The short range forces may give rise to covalent or hydrophobic bonds or hydrogen bonding or steric effect (Buamah, 2009). On the other hand, the long range forces give rise to electrostatic attractions (Yang 1999). Based upon these adhesive forces four principal types of adsorption have been identified: namely, ion exchange, chemical adsorption, physical adsorption and specific adsorption (Yang 1999; Buamah, 2009). Arsenic removal by adsorptive processes can be accomplished in two ways, i.e., adsorptive media filtration or flow through a column of ion-exchange resin. Different adsorptive and ion-exchange medias are discussed in the next section.
Adsorptive media
In the past, the most commonly used adsorptive media for As removal had been activated alumina. However, in recent years, several new granular adsorptive filter media have been developed which have shown high effectiveness in As removal from water (Petrusevski et al., 2007). These media can be categorized into two major groups i.e., metal oxide coated media and metal oxide based media. The primary mechanism of As removal by these media is chemical adsorption which involves a reaction among an adsorbate (e.g., As) and adsorbent (media) resulting in a change in the chemical form of the adsorbate. Sharing of electrons between adsorbent and adsorbate occurs at the adsorptive site of the adsorbent yielding process irreversibility (Buamah, 2009; Buamah et al., 2008). In aqueous systems the surfaces of metal oxide adsorptive media grains get covered with hydroxyl groups (Buamah, 2009; Buamah et al., 2008). Anions such as As(V) are then adsorbed onto metal oxide based media via a ligand exchange reaction in which hydroxyl surface groups are replaced by the sorbing ions as shown in the Eqs. 2.13, 2.14 and 2.15 (Buamah, 2009; Buamah et al., 2008). In these Eqs. S represents the surface of metal oxide coated media.

\[
S - OH + H_3AsO_3 \rightarrow S - H_2AsO_3 + H_2O \quad (2.13)
\]

\[
S - OH + H_2AsO_4^+ \rightarrow S - HAsO_4^+ + H_2O \quad (2.14)
\]

\[
S - OH + HAsO_4^{2-} \rightarrow S - AsO_4^{2-} + H_2O \quad (2.15)
\]

In the complex adsorptive environment of media As(III), which exists as an uncharged species in the pH range of 6-9, may also be removed because of physical and specific adsorption mechanisms. Physical adsorption generally results from the action of van der Waals forces that hold the adsorbate, i.e., As(III), to the atoms on adsorbent surface (Buamah et al., 2008; Buamah, 2009). Unlike As(V), the adsorbed As(III) is not affixed to a specific site but free to undergo translational movements.

Latest research regarding As removal has been focused on the development of efficient As adsorptive media. One such promising adsorption media is Iron Oxide Coated Sand (IOCS) (Fig. 2-8 b) which has been developed by UNESCO-IHE. IOCS has shown efficient As(III) and As(V) removal capacities during field trials in Bangladesh and at centralized applications in Greece and Hungary (Petrusevski et al., 2007). Natural geological materials have also demonstrated strong affinity for both As(III) and As(V) (Bundschuh et al., 2011). Pretreatment of the zeolite with copper has shown to enhance As adsorption capacity of the zeolite (Beamguard, 2006). Naturally occurring glauconitic sand after being treated with KMnO₄ (known as green sand) (Fig. 2-8) can also remove As from water. The principle behind the As removal by green sand is multi-faceted, including oxidation, ion exchange and adsorption (USEPA, 2000). Some other commercial adsorptive media include Aquamandix (Figure 2-8) Aqua-Bind MP, ArsenX, Bayoxide E33 ferric oxide, GFH, MEDIA G2 etc.

Ion exchange resins
For As removal from water synthetic anion exchange resins have been proven to be very effective to produce an effluent with less than 1 µg/L As concentrations (Johnston and Heijnen, 2001). According to USEPA (2000) a consistent removal to below 3 µg/L can be achieved by anion exchange technology. Korngold et al. (2001) reported more than 99% As(V) removal using chloride based ion exchange resins. Conventional sulphate and nitrate selective resins are well suited for As(V) removal.
The removal through an ion-exchange resin involves short-range forces which occur within the porous lattice of resin grains which contain a fixed charge. The electrostatic attachment of ionic species to sites of opposite charge at the surface of an ion exchange media grain occurs with a subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity. Eqs. 2.16 and 2.17 represent the exchange of dissolved As species with the Cl ions on the resin grains. The ion exchange treatment procedure includes continuous passage of feed water through a packed bed of ion exchange resin beads until the resin is exhausted. At that stage, the bed is regenerated by rinsing with a regenerant. The principle challenge with ion exchange resin treatment is the absence of removal for As(III). This is because of the uncharged nature of As(III). Therefore, waters containing As(III) typically require a pre-oxidation step before contact with ion exchange resin bed. Another problem in this treatment is the potential interference from other anions. If the feed water contains sulphates, nitrates, chloride or other anions, the As removal may be significantly reduced (Johnston and Heijnen, 2001, Korngold et al., 2001; Feenstra et al., 2007). Some commercially available ion exchange resins include Dowex 11, Ionac ASB-2 and Dowex SBR-1 (USEPA, 2000).

\[ R - Cl + H_2AsO_4^- \rightarrow R - H_2AsO_4 + Cl^- \]  \hspace{1cm} (2.16)

\[ 2R - Cl + HAsO_4^{2-} \rightarrow R_2 - HAsO_4 + 2Cl^- \] \hspace{1cm} (2.17)

The effectiveness of As treatment by adsorption and ion exchange is more likely to be affected by characteristics and contaminants other than As compared to precipitative processes discussed in previous section. Therefore, adsorption and ion exchange media treatment techniques tend to be used more often when As is the only contaminant to be
treated, for relatively smaller systems, and as an auxiliary process for treating effluent from larger systems (Petrusevski et al., 2007).

2.9.4 Membrane separation processes

A water treatment membrane is a selective barrier which allows some constituents to pass while blocking the passage of others. Membranes split a feed stream into two parts i.e., retentate and permeate fractions. Membrane processes can remove As very efficiently through filtration, electric repulsion and adsorption of As bearing compounds (Petrusevski et al., 2007). Pressure driven membranes can be classified, on the basis of pore size, into four categories. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). NF and RO are high pressure processes, requiring more energy. Typical pressure range and recoveries of different membrane processes can be observed in Table 2-8 (EPA, 2000). The percentage of product water that can be produced from the feed water is known as recovery (USEPA, 2000). Membrane filtration is capable of removing both As(III) and As(V), however As(V) removal efficiency is higher than As(III) (Petrusevski et al., 2007). Membrane processes produce a large volume of residuals and tends to be more expensive compared to other As removal methods. They are therefore used less frequently than precipitative/coprecipitative, adsorptive and ion exchange processes (USEPA, 2002; Petrusenski et al., 2007). A cross sectional view of UF membrane under Scanning Electron Microscope (SEM) has been shown (Fig. 2-9).

Table 2-8: Typical pressure ranges and recoveries for membrane processes.

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Pressure range</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>5 – 45 psi</td>
<td>to 99 %</td>
</tr>
<tr>
<td>UF</td>
<td>7 – 100 psi</td>
<td>to 95 %</td>
</tr>
<tr>
<td>NF</td>
<td>50 – 150 psi</td>
<td>to 85 %</td>
</tr>
<tr>
<td>RO</td>
<td>100 – 150 psi</td>
<td>30 – 85 %</td>
</tr>
</tbody>
</table>


Figure 2-9: Cross section of UF membrane under SEM.
2.9.5 **Subsurface immobilization**

The application of subsurface treatment for the removal of As from groundwater is a relatively new approach (Sarkar and Rahman, 2001; van Halem 2011). In contrast, for removing Fe from groundwater, subsurface immobilization method (Fig. 2-10) has been used in central Europe for many decades. In strongly reducing environments As gets mobilized into groundwater because of the reductive dissolution of As bearing minerals. The process can be reversed and loose As can be immobilized again by pumping in aerated water periodically into an anoxic aquifer. The injected water oxidises dissolved Fe(II) which is then precipitated on the soil grains, resulting in the formation of adsorptive surfaces of iron hydroxides. Arsenic ions get adsorb on these surface sorption sites and become immobile. When the flow is reversed (abstraction mode), As free water can be obtained. Apart from As adsorption, there may also be As immobilization through coprecipitation while Fe(II) changes to ferrihydrite (van Halem, 2011). Subsurface As removal has the potential to be a cost-effective way to provide safe drinking water in rural areas in decentralized applications (van Halem, 2011). A remarkable advantage of this process is no production of As-rich waste above surface.

2.9.6 **Biological processes**

Biological and microbiological removal methods can present economically viable and environmentally harmless solution for the As contamination problem. Indigenous bacterial species can play an important role in catalyzing many of the physical-chemical As removal processes. Further, a wide range of bacteria have been reported with having the ability to synthesize and oxidize As(III) (Duarte et al., 2009). New developments in the biotechnological As removal have been focused on phytoremediation and biofiltration processes. In phytoremediation, plants and fungal biomass is used as a renewable adsorbing material. Aquatic plants like Azolla and Spirodella (duckweed) species have a significant As removal capacity by uptake (Feenstra et al., 2007). According to Duarte et al. (2009), the adsorbing capacity of this biomass is superior to that of activated carbon and some synthetic resins used in water treatment. Although biological methods seem very promising for efficient As remediation, relatively little is known about their capacity. Biological technology is still confined to laboratory scale investigations and need to be evaluated under full scale conditions to prove their viability.

![Figure 2-10: Principle of subsurface iron removal. Injection (left) and abstraction (right) (van Halem, 2011).](image)
### 2.9.7 Summary of arsenic removal method

#### Table 2-9: Summary of arsenic removal processes.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Removal efficiency</th>
<th>Institutional experience and issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>As(V)</td>
<td></td>
</tr>
<tr>
<td>Coagulation/Filtration (Fe salts)</td>
<td>+</td>
<td>Well proven at central level. Piloted at community and household levels. Phosphates, silicates and other anions may reduce As removal efficiency. Generates As rich sludge. Potential reductions of filter run times on adoption to an existing facility. Ideal pH 6-8.</td>
</tr>
<tr>
<td>Coagulation/Filtration (alum)</td>
<td>-</td>
<td>Well proven at central level. Piloted at community and household levels. Phosphates, silicates and other anions may reduce As removal efficiency. Generates arsenic rich sludge. Potential reductions of filter run times on adoption to an existing facility. Ideal, relatively narrow, pH 6-6.5.</td>
</tr>
<tr>
<td>Fe/Mn oxidation (air)</td>
<td>-/+</td>
<td>Conventional groundwater treatment plants with Fe/Mn removal have shown As removal. Ideal pH 6-8.</td>
</tr>
<tr>
<td>Fe/Mn oxidation (chemical oxidant)</td>
<td>++/+ +/++</td>
<td>Well proven at central level. Piloted at community and household levels. The adoption to filtration may change filter run times. Ideal pH 6-8.</td>
</tr>
<tr>
<td>Lime softening</td>
<td>+</td>
<td>Conventional softening plants have shown arsenic removal capacity. pH adjustment required after treatment. Ideal pH &gt;10.5.</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>+</td>
<td>Proven as an auxiliary treatment at central level. Used in household systems. Waters contaminated with turbidity, Fe, Mn, organics require pre-treatment. High organic content can reduce arsenic sorption. Regular regeneration required. Ideal pH 5.5-6.5.</td>
</tr>
<tr>
<td>Iron oxide coated and iron oxide based media</td>
<td>+</td>
<td>Piloted at community and household levels. Arsenic removal can be reduced due to competition from co-existing anions. Media regeneration is required. Need to be evaluated in different environmental conditions. Ideal pH near 8.0.</td>
</tr>
<tr>
<td>Manganese green sand filtration</td>
<td>++</td>
<td>Popular filtration media in the US at central level. Effectiveness strongly depends upon influent water quality in terms of Fe. Problems of Mn leaching can encounter. Regeneration of the media is required.</td>
</tr>
<tr>
<td>Ion exchange resins</td>
<td>-</td>
<td>Piloted at central and house hold levels. Relatively high cost method. Interference from sulphates and TDS. Regeneration produces arsenic rich brine. Media clogging due to organics. Ideal pH 6.5-9.0.</td>
</tr>
<tr>
<td>Membrane Technology</td>
<td>++</td>
<td>Shown effective arsenic removal in lab and pilot studies. Research needed for increasing recovery rates, especially low pressure membranes. Relatively expensive, especially when operated at high pressure.</td>
</tr>
<tr>
<td>Sub-surface/In-situ immobilization</td>
<td>++</td>
<td>Limited experience in context of arsenic. Pilot scale studies are ongoing. Major advantage is no arsenic rich sludge. Evaluated in different geochemical settings is required</td>
</tr>
<tr>
<td>Biological processes</td>
<td>?</td>
<td>Lab scale studies have shown promising potential. Limited understanding of the biochemical mechanisms.</td>
</tr>
</tbody>
</table>

Key: +++ Consistently >90 % removal
+ + Generally 60-90% removal
+ Generally 30-60% removal
- <30 % removal

Sources: Johnston and Heijnen et al. (2001); Feenstra et al. (2007); Duarte et al. (2009); Buamah (2009).
2.10 Selection of appropriate arsenic removal technology

Selection of the most appropriate technology for implementation on an already existing groundwater treatment system needs careful pre-evaluation of certain aspects. From the perspective of plant managers, the main goal is to install an efficient process which can remove As to the target levels, consistently and cost effectively. The primary factors which should be taken into consideration when selecting a treatment technology include water quality characteristics (i.e., pH, initial concentrations of As(III), As(V) and Fe), target finished water As concentration, ease of implementation on an existing system, residual management and the cost (USEPA, 2005; USEPA, 2003). Concentrations of anions such as sulphates, phosphates, silicates, nitrates etc. may also be considered on a secondary level. Many of the most efficient and cost effective As removal processes are Fe-based methods. Co-removal of As with Fe removal can attain high As removal efficiency in optimized conditions. Therefore, the level of Fe in the source water is suggested as a principal consideration in the selection of an optimal treatment technology (USEPA, 2005). USEPA’s National Risk Management Research Laboratory (2005) has provided a general method, based upon the source water Fe to As ratio to decide upon the adoption of the most appropriate As removal process for a particular situation (Fig. 2-11). The process selection process of USEPA has been discussed below. It is worth-mentioning that this process is very basic and meant to be used as a general “rule of thumb.” The process selection method provides guidance on three cases of source water quality;

If source water contains high Fe concentrations (> 0.3 mg/L) and high Fe to As ratio (20:1 or more), typical Fe removal processes such as aeration-filtration can be used to promote As removal from drinking water (Section A of Fig. 2-11).

If source water contains high Fe concentrations (> 0.3 mg/L) but low Fe to As ratio (< 20:1), then a modified treatment process such as coagulation/filtration with the addition of Fe salts should be tested (Section B of Fig. 2-11).

If source water contains low Fe levels (<0.3 mg/L), technologies such as adsorptive media and ion exchange are best suited (Section C of Fig. 2-11).

Figure 2-11: Arsenic treatment selection guide of USEPA.
USEPA has also indicated seven best available technologies (BATs) (USEPA, 2000) which may also be considered while selecting an appropriate technology. Table 2-10 presents these technologies with their maximum removal percentages when total As is present in As(V) form. In certain situations only an adjustment in pH may be sufficient to increase the As removal efficiency of a treatment system. For example, in lime softening plants, a slight optimisation of pH may increase As removal efficiency significantly. Pre-evaluation of As speciation in raw water may also provide guidance regarding the strategy to be adopted for achieving an optimised As removal. Therefore, careful investigation of the existing As removal processes should be carried out before considering implementation of a new technology on an existing treatment system. Another important consideration in the phase of technology selection is the residual production and management. Piloting the potential mitigation strategies is an essential procedure to optimize treatment variables and avoid implementing a strategy that may not work for unforeseen reasons (USEPA, 2005).

2.11 Sorption chemistry of arsenic onto iron (oxy)hydroxides
The natural and synthetic Fe-oxides play a vital role in most of the As removal processes. There are atleast sixteen types of Fe-oxides, depending upon the arrangement of atoms, which get covered with hydroxide ions and give rise to different oxy-hydroxides and hydroxides of Fe, when exposed to aqueous environments. Some examples of Fe oxides, oxy-hydroxides and hydroxides are: haematite (\(\alpha-Fe_2O_3\)), magnetite (Fe_3O_4), goethite (\(\alpha-FeOOH\)), ferrihydrite (Fe_5O_8H_4O_2), akaganeite (\(\beta-FeOOH\)) etc. When an Fe salt (coagulant) undergoes hydrolysis in oxidizing environment, different types of (oxy)hydroxides are formed depending upon the pH and other ions present in the system. Matijvic and Scheiner (1978) reported the formation of akaganeite (\(\beta-FeOOH\)) when FeCl_3 was allowed to hydrolyse near neutral pH. Generally, as the time passes the freshly formed amorphous hydroxides and oxyhydroxides (e.g, ferrihydrite) transform to more stable and crystalline forms (e.g, goethite) and in complex aqueous environments with a variety of ions, it becomes extremely difficult to characterise the type of Fe-oxide present at a particular time. To simplify, from now onwards, the term iron hydroxide (Fe(OH)_3) will be used to represent all types of hydroxides and oxyhydroxides of Fe(III) formed in the aqueous phase.

<table>
<thead>
<tr>
<th>Treatment Technology</th>
<th>Maximum Removal of As(V) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion exchange</td>
<td>95</td>
</tr>
<tr>
<td>Activated Alumina</td>
<td>95</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Modified coagulation filtration</td>
<td>95</td>
</tr>
<tr>
<td>Modified lime softening (pH&gt;10.5)</td>
<td>90</td>
</tr>
<tr>
<td>Electrodialysis reversal</td>
<td>85</td>
</tr>
<tr>
<td>Oxidation/filtration (Fe:As=20:1)</td>
<td>80</td>
</tr>
</tbody>
</table>

Figure 2-12: Variation of Fe-hydroxide surface charge with pH.

The adsorption of As on Fe(OH)₃ has been extensively studied. Both As(III) and As(V) exhibit a significant affinity for Fe(OH)₃. Metal oxides generally are characterized by a certain specific pH at which the net charge of the oxide surface is neutral. This pH is called point of zero charge (PZC). The PZC for Fe(OH)₃ occurs between pH values of 7 and 9 (Fig. 2-12) (Cornell and Schwertmann, 1996; Peacock and Sherman, 2004). The extent of sorption of an anion generally decreases at pH values above the PZC of the oxide. Since As(V) is charged at pH values above 4, it exhibits typical adsorption behaviour of anions onto the surface of Fe(OH)₃. The adsorption of As(V) increases at low pH in the pH range of 4 to 9 (Manning et al., 1998; Sun and Doner, 1996) while the adsorption of As(III) increases at high pH (Goldberg and Johnston, 2001; Holm, 2002). According to Dixit and Hering (2003), As(III) adsorption onto Fe(OH)₃ is relatively insensitive to pH values which are commonly encountered in the aquatic environments, though slightly favouring the pH range of 5 to 8. Generally As(V) is more strongly adsorbed to Fe(OH)₃ than As(III) (Bowell, 1994). However, As(III) adsorption is greater than As(V) when the solution pH is above 8 (Goldberg and Johnston, 2001). Both macroscopic and microscopic test methods have been utilized to investigate the adsorption mechanisms of As(III) and As(V) on the surface of Fe(OH)₃ (Sun and Doner, 1996; Raven et al., 1998; Manning et al., 1998; Goldberg and Johnson, 2001; Nayak et al., 2006; Carabante, 2012; Farrel and Chaudhary, 2013). Direct experimental observations of the adsorption mechanism have been obtained using different spectroscopic techniques which include Fourier Transformed Infrared Spectroscopy (FTIR)(Sun and Doner, 1996; Carabante, 2012), Raman Spectroscopy (Goldberg and Johnson, 2001) and Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS)(Manning et al., 1998). Generally, the adsorption of As decreases with increasing ionic strength when the ions form outer sphere surface complexes, whereas ionic strength has little effect on As adsorption when inner sphere complexes are formed (Bang and Meng, 2004). However, Goldberg and Johnson (2001) reported a slight different results, that As(V) adsorption onto Fe(OH)₃ increased with increasing ionic strength and As(III) adsorption decreased on Fe(OH)₃ when ionic strength increases. Goldberg and Johnson (2001) summarized the results of their investigations that As(V) forms inner sphere complexes on the Fe(OH)₃ surface and As(III) not only forms outersphere complexes, but also inner sphere complexes.
It should be noted that in outer sphere surface complexation the adsorbate ion remains bounded to the hydration shell so it does not bind directly to the surface and the attraction is purely electrostatic (Fig. 2-13). On the other hand, in inner sphere surface complexation the adsorbate ion bonds to a specific site on the surface (Fig. 2-13), this ignores the overall electrostatic interaction with bulk surface (i.e. a cation could bind to a mineral below the mineral pH). Although there is a general consensus that As(V) forms inner sphere surface complexes on the surface of Fe(OH)$_3$, the exact nature of As(V) surface complexes remains controversial (Pedersen, 2006). Possible surface complexes of As(V) tetrahedra on Fe(OH)$_3$ surface are shown in Fig. 2-14, where 2C represents a bidentate complex resulting from corner sharing, 2E represents a bidentate complex resulting from edge sharing and 1V represents a monodentate complex resulting from corner sharing between As(V) tetrahedra and the Fe(OH)$_3$ surface. Most researchers believe that a combination of all these complexes occur. As(III) appears to associate with the Fe(OH)$_3$ surface through a bidentate binuclear surface complex (Manning et al., 1998).

**Figure 2-13:** Formation of inner sphere and outer sphere complexes.

**Figure 2-14:** Surface complexes of As(V) tetrahedra on iron oxides (Sherman and Randall, 2003).
2.12 Groundwater arsenic levels in the Netherlands

The Netherlands is a small and densely populated country with an approximate area of 37,400 km² and a population of about 16.3 million. The country lies in the delta of the three major North West European rivers, including the Rhine, the Meuse and the Schelde. Since 1853, the centralized public drinking water supply has been started in the Netherlands (Stuyfzand et al., 2008) and presently more than 99% of the Dutch population has access to public water supply services (Vewin, 2006). Groundwater is a major source of drinking water in the Netherlands; about two-third of the country obtains its drinking water from groundwater and the rest relies on natural dune water and surface water resources (Vewin, 2006; Buamah, 2009). Presently there are ten water supply companies in the Netherlands supplying almost 1.2 billion m³ water annually (Vewin, 2013). The water companies and their area of distribution has been shown (Appendix I). In 2008, Stuyfzand et al. investigated the As concentrations in groundwater throughout the Netherlands, taking into account the source water quality data from 241 well fields. They found that the total As concentration of groundwater in the Netherlands ranged from 0.1 -70 µg/L (Stuyfzand et al., 2008). In total 8 drinking water production sites were identified where As levels above 10 µg/L were noticed in the source water. These sites included Laren, Loosdrecht, Zwijndrecht, Dorst, Oostrum, Tolkamer, Klotputten and Hammerflier. The spatial distribution of As in the Netherlands and locations of water abstraction sites with elevated As levels are shown (Fig. 2-15). Among these sites Tolkamer and Oostrum had been abandoned, while water treatment methods applied at the remaining 6 sites successfully reduced As to below the Dutch national standard, i.e., 10 µg/L. According to Stufzand et al. (2008), the elevated concentrations of As were generally observed in anoxic sand aquifers and deep anoxic river bank filtration systems.

![Figure 2-15: Mean total As concentration in the raw water from 241 water supply wells for public drinking water supply in the Netherlands, in 2008 (Stuyfzand et al., 2008).](image)
2.13 Water treatment plant of Dorst

Dorst is one of the drinking water production sites in the Netherlands which make use of groundwater with elevated As levels (Fig. 2-16). The WTP at Dorst treats approximately 9 million m$^3$ of drinking water per year which is supplied to the Noord Brabant communities of Bavel, Breda, Dorst, Prinzenbeek, Galder, Teteringen, Ulvenhout and Etten-Leur. The average As concentration in the source groundwater of WTP Dorst is 12 µg/L. Besides As, the source water also contains an average Fe concentration of 1.4 mg/L, Mn concentration of 0.04 mg/L and NH$_4^+$ concentration of 0.6 mg/L. The average concentrations of different elements and other water quality parameters in the source water of WTP Dorst and the plant effluent are presented (Appendix II). The source water at Dorst is pumped from approximately 120-190 meters deep glauconitic sandy aquifer and it is believed that the principle mechanism of As mobilization would be reductive dissolution of As-bearing minerals. The raw water at WTP Dorst is treated by applying cascade aeration and subsequent rapid sand filtration after which the plant effluent contains, at an average, 6 µg/L of As, less than 0.01 mg/L of Fe and less than 0.01 mg/L of Mn. Although the average concentration of As in the effluent of WTP Dorst is well below the EU’s drinking water standard and WHO provisional guideline value, it does not comply with the Brabant Water’s relatively stringent As standard of 5 µg/L.

Groundwater is pumped through 17 wells of 150 m$^3$/h capacity each in WTP Dorst to produce 2000m$^3$/h. The groundwater from all the pumping wells is mixed and then used as raw water for drinking water production. Since the groundwater is abstracted from very deep aquifer and where it had been in equilibrium with the soil for hundreds of years, the overall source water quality is expected to remain consistent according to previous investigations. At the treatment plant, the water is treated in 10 parallel treatment trains. The process scheme has been provided (Appendix III). The effluents from the 10 rapid sand filters are combined and stored for subsequent distribution to various communities. Filtration velocity of 5 m/h on average is maintained. Table 2-11 shows the details related to the filtration process of Dorst. No chlorination is applied to the water before the distribution. The filters are regularly backwashed averagely after 96 hours of continuous filter operation and the wash water is treated separately in a side stream with FeCl$_3$ coagulation, sand filtration and UV disinfection before its inflow to the finished water storage tank.

3. MATERIALS AND METHODS

3.1 Investigation of arsenic removal at WTP Dorst

3.1.1 Procedures and equipment

In order to investigate the As removal mechanism at WTP Dorst a 6 week sampling and data collection plan was implemented. Three locations were selected along the treatment train of WTP Dorst from where water samples were collected once every week to measure the dissolved and particulate concentrations of As, Fe and Mn, and once every two weeks for As speciation analysis. The process flow diagram for the WTP Dorst (Fig. 3-1) indicates the sampling locations selected for the evaluation and analyses. The sampling locations included: (1) the raw water inflow to plant (IN); (2) the pre-filtration step i.e., after the cascade aerator (PF) and (3) after the filtration process, i.e., from the effluent of
the filters (AF). Over the period of six weeks, in total 6 samples were collected for the determination of total and dissolved As, Fe and Mn concentrations and in total 3 samples for the As speciation analysis. For As speciation analysis field speciation protocol developed by Clifford et al. (1983) was used and the kits were prepared on site. All the samples from weekly and twice monthly sampling were sent to Aqualab Zuid laboratory on the same day for the analysis of inorganic constituents. High density polyethylene (HDPE) bottles of 125 mL capacity were used to preserve the samples until they reached the laboratory. The sample bottles were prepared and supplied by Aqualab Zuid and contained 250 μL of concentrated ultra-pure nitric acid (HNO₃). Analysis of As, Fe, and Mn in water samples were accomplished at Aqualab Zuid laboratory by ICP-MS in accordance with NEN-EN-ISO 17294-2.

For weekly determination of total, dissolved and particulate concentrations of As, Fe and Mn, samples were collected using a 400-mL glass beaker. Before the sampling, the beaker was rinsed thoroughly with the water to be collected. The pH was measured on site as soon as the samples were collected with the help of a multi-probe device manufactured by HACH. At all the sampling locations sampling taps were present except at the PF step. Therefore, the treatment plant crew collected the samples directly from the supernatant of the filters (the water that stands at the top of filter bed and represents pressure head). All the sampling taps were flushed for atleast 1 min prior to collecting the samples. For determining the particulate concentrations of As, Fe and Mn, 125 mL of sample from each location was filtered using a 60-mL disposable plastic syringe and 0.45-μm membrane filters. The filtered samples were then preserved in the HDPE sampling bottles. After the completion of sampling at all the locations, the samples were sent to the laboratory for analysis. The sampling procedure has been illustrated step-wise (Fig. 3-2). All glass beakers, plastic syringes, and membrane filters were rinsed with De-ionized (DI) water and air dried before every sampling event.

Table 2-11: Filtration at WTP Dorst.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of filters</td>
<td>10</td>
</tr>
<tr>
<td>Design capacity</td>
<td>200 m³/h, 7.4 m/h</td>
</tr>
<tr>
<td>Minimum capacity</td>
<td>50 m³/h, 1.85 m/h</td>
</tr>
<tr>
<td>Maximum capacity</td>
<td>200 m³/h, 7.4 m/h</td>
</tr>
<tr>
<td>Bed height</td>
<td>1.8 m</td>
</tr>
<tr>
<td>Surface area</td>
<td>27 m²</td>
</tr>
<tr>
<td>Grain size of filter media</td>
<td>1 – 1.6 mm sand</td>
</tr>
<tr>
<td>Depth of supernatant water</td>
<td>15 – 50 cm</td>
</tr>
<tr>
<td>Filter run time</td>
<td>96 h</td>
</tr>
</tbody>
</table>
Figure 3-1: Process flow diagram of WTP Dorst, sampling schedule and sampling locations selected for investigation.
The speciation procedure involved collection of samples from the 3 selected locations using a 400 mL glass beaker. After that 125 mL from the collected sample was transferred to a sample bottle (identified as bottle A in Fig. 3-3) for the analysis of total As. About 250 mL of the sample was then filtered through a 0.45 µm filter and stored in another bottle (designated as B in Fig. 3-3) to analyse total dissolved As in the sample. Half of the filtered 250 mL sample in bottle B was then passed through a column packed with the ion exchange resin.

The resin columns used were 12 cm × 15 mm in size and made of polypropylene. Each column was packed with about 20 g of the resin, yielding a resin depth of approximately 10.5 cm. The sample was allowed to flow into the column slowly in a drop wise manner and the effluent of the column was collected in another 125-mL bottle (identified as bottle C in Fig. 3-3). The pH of each sample was measured prior to As speciation and was found to be in the range of 7.6-7.9. In this pH range, As(III) was completely protonated as \( \text{H}_3\text{AsO}_3 \), and As(V) was present in ionic forms (i.e., \( \text{H}_2\text{AsO}_4^- \) and \( \text{HAsO}_4^{2-} \)). Therefore, the resin retained the As(V) and allowed As(III) (i.e., \( \text{H}_3\text{AsO}_3 \)) to pass through the column. Samples stored in bottles A, B and C were then sent to the laboratory for the analysis of total As using ICP-MS. The total As concentration of the resin-treated sample in bottle C was the total dissolved As(III) concentration. As(V) concentration was calculated by subtracting As(III) from the total soluble As concentration of the sample in bottle B.

Sampling for As speciation analysis was carried out once every two weeks. The separation of As(V) from As(III) was carried out on site using a chloride-form strong base anion exchange resin (Amberlite® Ira - 400(Cl)) (Fig. 3-4) manufactured by ALDRICH and then the Aqualab Zuid laboratory measured the total concentration of separated As species. It should be noted that in order to validate the field speciation protocol, the samples were sent to the laboratory for As speciation by HPLC-ICPMS method. The results were consistent with the results of on site speciation protocol. Fig. 3-3 illustrates the procedure of As speciation protocol adopted in this study.

3.2 Bench-scale evaluation and optimization of AOCF

3.2.1 Reagents and stock solutions

All chemicals used in bench-scale experiments were reagent grade and were used without any additional purification. All solutions were supplied by Aqualab Zuid laboratory where they were prepared with DI water. For the production of DI water, the water was pretreated by reverse osmosis (RO) and then distilled. All kinds of glass and plastic ware were acid-washed before use. All low concentration stock solutions i.e., secondary stock solutions, were freshly prepared for each experiment from the concentrated primary stock solutions whenever needed. Stock solution for FeCl₃ (2 g/L Fe) was prepared from FeCl₃.6H₂O, FeSO₄ (1.8 g/L Fe) was from FeSO₄.7H₂O, alum (1.2 g/L Al) was from Al₂(SO₄)₃·18 H₂O and KMnO₄ (0.02 M) from the solid KMnO₄. In order to adjust and maintain pH, dilute hydrochloric acid solution, HCl (10 ml 37% diluted to 1 L) and dilute sodium hydroxide solution, NaOH (10 ml 50% diluted to 1 L) were used. The bottles used for the samples contained 250 µL of concentrated ultra-pure nitric acid (HNO₃). Required experiments were performed using source water of WTP Dorst which was collected at the inlet (IN) of the treatment process (Fig. 3-1). The source water contained at an average 12 µg/L of As, 1.4 mg/L of Fe and 0.04 mg/L of Mn.
3.2.2 **Experimental setup**

Polyethylene jerry cans were used for collecting and storing source water from WTP Dorst which was subsequently used in the bench-scale experiments. The experiments were conducted using a jar test apparatus (Fig. 3-5) which comprised of a set of six jars, each having 1.8 litres capacity. The device consisted of six paddle stirrers that kept a constant uniform stirring rate in all the beakers. The device was provided with a double wall pass warm water to allow experiments at different temperature ranges. A vacuum system allowed collection of water samples from each jar. An arrangement for simultaneous and individual dosing of chemicals was also provided with the assembly of the jar test apparatus which was used during the experiments. A multi-probe device (multi HQ40d) manufactured by HACH (Fig. 3-6) was used to measure pH, temperature and oxidation reduction potential (ORP) of the solutions. 60 mL syringes and 0.45 µm membrane filters were used to filter the water samples for determining the dissolved concentration of the elements of interest. For the preservation of water samples before analysis, 125 mL HDPE bottles were used which were prepared and supplied by Aqualab Zuid laboratory.

3.2.3 **Methodology**

At bench-scale, optimization of AOCF technology was carried out in three steps. Firstly, the most suitable type of coagulant was determined which could achieve high As removal from the source water of WTP Dorst. Three commonly applied coagulants, i.e., FeSO₄, FeCl₃ and Al₂(SO₄)₃ were investigated for this purpose. After the selection of a suit-
able coagulant, the doses of KMnO₄ and the selected coagulant were determined which could achieve residual As concentrations of less than 1 µg/L. The third and final step of bench scale optimization was to determine the optimum process pH for AOCF technology.

Selection of suitable coagulant
For determining the most suitable coagulant for the source water of WTP Dorst three commonly used coagulants, i.e., FeSO₄, FeCl₃ and Al₂(SO₄)₃ were tested in bench-scale experiments. In this thesis, one jar test will mean one run with 6 jars, each simulating a different process condition. The dosing of the coagulants was varied from no coagulant addition i.e, 0 mg/L to 10 mg/L as Fe(II), Fe(III) or Al(III). An increment of 2 mg/L coagulant dose was applied in every successive jar. These experiments were performed at a pH of 8, since the process pH at WTP Dorst varies between 7.6 and 7.8. In order to determine the effect of pH on As removal efficiency of the coagulants, only FeSO₄ and FeCl₃ were used and the pH was varied in the range of 5 and 8.5. Both coagulants were dosed at 6 mg/L as Fe(II) or Fe(III) for determining the effect of pH.

Determination of optimum oxidant-coagulant combination dose
To determine the optimum combination of KMnO₄ and coagulant dose different combinations of KMnO₄ and selected suitable coagulant (FeCl₃) were tested at pH 8. FeCl₃ dose was fixed at 1 mg/L, 2 mg/L and 6 mg/L as Fe(III) in 3 jar tests and for each Fe(III) dose the KMnO₄ dose was varied between 0.5 mg/L and 2.5 mg/L. An increment of 0.5 mg/L KMnO₄ was applied in every successive jar. One of the six jars, in each jar test, was neither dosed with oxidant nor with the coagulant and was used as a control for comparison with baseline conditions.
Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic

Figure 3-4: Anion exchange resin Amberlite® Ira-400(Cl).

Determination of optimum process pH
The experiments performed for optimizing the doses of KMnO₄ and FeCl₃ were performed again but at a slightly lower pH of 7.5 in order to determine the effect of pH on As removal at same oxidant and coagulant dose. A further investigation for studying the pH dependence of As removal was conducted with the help of 2 jar tests in which pH was varied between 6 and 11 and the dosing combinations of 2 mg/L KMnO₄, no FeCl₃ and 2 mg/L KMnO₄ and 6 mg/L FeCl₃ as Fe(III) were applied.

Jar test procedure
Jar tests were performed open to the air to simulate a conventional coagulation process in aerated environment. Each jar was filled with 1.8 L of raw water (source water of WTP Dorst). The jar testing procedure was initiated with the addition of pre-determined aliquots of chemicals (KMnO₄, FeCl₃, FeSO₄, alum etc.) followed by rapid mixing at 300 RPM for 1 minute. If more than one chemical were added, a 20 second interval between the additions of two successive chemicals was maintained and the rapid mixing phase was also prolonged the same duration. In this way complete mixing of each chemical was ensured. In the AOCF experiment, dosing of the oxidant (KMnO₄) preceded the addition of coagulant. After the rapid mixing phase, slow mixing at 50 RPM for 15 minutes was applied which was followed by a final 30 minutes quiescent settling phase. The pH was pre-adjusted and maintained during the coagulation experiments. After each test, approximately 300 mL of the supernatant was sampled from 3 cm below the surface of water, 125 mL filtered immediately through 0.45 µm membrane filter, and preserved in sample bottles containing concentrated HNO₃.

Analysis of water samples
The samples were analysed for total As, Fe and Mn with ICP-MS in accordance with NEN-EN-ISO 17294-2 at Aqualab Zuid laboratory.
3.3 Pilot scale evaluation and optimization of AOCF

3.3.1 Reagents and stock solutions

Mainly two chemicals i.e., FeCl₃ and KMnO₄ were used in the pilot experiments. Stock solution of FeCl₃ (2 %) was purchased from Breustedt Chemie B.V. KMnO₄ solution (0.03 M) was prepared onsite from solid KMnO₄ purchased in powdered form from the treatment plant of Eindhoven. The 125 mL HDPE bottles used for the preservation of samples for As, Fe and Mn contained HNO₃ as a preservative. Samples for NH₄⁺, NO₂⁻ and NO₃⁻ analysis were preserved without acidification. The experiments were performed using the source water of WTP Dorst which contained average concentrations of 12 μg/L As, 1.4 mg/L Fe, 0.04 mg/L Mn and 0.6 mg/L NH₄⁺. The filters of the pilot setup were backwashed with the effluent of WTP Dorst.
3.3.2 Pilot setup

The pilot plant was installed in the main filtration building of WTP Dorst in June 2013. It was designed so that it could represent a pilot scale physical model of the WTP Dorst where process conditions (e.g., residence time of water in different unit processes) similar to the full scale treatment plant could be simulated. The pilot plant consisted of a pair of aeration cascades (Fig. 3-7), a pair of filtration columns (300 mm dia) (Fig. 3-8), a pair of dosing pumps (Fig. 3-9), a pair of containers for FeCl3 and KMnO4 solutions storage (Fig. 3-9) and a network of pipes, sampling points and drains. The schematic diagram of the pilot set-up has been shown (Fig. 3-10). Each dosing pump could dose two columns simultaneously. In one of the columns, virgin sand media (VS media) (1-1.6 mm effective size) was filled and in the other column, the metal oxide coated filter media (MOCS media) extracted from the filters of WTP Dorst was placed (1-1.6 mm effective size). Fig. 3-11 shows the two types of sand media which were used in the pilot study. In each column, the height of the filtration bed was similar to that of WTP Dorst, i.e., 1.8 m. Transport of water between the raw water intake point and cascade aerators and between the cascade aerators and filtration columns was accomplished through 30 mm flexible plastic hoses purchased from Tricoflex Nobel Plastiques. Hard PVC was the construction material used for cascade aerators, filtration columns and various pipe and valve fixtures. For facilitating the sampling at different locations in the treatment train, sample points were provided made of stainless steel. The samples were collected in a 400 mL glass beaker which was pre-rinsed with the water to be sampled. For obtaining dissolved concentrations of different elements 0.45 µm membrane filters and 60 mL plastic syringes were used. 125 mL HDPE bottles were used to preserve samples before analysis in laboratory. The samples were stored at 4 degree celsius. A multi-probe device manufactured by HACH was used for the in situ measurements of pH, ORP and temperature.

The wastewater from the backwashing and excess effluent of the filters were collected, combined and drained to wastewater line of the full scale process types of sand media were used in pilot scale evaluation of AOCF. In one filter VS media was used and in the other filter MOCS media was used. The primary reason to use VS media besides MOCS media obtained from WTP Dorst was to investigate the effect of sand media age (coating) on the efficiency of AOCF technology. The dosing in both the pilot filters was started after the effluent quality similar to that of WTP Dorst was achieved. During the ripening phase of pilot filters, effluent water quality was regularly monitored to investigate the start-up of different removal processes with time. The dosing of the chemicals was increased step-wise to optimize As removal. The detailed methodology of pilot plant operation and sampling during ripening and dosing phases of pilot study has been discussed below.

Start-up of arsenic, iron, manganese and ammonium removal

Before the implementation of AOCF on the pilot scale model of WTP Dorst, both the filters were required to produce effluent with a similar water quality as WTP Dorst produced. Therefore, the change in water quality during the ripening period was monitored to gain insight into the start-up of different removal processes. The ripening of filters continued for a period of 2 months, i.e., from 9-July-2013 to 9-Sep-2013. On the day of pilot plant start-up, the media in both the columns were backwashed for 20 minutes in order to flush out the lose small sized par-
Following the initial backwashing, the normal filter operation was started-up at a filtration velocity of 1 m/h. The decision to apply in the start a slower filtration rate of 1 m/h was based on recommendations in the literature and from the discussions with the filter start-up experts. As soon as the nitrification i.e., NH$_4^+$ removal, started in each filter, the filtration velocity was increased to 5 m/h. The filtration velocity in the filter with MOCS media was increased on 2-Aug-2013 and the filtration velocity in the filter with VS media was increased on 14-Aug-2013. Samples were collected from the aerated streams coming out of the cascade aerators (i.e., influent of the filters/supernatant) and from the effluent of the filters were collected 2 to 3 times per week. The samples were sent to the laboratory after necessary preservation measures for the analysis of total As, Fe, Mn, NH$_4^+$, NO$_2^-$ and NO$_3^-$. For determining the dissolved concentrations of the elements, samples were filtered through 0.45 µm membrane filters and afterwards sent to the laboratory for analysis. The pH, ORP, temperature and the height of supernatant of the filters were measured every day and a log-book was maintained throughout the duration of the ripening period. Both the filters were backwashed averagely twice a week. The criteria of putting the filters on backwash was not the deterioration of water quality, but the head loss through the filter bed, even when the filtration velocities were increased to 5 m/h. The backwashing was carried out only with water during the ripening phase of the filters. The procedure included sending a strong flow of water in reverse direction for 10 min to obtain the bed expansion of 20%.

Evaluation and optimization of AOCF

After the 8 week ripening period of both the filters was over, the pilot scale evaluation of the AOCF started. The filters were operated with a continuous inflow (285 L/h) mode keeping the effluent valve completely open from the start of the filter run. The dosing of chemicals was started on 9-Sep-2013 and step-wise increased over time to optimise the As removal and to evaluate the effect of AOCF on the removal of Fe, Mn &

Figure 3-7: Cascade aerators of the pilot plant (outside and inside view).
NH₄⁺. From 9-Sep-2013 till 2-Oct-2013 a combination of 1 mg/L KMnO₄ and 1.7 mg/L Fe(III) was applied, from 2-Oct-2013 till 10-Oct-2013 a combination of 1.3 mg/L KMnO₄ and 1.7 mg/L Fe(III) was dosed, from 10-Oct-2013 till 17-Oct-2013 a combination of 1.3 mg/L KMnO₄ and 2 mg/L Fe(III) was applied, and finally from 17-Oct-2013 till 15-Nov-20 a KMnO₄ dose of 1.7 mg/L and an Fe(III) dose of 2 mg/L was applied. Different dosing combinations which were maintained throughout the period of the pilot scale study (Table 3-1).

Both the chemicals were dosed in the cascade aerators in such a manner that the KMnO₄ was dosed before the application of FeCl₃. KMnO₄ in the first step (first tray) and FeCl₃ was dosed in the third step of the cascade aerator. The fall of water from a higher to lower step of the cascade aerator ensured the complete mixing of both the chemicals until the water reached the filters. ORP and pH measurements in combination with the dosing pump settings were used to control the doses of KMnO₄ and FeCl₃ in water. The dosing solutions were prepared 2 to 3 times per week depending upon the setting of chemical inputs. The samples were collected approximately 3 to 5 times per week at different instances during the filter runs and a log-book was maintained with the information regarding the sampling time, pH, ORP and the parameters which were analysed. Sometimes more than one samples were collected in a filter run to evaluate the changes in water quality over time during the filter run at a particular combination of chemical dosing. Filter influent samples were collected from the aerated - dosed water stream outcoming from the cascades. Effluent samples were collected from the filtrate sampling tap. Both the filters were backwashed whenever required. The criteria of putting filters on backwash was the deterioration of effluent water quality which was checked daily by filtering the effluents with 0.45 µm filter. The normal operation was stopped when particulate Fe was observed in the membranes after filtration of about 100 mL of each effluent. The backwashing was carried out with a combination of water and compressed air, unlike the start-up phase when the backwashing was accomplished only with the water. The procedure included a start with sending a strong flow of water in reverse direction for 4 min, followed by a air-water rinsing for 5 min and finally

Figure 3-8: Pilot columns filled with VS media and MOCS media.
sending again a strong flow of water in reverse direction for 3 min. A 20 % expansion of filter media was aimed during the backwashing process.

**Analysis of water samples**

For the analysis of total As, Fe and Mn, ICP-MS in accordance with NEN-EN-ISO 17294-2 was used, for NH$_4^+$ a discrete analysis system and spectrophotometric detection, in accordance with NEN-EN-ISO 6604 was used, for NO$_2^-$, a discrete analysis system and spectrophotometric detection, in accordance with or derived from NEN-EN-ISO 6604 was used and for NO$_3^-$, ion chromatography, in accordance with NEN-EN-ISO 10304-1 (low level) or a discrete analysis system and spectrophotometric detection, in accordance with or derived from BS-EN-ISO 6604 (high level) was used.

![Figure 3-9: Dosing pumps and storage containers.](image)

**Table 3-1: Combinations of KMnO$_4$ and FeCl$_3$ doses during the pilot scale optimization of AOCF.**

<table>
<thead>
<tr>
<th>From (Date)</th>
<th>To (Date)</th>
<th>KMnO$_4$ dose</th>
<th>FeCl$_3$ dose as Fe(III)</th>
<th>Number of sampling events</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 - Sep - 2013</td>
<td>2 – Oct - 2013</td>
<td>1 mg/L</td>
<td>1.7 mg/L</td>
<td>16</td>
</tr>
<tr>
<td>2 – Oct - 2013</td>
<td>10 – Oct - 2013</td>
<td>1.3 mg/L</td>
<td>1.7 mg/L</td>
<td>8</td>
</tr>
<tr>
<td>10 – Oct - 2013</td>
<td>17 – Oct - 2013</td>
<td>1.3 mg/L</td>
<td>2 mg/L</td>
<td>5</td>
</tr>
<tr>
<td>17 – Oct - 2013</td>
<td>15 – Nov - 2013</td>
<td>1.7 mg/L</td>
<td>2 mg/L</td>
<td>18</td>
</tr>
</tbody>
</table>
Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic

**Figure 3-10:** Schematic diagram of the pilot plant.

**Figure 3-11:** Filtration media used in pilot investigations. VS media (left) and MOCS media (right).
4. RESULTS AND DISCUSSION

4.1 Arsenic removal processes at WTP Dorst

The summary of As analytical results of the samples collected from selected three locations (Fig. 3-1) at WTP Dorst have been provided (Table 4-1). Total As concentrations at IN (inlet) ranged from 10.9 μg/L to 12.1 μg/L with an average concentration of 11.7 μg/L. Total As concentrations at PF (pre-filtration) ranged from 11.5 to 12.3 μg/L, with an average of 11.8 μg/L. Samples collected at AF (after filtration) contained total As concentrations ranging from 5.5 μg/L to 6.5 μg/L with an average concentration of 6.1 μg/L. Therefore, in general, no reduction of total As was observed between the IN and PF (i.e., during the cascade aeration). However, during the filtration through the sand media As was significantly reduced to an average As removal of 48%. The total As concentration recorded at each sampling location throughout the six week sampling phase, as well as removal percentages calculated for each sampling event are shown (Fig. 4-1). It can be seen that at individual sampling events the percentage removal of As was sometimes recorded between 50 to 60 percent.

For measuring soluble As(III) and As(V) concentration at the selected sampling locations, samples were first filtered through 0.45 μm membrane filters and then analysed for As(III) and As(V). Table 4-1 shows that As(III) concentrations averaged 11.2 μg/L at the IN, 10.2 μg/L at the PF, and 1.0 μg/L at the AF sampling location. Average As(V) concentrations were 0.67 μg/L at the IN, 1.2 μg/L at the PF, and 5.0 μg/L at the AF location. At IN and PF sampling locations, As(III) made up the majority of the total soluble As, however at AF As(V) formed the major part of total dissolved As. The charts showing the fractions of the total As concentration made up by particulate As, As(III), and As(V) at different sampling locations have been presented (Figs. 4-2, 4-3, 4-4). The dominance of As(III) at IN and PF can be explained by the facts that WTP Dorst pumped water from a deep anoxic aquifer where conditions were expected to favor reduced form of As and generally when atmospheric oxygen is the only oxidizing agent, transformation of As(III) to As(V) is expected to be very slow. Bissen and Frimmel (2003) studied As(III) oxidation kinetics and reported that 55 % of total As(III) was oxidized in 5 days when the groundwater was purged with air and pure oxygen. At WTP Dorst cascade aeration was the only treatment between IN and PF and the residence time of water between IN and PF was approximately 5 minutes which was not adequate for the complete oxidation of As(III). The results show that at AF As(V) was the main constituent of total As which raised questions regarding the mechanism of As(III) oxidation in the filter bed. It is well-known from the literature that solid-liquid interfaces in the presence of dissolved oxygen may catalyze the oxidation process of As(III). Ferric iron deposited on the surface of filter sand grains, may facilitate the conversion of As(III) to As(V) by catalytic effects and by direct reaction (Sarkar and Rehman, 2001). It has also been reported that Mn-oxides produced during auto-catalytic Mn removal process can lead to a faster oxidation of As(III) in a time scale of only few minutes (Sevil, 2005). Besides physical-chemical processes, biological mechanisms may also play a role in the oxidation of As(III). However, which mechanism was responsible for As(III) oxidation in the filter bed of WTP dorst remained a question in this study. It should be noted that from the perspective of human health, presence of As(V) form is much preferred than As(III) presence since the toxicity of As(III) is several times higher than As(V).
Determination of the concentration of particulate As at the 3 selected locations provided further insight into the removal mechanism. The results of analysis (Table 4-1) show that particulate As concentrations averaged 0.03 μg/L at the IN, 1.4 μg/L at the PF sampling location, and 0.05 μg/L at the AF sampling location. The increase of particulate As at PF was due to the sorption and coprecipitation of As onto the Fe (OH)₃ flocs formed after the anoxic groundwater came in contact with the atmospheric oxygen because of cascade aeration treatment. It is clear that that an average 62 % of the total Fe was oxidized and converted to Fe(OH)₃ flocs until the water reached PF, on the other hand the entire total Mn remained dissolved in water (Table 4-2). Therefore, the sorption of As could only be attributed to the hydroxides of Fe present at PF sampling point. The average pH was 7.6, 7.7 and 7.7 at the IN, PF, and AF respectively. These pH values are in the range (pH 5.5 to 8.5) where As removal efficiency by Fe(OH)₃ is generally not affected (Sorg, 1993). An interesting aspect of As sorption onto Fe(OH)₃ was that only 1.1 μg/L of As was sorbed or co-precipitated with 0.88 mg/L of total precipitated Fe. It means a sorption of only 1.25 μg As/mg of precipitated Fe took place between IN and PF or in other words, 1.25 μg As/mg of Fe was sorbed in approximately 5 min since the residence time of water between IN and PF was calculated to be approximately 5 min. This low extent of As sorption onto the precipitating phase of Fe may be explained by the presence of As(III) and competitive effects from other anions presents in the source water of Dorst, most importantly silicates and bicarbonates. The source water quality data of WTP Dorst show that an average concentration of 18 mg/L silicates and 251 mg/L bicarbonates were present in the raw water of WTP Dorst. Complete oxidation/precipitation of Mn and approximately 38 % of Fe oxidation/precipitation was accomplished inside the filter bed. Roughly 67 % of the total As was co-precipitated and removed in the filter bed as well.
Table 4-1: Summary of As analytical results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample location</th>
<th>Units</th>
<th>Number of samples</th>
<th>Minimum concentration</th>
<th>Maximum concentration</th>
<th>Average concentration</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (total)</td>
<td>IN</td>
<td>μg/L</td>
<td>6</td>
<td>10.9</td>
<td>12.1</td>
<td>11.7</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>PF</td>
<td>μg/L</td>
<td>6</td>
<td>11.5</td>
<td>12.3</td>
<td>11.8</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>AF</td>
<td>μg/L</td>
<td>6</td>
<td>5.5</td>
<td>6.5</td>
<td>6.1</td>
<td>0.36</td>
</tr>
<tr>
<td>As (total soluble)</td>
<td>IN</td>
<td>μg/L</td>
<td>6</td>
<td>10.8</td>
<td>12.0</td>
<td>11.6</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>PF</td>
<td>μg/L</td>
<td>6</td>
<td>10</td>
<td>11.2</td>
<td>10.7</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>AF</td>
<td>μg/L</td>
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<tr>
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<tr>
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<td>PF</td>
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<tr>
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<tr>
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<td>1.0</td>
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<td>1.2</td>
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<tr>
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<td>AF</td>
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From the results, it can be estimated that the Fe and Mn oxide coating which had been developed over the period of 17 years on the filter media grains also played a vital role in As adsorption during the passage of water through the filter bed. Careful visual observation of the sand grains indicated a brownish-black thick coating on the grains of filter media which could be attributed to the deposition of Fe and Mn oxides on the sand grains. According to Petrusevski et al. (2007) As exhibit a great tendency to adsorb to the positive adsorption sites present on the surface of the metal oxide based coating on the grains and in fact this is the principle As removal mechanism of IOCS which is a by product of many ground water Fe removal plants. It can be noted from the As speciation results that during the flow of water through the filter bed As(III) was almost completely transformed to As(V). This oxidation of As may be accomplished by the Mn-oxides formed during the autocatalytic removal of Mn. When MnO₂ oxidizes As(III) by the reaction \( H_3AsO_3 + MnO_2 \rightarrow HAsO_4^- + Mn^{+2} + H_2O \), Mn^{+2} ions are formed which can adsorb onto the MnO₂ and give it a positive surface charge. These positively charged sites on MnO₂ surface facilitate the removal of As(V) (Bajpai and Chaudhary, 1999). Therefore, it seems convincing that the oxides of Fe and Mn played a vital role in the As(III) oxidation and subsequent removal through the filter bed. The oxidation can be primarily attributed...
to the oxides of Mn and the sorptive removal to the oxides of Fe. Further research to evaluate the oxidative and adsorptive capacity of filter media grains obtained from WTP Dorst in controlled laboratory conditions is necessary to understand the mechanisms completely.

<table>
<thead>
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<th>Parameter</th>
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<td></td>
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</tbody>
</table>

Total Fe: IN mg/L 6 1.3 1.5 1.4 0.05
| PF mg/L 6 1.3 1.5 1.4 0.07
| AF mg/L 6 <0.01 <0.01 <0.01 -

Total Mn: IN mg/L 6 0.04 0.05 0.04 0.005
| PF mg/L 6 0.03 0.04 0.04 0.005
| AF mg/L 6 <0.01 <0.01 <0.01 -

Dissolved Fe: IN mg/L 6 1.3 1.4 1.4 0.05
| PF mg/L 6 0.3 0.7 0.52 0.16
| AF mg/L 6 <0.01 <0.01 <0.01 -

Dissolved Mn: IN mg/L 6 0.04 0.05 0.04 0.005
| PF mg/L 6 0.03 0.04 0.04 0.005
| AF mg/L 6 <0.01 <0.01 <0.01 -

4.2 Bench scale evaluation and optimization of AOCF

4.2.1 Determination of suitable coagulant

Before interpreting the results of bench-scale experiments with the source water of WTP Dorst, one must note that the previous section has discussed in detail that more than 95 % of the total As in the groundwater abstracted and used at WTP Dorst occurs as As(III). The effects of nature of coagulant and coagulant dose on As removal at pH 8 are presented (Fig. 4-5). Concentration of total metal added as coagulant ranged from 2 to 10 mg/L. It corresponds to 5.44 mg/L to 27.2 mg/L of FeSO₄, 5.8 mg/L to 29.1 mg/L of FeCl₃ and 25.4 mg/L to 126.8 mg/L for alum (Al₂(SO₄)₃). It can be noted (Fig. 4-5) that for both the Fe based coagulants As removal increased with the increase in coagulant dose. At the highest coagulant dose, i.e., 10 mg/L Fe(II) and Fe(III), the As removal was 82 % and 90 %, respectively. However, the As removal remained between 14 % and 25 % for the entire range of alum dosing.
Figure 4-2: Inlet (IN) As speciation and particulate concentration.

Figure 4-3: Pre- filtration (PF) As speciation and particulate concentration.

Figure 4-4: After filtration (AF) As speciation and particulate concentration
The maximum As removal could be achieved at an alum dose of 10 mg/L as Al(III). The significantly lower As removal efficiency of alum may be attributed to the oxidation state of As, i.e., it was As(III) in the raw water and to the coagulation pH which was not optimum for alum coagulation. According to USEPA (2000), the suitable pH range for alum coagulation is 5 to 7. Both Al and Fe hydroxides possess an adsorptive capacity for dissolved As species in water. When Fe or Al based salt such as FeSO₄, FeCl₃ or Al₂(SO₄)₃ are dissolved in water, they hydrolyse to produce insoluble reaction products; amorphous hydroxide phases. Two mechanisms play vital role in As removal through coagulation. One is co-precipitation of As (inclusion, occlusion, entrapment) and the other is adsorption on the surface sites provided by the hydrolyzing reaction products of the added coagulants. For this reason, it could be expected that with an increase of coagulant dose, an enhanced As removal would be observed. The results (Fig. 4-5) show that FeCl₃ exhibited the most efficient As removal, followed by FeSO₄. Through the entire range of coagulant dosing, the As removal was on average 10 % higher in case of FeCl₃ in comparison to FeSO₄. The residual or dissolved concentrations of Fe in case of both FeCl₃ and FeSO₄ were negligible which means that complete precipitation of Fe took place even when Fe(II) was added.

Therefore, the relatively lower As removal efficiency exhibited by FeSO₄ can only be attributed to the presence of increased amount of sulphate ions which were added to the solutions with FeSO₄. It is worth-mentioning that each milligram of FeSO₄ added to water gives approximately 0.65 mg of sulphates to the solution. Sulphates possess a tendency to compete with As for the adsorption sites at the surface of Fe(OH)₃. Qiao et al. (2012) have studied the effects of sulphates on As(III) and As(V) removal and have reported a decrease in As removal at all the sulphate concentrations in the range of 5 to 40 mg/L. Wilkie and Hering (1995) had also reported competitive effects from sulphates towards As. It can be noticed from the results (Fig. 4-5) that even when no coagulant was dosed, an As removal of 20 % to 30 % was observed. This was due to the presence of 1.4 mg/L dissolved Fe(II) in the source water of WTP Dorst. Towards the end of each jar test, the initially dissolved concentration of Fe(II) was completely oxidized and precipitated, which not only was the reason for As removal in un-dosed jars, but also contributed to the total As removal in the dosed jars.

![Figure 4-5: Effect of coagulant type and dose on As(III) removal at pH 8.](image-url)
The two Fe based coagulants, FeSO₄ and FeCl₃, were evaluated in different pH conditions as well, keeping the doses fixed at 6 mg/L in terms of Fe(II) and Fe(III) respectively. The results presented (Fig. 4-6) reflect the typical pH dependent removal behavior of As(III) by coagulation through Fe salts. Pallier et al (2011) reported that As(III) removal depend only on coagulant dose and surface adsorption sites of Fe(OH)₃ rather than on coagulation pH. However, the results are not consistent with their observations. The reason for this difference may be the fact that they had used much higher coagulant doses and narrower pH range for their evaluation. The pH dependent As removal which has been presented (Fig. 4-6) was, however, consistent with Qiao et al. (2013) who also reported pH dependency of As(III) removal in a similar manner. It can be noticed that the percentage As removal for both the coagulants generally showed an increasing trend in the pH range of 5 to 8.5. This kind of similarity in removal behavior with pH can be attributed to the similar final adsorptive phase formed by both type of coagulants, i.e., Fe(OH)₃. The only difference was the mechanism of Fe(OH)₃ formation, which for FeCl₃ was comparatively straight forward and included dissolution of FeCl₃ and then immediate formation of insoluble hydrolysis products. In contrast, in case of FeSO₄, the Fe(II) was oxidized first to Fe(III) and then this insitu formed Fe(III) followed the same process as Fe(III) provided by FeCl₃ to form the insoluble hydroxide phase. This difference of Fe(OH)₃ formation mechanism may also be responsible for the lower As removal by FeSO₄ (compared to FeCl₃), besides the interaction from sulphates. It might also be possible that during the oxidation of Fe(II) in the presence of air, flocs of Fe(OH)₃ grew much immediately which resulted in the reduced availability of surface sorption sites to the dissolved As in water.

From the evaluation of coagulant type in different process conditions i.e., different coagulant doses and pH, it became clear that the maximum As removal from the source water of WTP Dorst could be achieved with FeCl₃. Previously, Gupta and Cheng (1978); Cheng et al. (1994); Hering et al. (1997); and Donmez and Akbal, (2011) have also reported similar As removal efficiency of FeCl₃ in their experiments. Therefore, FeCl₃ was selected as a coagulant to be used in further evaluation of AOCF and from here onwards all the experiments, either at bench-scale or pilot scale, were performed with FeCl₃.

![Figure 4-6: Effect of pH on As(III) removal efficiency by Fe based coagulants (coagulant dose = 6 mg/L as Fe).](image-url)
4.2.2 **Determination of optimum oxidant – coagulant combination dose**

Before the discussion of results related to this section it is important to discuss the oxidation processes of different constituents of the source water of WTP Dorst. The source water used in bench-scale scale jar tests contained on average 1.4 mg/L of Fe(II), 11.7 µg/L of As(III) and 0.04 mg/L of Mn(II). According to the stoichiometric calculations based on the Eqs. 4.1, 4.2 and 4.3, the KMnO₄ dose required for the oxidation of 1 mg/L Fe(II) is 0.94 mg/L, for 1 mg/L As(III) is 1.58 mg/L and for 1 mg/L Mn(II) is 1.92 mg/L. In situations where Fe(II) co-exists with As(III), KMnO₄ reacts with Fe(II) and oxidizes it to Fe(III) before it can oxidize As(III) to As(V) (Guan et al., 2009). Therefore, an additional amount of KMnO₄ is always required to oxidize both the Fe(II) and the As(III) completely. The oxidation of Mn(II) may also consume permanganate, however it is oxidized after the redox potential of the aqueous system goes above the oxidation range of As(III). It is also worth-mentioning that according to USEPA (1999) the actual amounts of KMnO₄ required in practice have been found to be less than that indicated by stoichiometry. It may be due to the catalytic influence by MnO₂ formed during the oxidation reactions (O’ Connell, 1978).

\[ 3\text{Fe}^{2+} + \text{KMnO}_4 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_3(s) + \text{MnO}_2(s) + \text{K}^+ + 5\text{H}^+ \]  
\[ 3\text{H}_3\text{AsO}_3 + 2\text{KMnO}_4 \rightarrow 3\text{HAsO}_4^{2-} + 2\text{MnO}_2(s) + 2\text{K}^+ + 4\text{H}^+ + \text{H}_2\text{O} \]  
\[ 3\text{Mn}^{2+} + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2(s) + 2\text{K}^+ + 4\text{H}^+ \]

For determining the most suitable KMnO₄-FeCl₃ dosing combinations for AOCF a series of jar tests was performed at pH 8. Varying amounts of KMnO₄ in combination with different fixed Fe(III) doses were applied. The results (Fig. 4-7) show that at pH 8 the residual As decreased with increase in the concentration of KMnO₄ at all the three doses of FeCl₃ i.e., 6 mg/L, 2 mg/L, and 1 mg/L as Fe(III). The minimum amount of KMnO₄ required to achieve a residual As concentration of less than 1 µg/L was 0.5 mg/L with a subsequent Fe(III) dose of 6 mg/L. At Fe(III) dose of 2 mg/L, 1 mg/L of KMnO₄ was required to reduce the residual As concentration to below 1 µg/L. In cases, when only 1 mg/L of Fe(III) was added and in cases when no coagulant was dosed for treatment, residual As could not be reduced to less than 1 µg/L, even at the highest KMnO₄ dose of 2.5 mg/L. It should be noted (Fig. 4-7) that the oxidation of Fe(II) and subsequent precipitation to remove As (initial As was approximately 12 µg/L) concentration was occurred even if no KMnO₄ was added (control data did not show any dissolved Fe left in jars after the tests). It was because the experiments were performed open to air and during the complete duration of one jar test complete oxidation of Fe(II) was expected.

4.2.3 **Determination of optimum process pH**

In order to investigate the effect of pH on As removal by AOCF jar tests (similar to that were performed in the previous section) were performed at a slightly lower pH i.e., pH 7.5. The results of As removal with different KMnO₄-FeCl₃ dosing combinations are presented (Fig. 4-8). A general trend of increased As removal at higher KMnO₄ dose was consistent with the results at pH 8 (Fig. 4-7). However, slightly lower residual As concentrations were achieved at each KMnO₄-FeCl₃ combination. It can be noted that at a Fe(III) dose of 2 mg/L in combination with 0.5 mg/L of KMnO₄ residual As was adequately reduced to lower than 1 µg/L. Similarly, a KMnO₄ dose of 1 mg/L in combination with Fe(III) dose of 1 mg/L was also adequate to reduce As
to less than 1 µg/L. It seemed that the removal of As by AOCF was strongly dependent upon the process pH, therefore another series of bench-scale experiments was performed to investigate further the effect of pH on As removal. The influence of pH was evaluated in a broader pH range of 6 to 11. The results (Fig. 4-9) show that the residual As concentrations were lower at low pH values, i.e., at and below neutral pH. However, the residual As for both the dosing combinations (KMnO₄=2 mg/L, Fe(III)=6 mg/L, and only KMnO₄=2 mg/L), increased consistently with an increase in pH, especially in the range 8 to 11. This trend of pH dependent As removal may be ascribed to the pH dependent properties of Fe-hydroxides formed insitu i.e., by the precipitation of initially dissolved Fe(II) and those formed by the hydrolysis of FeCl₃. The adsorption onto the surface of Fe-hydroxides directly correlates with the pH of the solution in which hydroxides exist. The point of zero charge (PZC) of Fe(OH)₃ is reported to vary between 7 and 9. AT the PZC the net charge on the precipitated Fe(OH)₃ surface is zero, below the PZC the surface of Fe(OH)₃ possesses higher number of positively charged adsorption sites, and the surface possess an overall negative charge above the PZC.

The significant variation in the residual As concentration with pH (Fig. 4-9) can be adequately explained by the variation of number of surface adsorption sites with the pH. The pH also influenced the speciation of As(V), which was the principle form of As after a KMnO₄ dose of 2 mg/L was applied. As(V) became more negatively charged with increasing pH (Fig. 2-5) and hence a more repulsion started to occur between the net negatively charged surfaces and the negatively charged As(V) ions. This repulsion reduced the overall As sorption and subsequent removal.

The pH dependence of As removal in AOCF may also be discussed from another perspective. It has been reported that depending upon the pH, different amounts of MnO₂ are formed in situ by the reduction of KMnO₄ (Weast, 1990; Guan et al., 2009). In acidic conditions the oxidation half-reaction by permanganate is Eq. 4.4: 

Figure 4-7: Residual As concentrations at different KMnO₄-FeCl₃ combinations at a pH 8.
Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic

\[ \text{MnO}_4^- + 8 \text{H}^+ + 5 e^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O} \quad \text{E}_0 = +1.51 \text{ V} \quad (4.4) \]

And under weak acidic, neutral and weak alkaline conditions, the half-reaction is Eq. 4.5;

\[ \text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 e^- \rightarrow \text{MnO}_2(s) + 4\text{OH}^- \quad \text{E}_0 = +0.588 \text{ V} \quad (4.5) \]

The reactions show that as the pH increases from acidic towards mild acidic region, the formation of soluble Mn\(^{2+}\) ions is suppressed. Instead, the oxidation of both the Fe(II) and As(III) produce solid Mn-oxides in neutral to mild alkaline pH values. MnO\(_2\) have been reported to exhibit adsorption capacity for As(V) (Guan et al., 2009; Bajpai and Chaudhary, 1999). Therefore, it may be possible that the better As removal observed at mild acidic, neutral and mild alkaline pH values (i.e., 6 to 8) was due to the presence of solid Mn-oxides. However, as a matter of fact, Mn-oxides exhibit significantly lower As adsorption compared to Fe-oxides. Guan et al. (2009) reported only up to 5.6% of As(V) removal by MnO\(_2\) formed in situ in their study.

**Figure 4-8: Residual As concentrations at different KMnO\(_4\)-FeCl\(_3\) combinations at pH 7.5.**

**Figure 4-9: Influence of pH on As(V) removal.**
4.2.4 Summary of bench-scale investigations

FeCl₃ was identified as the most appropriate coagulant for use in As removal effort from the source water of Dorst. It showed an overall better As removal efficiency than its competitors, i.e., FeSO₄ and alum, at all the pH values between 5 and 8.5. However, reduction of As to less than 1 µg/L was not achieved with only Fe(III) dose in the range of 2-10 mg/L. When advanced oxidation with KMnO₄ was combined with the FeCl₃ coagulation treatment, significant increase in As removal was noticed and residual As levels lower than 1 µg/L were achieved with various KMnO₄-FeCl₃ combination dosings. Table 4-3 presents the optimized oxidant-coagulant dosing combinations and related pH values which lowered residual As concentration to less than 1 µg/L.

Table 4-3: Optimized dosing combinations and respective pH values.

<table>
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<tr>
<th>pH</th>
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<tr>
<td>8</td>
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4.3 Pilot scale evaluation and optimization of AOCF

4.3.1 Start-up of arsenic, iron, manganese and ammonium removal

Start-up of arsenic removal

Two types of filtration media were used in pilot scale evaluation of AOCF. In one filter VS media (virgin sand media) was used and in the other filter MOCS (metal oxide coated sand media) extracted from the full scale filters of WTP Dorst was used as filtration media. The principle reason to use VS media besides MOCS media was to investigate the effect of sand media age and its surface metal oxide coating on the As removal efficiency of AOCF technology. Before the implementation of AOCF technology at a pilot scale model of WTP Dorst, achieving pilot effluent quality comparable to that of WTP Dorst was a pre-requisite to obtain Dorst-like conditions. Therefore, both the filters were ripened over a period of 8 weeks to achieve desired filtrate quality. During this period samples were regularly collected to monitor the changes in overall effluent quality of both the filters. The updates regarding As removal during the ripening phase by both types of filter media are shown (Figs. 4-10 and 4-11). It can be noticed that in both the filters As removal started soon after the inflow to the pilot plant was initiated, indicating the physical-chemical nature of the As removal mechanism. A general increase in total As concentrations of both the effluents was observed which can be attributed to the fact that the filtration velocity in each filter was fixed at 1 m/h in the starting few weeks and after the start of NH₄⁺ removal in the filters it was increased to 5 m/h. In filtration processes the removal of Fe(OH)₃ flocs is generally better accomplished at lower filtration rates which results in a better removal of adsorbed As as well, if present. It can also be noticed from the the results (Figs. 4-10 and 4-11) that an averaged 6 µg/L total As concentration was achieved in the effluent of MOCS media which was slightly lower than the average total As concentration achieved in the effluent of VS media, i.e., 7.5 µg/L. This marked difference in removal efficiencies of the two media can be attributed to the presence of adsorptive Fe and Mn oxide based
coating on the sand grains of MOCS media. It has been reported in the literature that Fe and Mn oxides (e.g. Fe₂O₃, FeOOH, Mn₃O₄, MnO₂), when formed in the filter bed and deposited on media grains, can remove significant amounts of dissolved As by providing positively charged sorption sites depending upon the pH (Petrusevski et al., 2007). The MOCS extracted from the full-scale filters of WTP Dorst had been in use for over 17 years which had resulted in the development of a thick oxide based coating on the particles of sand. The Fe content of the raw water, pH and length of time in use generally are the influencing factors to the rate of growth of the Fe and Mn oxide coating (Buamah, 2009). In contrast, the VS media did not possess the metal oxide coating which could be observed by the visual analysis of both types of filter media (Fig. 2-11). For VS media it was expected that the As removal efficiency would increase gradually over the period of few weeks, however during the complete 8 weeks of ripening period the average effluent As concentration remained consistently 7.5 µg/L. Infact, the residual As concentrations increased slightly after the filtration velocity was increased to 5 m/h. It is worth-mentioning that the average effluent As concentration of MOCS filter (6 µg/L) was similar to the average effluent As concentration of WTP Dorst (6.1 µg/L). Furthermore, both types of filter media were efficient enough from the start to produce effluents with an average As concentration of lower than the accepted drinking water limit, i.e., 10 µg/L.

**Start-up of iron removal**

The developments regarding influent and effluent Fe concentrations of both the filters have been presented (Figs. 4-12 and 4-13). In the raw water 1.4 mg/L of Fe(II) was present. Right from the start, Fe removal was being adequately removed in both the filters. It can be noticed that after the cascade aeration approximately 0.6 mg/L of Fe was still in the dissolved Fe(II) form. However, while passing through the filters the entire dissolved concentration of Fe(II) was oxidized and removed to produce effluents having less than 0.01 mg/L of total average Fe concentration. A slight upward trend in dissolved Fe concentrations in both the influents can be observed (Figs 4-12 and 4-13).

![Figure 4-10: Influent and effluent As concentration during start-up (VS media).](image-url)
This increase in dissolved influent Fe concentrations was consistent for both the filters and was due to the increase in filtration velocity from 1 m/h to 5 m/h. Actually, when the filtration velocity was increased it resulted in decreased contact time of water in the aeration process and therefore, the precipitation of Fe occurred to a lower extent before the water entered the filtration beds. When water, with some concentration of dissolved Fe(II), enters into a rapid sand filter, the dissolved Fe is simultaneously being removed by two processes i.e., a part of the dissolved Fe adsorbs to the filter media due to its positively charged ionic nature and then gets oxidized at the surface of sand grain in the presence of dissolved oxygen, on the other hand the remaining part of Fe(II) is simultaneously being oxidized in the aqueous phase into solid reaction products i.e., Fe(OH)₃ flocs which subsequently get removed by settling, sorption and straining in the filter bed.

**Figure 4-11: Influent and effluent As concentration during start-up (MOCS media).**

**Figure 4-12: Influent and effluent Fe concentration during start-up (VS media).**
Figure 4-13: Influent and effluent Fe concentration during start-up (MOCS media).

Start-up of Mn removal
The developments regarding the Mn removal by both the filter media have been shown (Figs. 4-14 and 4-15). It has been discussed in previous sections that the full scale filters of WTP Dorst removed Mn by autocatalytic oxidation/adsorption mechanism. Therefore, the Mn removal was expected to started in MOCS media as soon as the filtration was initiated. It can be noted from the results (Fig. 4-15) that the MOCS produced consistently an effluent with a total Mn concentration of less than 0.01 mg/L throughout the ripening phase. However, the VS media took approximately 5 weeks (40 days) until the effluent Mn levels started to decrease, though not lowered to less than 0.03 mg/L. It can be noted that even after a period of 6 weeks ripening, the Mn was not completely removed to below 0.02 µg/L (BW standard) in VS filter media. The reason for slow start-up of Mn removal in VS was the absence of catalytic/adsorptive Mn-oxide coating on the grains of filter media. Basically in the rapid sand filters, the dissolved influent Mn(II) is first adsorbed onto the filter media and then gets oxidized thereby creating new and more adsorption sites that enhance further Mn removal. If the Mn oxide coating does not exist on the sand grains (as it was in case of VS media), the adsorption of Mn(II) and subsequent oxidation to MnO2 does not occur. In aqueous environments the oxidation of Mn(II) by atmospheric oxygen below pH 9 is a very slow process. That is why the removal mechanism of Mn is not similar to the removal mechanism of dissolved Fe in which dissolved Fe(II) precipitates as Fe(OH)3 fairly rapidly and get removed by physical separation. From the Figs. 4-14 and 4-15 it can also be observed that the concentration of particulate (oxidized) Mn was negligible in the influent of both the filters. In order to speed-up the ripening of VS media for Mn removal, besides low filtration velocity, backwashing without air was another technique which was adopted. Actually, when compressed air is passed through filter media, it scrubs-off freshly developed Mn deposits from the sand grains which could result in slow start-up of Mn removal. Another technique which could also be adopted for rapid Mn start-up was the continous or periodic inflow of higher Mn concentrations through the media. However, this option was not evaluated in this research. It was expected
that the desired Mn removal would be achieved through the VS media when the KMnO$_4$ would be dosed for the advanced oxidation of As(III). It can be noticed (Fig. 4-14) that when the filtration through VS media was started, some Mn was released from the media initially. Normally, such release of metallic ions can be expected from a newly placed filter media and this release has been reported to diminish with the flushing of filter media in time.

**Star-up of ammonium removal**

One of the particular characteristics of anaerobic groundwaters is the frequent presence of NH$_4^+$, the quantity of which is dependent upon the presence of organic matter in the soil. The developments regarding NH$_4^+$ removal in both the filters are shown (Figs. 4-16 and 4-17).

![Figure 4-14: Influent and effluent Mn concentration during start-up (VS media).](image)

![Figure 4-15: Influent and effluent Mn concentration during start-up (MOCS media).](image)
The raw water contained an average NH4+ concentration of 0.6 mg/L. It can be observed (Fig. 4-17) that from the start of pilot operation NH4+ was adequately being removed from the raw water by the MOCS media. In contrast, the VS media took approximately 4 weeks to start reducing NH4+ concentrations in the effluent to below 0.03 mg/L (Fig. 4-16). It can be observed from the results that as the NH4+ concentrations decreased in the effluent of VS media, the NO3- concentrations increased, suggesting the removal of NH4+ by bacteriological nitrification process which is catalysed through the metabolic activity of two groups of bacteria, i.e., nitros-bacteria and nitro-bacteria. The two step oxidation of NH4+ can be represented by the Eqs. 4.6, 4.7 and 4.8.

\[
2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \quad \text{(nitroso-bacteria)} \quad (4.6)
\]

\[
2NO_2^- + O_2 \rightarrow 2NO_3^- \quad \text{(nitro-bacteria)} \quad (4.7)
\]

**Total oxidation reaction**

\[
NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (4.8)
\]

To develop the bacterial species which carry out nitrification, aerobic conditions accompanied by continuous filtration is necessary. In order to promote the growth of nitrifying bacterial species in VS media, backwashing supernatant of the MOCS media was mixed with the influent of VS filter periodically for some days. A handful of sand was also exchanged between the filters to achieve an early start-up of NH4+ removal in VS media. It is worth-mentioning here that the complete oxidation of NH4+ to NO3- is necessary in any drinking water filtration/treatment system because the presence of NO2- in drinking water can pose serious health related risks for the consumer. Nitrite (NO2-) concentrations were also monitored during the ripening phase and found negligible in both the effluents when NH4+ was completely removed, suggesting a complete oxidation process.

\[R^2 = 0.4414\]
\[R^2 = 0.0056\]
\[R^2 = 0.8492\]

**Figure 4-16: Influent and effluent NH4+ concentration during start-up (VS media).**
4.3.2 Evaluation and optimisation of AOCF

Optimisation of As removal
Arsenic removal efficiency of AOCF technology was evaluated by applying different combinations of KMnO₄ and FeCl₃ doses at a pilot scale physical model of WTP Dorst. From 9-Sep-2013 to 2-Oct-2013, KMnO₄ and Fe(III) were dosed at 1 mg/L and 1.7 mg/L respectively, from 2-Oct-2013 to 10-Oct-2013, KMnO₄ and Fe(III) were doses at 1.3 mg/L and 1.7 mg/L respectively, from 10-Oct-2013 to 17-Oct-2013, 1.3 mg/L of KMnO₄ and 2 mg/L of Fe(III) were dosed and finally from 17-Oct-2013 to 15-Nov-2013 1.7 mg/L of KMnO₄ and 2 mg/L of Fe(III) were dosed to optimise As removal so that residual As concentration of less than 1 µg/L could be achieved. The developments regarding total As concentrations in the effluents of VS media and MOCS media over the entire 10 weeks study period have been shown (Figs. 4-18 and 4-19). It is evident from the results that the residual As concentration in the effluents of both the filter media remained consistently lower than 2 µg/L throughout the evaluation study and with all the dosing combinations tested in this pilot study. However, As concentrations lower than 1 µg/L could only be achieved in the effluent of VS media when a combination of 1.7 mg/L KMnO₄ dose and 2 mg/L of Fe(III) dose was applied.

It can be observed (Figs. 4-18 and 4-19) that as soon as the first dosing combination was applied, As level in effluent of VS media was lowered to between 2 and 1.5 µg/L. In contrast, the MOCS media which was obtained from the full scale filters of WTP Dorst reacted slowly to reach an equilibrium state to produce such low As concentrations, i.e., less than 2 µg/L. As. These low As concentrations in the effluents of both the filters were consistent with the results of previously carried out jar test experiments at similar KMnO₄ and FeCl₃ doses. For example, when a KMnO₄ dose of 1 mg/L and Fe(III) dose of 1.5 mg/L at was applied in a jar test to evaluate As removal at pH 8, a residual As concentration of less than 2 µg/L could be achieved. However, it must be realized that in lab scale jar tests the filtration is generally accomplished by 0.45 µm
membrane filters. In order to optimise the As removal and achieve lower effluent As concentrations, KMnO₄ dose was increased to 1.3 mg/L in both the treatment trains. Unexpectedly, no pronounced reduction in As concentrations was observed in both the effluents. The primary reason for not achieving further reduced residual As concentrations was the inadequacy of the permanganate dose to completely oxidize As(III). Since KMnO₄ was dosed in the first step of the cascade aerator, it was consumed by the oxidation of dissolved Fe(II), before it could completely convert As(III) to As(V). One potential measure to reduce the consumption of KMnO₄ by dissolved Fe(II) could be to introduce KMnO₄ after the atmospheric oxygen had oxidized a part of Fe(II). However, this option was not evaluated in the pilot study.

**Figure 4-18:** Effluent As concentration (total) after the implementation of AOCF (VS Media). AOCF implemented on 03-Sep.

**Figure 4-19:** Effluent As concentration (total) after the implementation of AOCF (MOCS Media). AOCF implemented on 03-Sep.
From 10-Oct-2013, Fe(III) dose was increased to 2 mg/L. With a 0.3 mg/L increase in the dose of coagulant (FeCl₃), only a slight increase of As removal by both the filter media was observed. The resulting effluent As concentrations were in the range of 1 and 1.5 µg/L. It seems that the level of As removal difficulty increases exponentially with the decrease in concentrations to be removed. The dosing requirements does not seem to be linear with respect to the As concentrations to be removed. At the dosing combination of 1.3 mg/L KMnO₄ and 2 mg/L Fe(III), As(III) still was not completely oxidized before it entered the filter media. Therefore, in order to achieve complete oxidation of As(III), the KMnO₄ dose was increased to 1.7 mg/L from 17-10-2013. The increase in KMnO₄ dose resulted in a residual As concentration of lower than 1 µg/L in the effluent of VS media. Arsenic levels less than 1 µg/L in the VS effluent remained consistent throughout the later duration of pilot scale investigation, as can be observed (Fig. 4-18). In contrast to the effluent of VS media, the As concentration in the effluent of MOCS media could not be lowered further, i.e., lower than 1 µg/L, though a decrease in dissolved As concentration in the influent was observed.

The comparison of dissolved and total As concentrations (Figs. 4-20 and 4-21) show that in both the effluents almost entire As concentration was in dissolved form. Further, it can be noticed that in the influents of both the filter media, the dissolved concentrations of As were comparable. Therefore, the relatively higher As concentration in the effluent of MOCS media may potentially be due to difference in sorption-desorption processes inside the two filter beds. The exact mechanism responsible for the difference in effluent As concentrations remained unclear and needs to be investigated in well controlled laboratory scale experiments. One possibility could be the difference in effective size of the sand grains of the two media. The sand grains of the MOCS media had grown in size because of continuous use over more than 17 years (development of metal oxide coating on the surface took place, the reason why this media is named metal oxide coated sand media). In contrast, the VS media grains had not grown to that extent after only 16 weeks of use in pilot scale groundwater treatment.

![Figure 4-20: Total and dissolved influent and effluent As concentrations after the implementation of AOCF (VS Media).](image-url)
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**Figure 4-21: Total and dissolved influent and effluent As concentrations after the implementation of AOCF (MOCS Media).**

**Effect on Fe and Mn removal processes**

The concentrations of total and dissolved Fe in the influents and effluents of VS and MOCS media respectively are shown (Figs. 4-22 and 4-23). It can be seen that the average dissolved Fe concentration in the influents of both the filter columns decreased over time. This decrease in dissolved concentrations can be attributed to step-wise increase in KMnO₄ dosing i.e., from 1 mg/L to 1.7 mg/L. However, even at 1.7 mg/L of KMnO₄, complete conversion of dissolved Fe to particulate reaction products could not be achieved. The 1.7 mg/L of KMnO₄, on the basis of stoichiometric calculations, was adequate to oxidize the entire 1.4 mg/L Fe(II) present in the raw water. Further, the water was aerated in cascade aerators as well. Therefore, it may be possible that the 0.2 to 0.3 mg/L of Fe, shown in the Figure as dissolved Fe in the influents, was not the dissolved Fe(II), rather it was Fe(III) which could not be filtered through 0.45 µm filtered. Another possibility could be the inadequate contact time of water in the air before the water entered into the filters. Total Fe concentrations (Figs 4-22 and 4-23) in the effluent of both the filters were lower than 0.05 mg/L during the filter runs.

Manganese removal remained undisturbed in case of filter with MOCS media after the AOCF technology had been implemented at the pilot scale model of WTP Dorst. Total and dissolved Mn concentrations in the effluents and influents of both the filters over the entire evaluation period have been provided (Figs. 4-24 and 4-25). It can be noticed that the effluent of VS media column contained relatively high concentrations of Mn for a few weeks after the dosing had been started. It was because, when the dose of 1 mg/L KMnO₄ and 1.7 mg/L Fe(III) was started on 9-Sep-2013, the Mn removal was not complete in the VS media. As discussed earlier, Mn removal is a auto-catalytic oxidative/adsorptive process which is accomplished by the presence of a Mn-oxide coating in the filter media. This coating requires time, in some cases, over the period many weeks, to grow and develop on the surface of media grains depending upon the inflow Mn concentration. Therefore, when the dosing of KMnO₄ was started, the dissolved Mn concentration in the
influent of both the filters increased which facilitated a rapid development of MnO₂ layer on the sand grains of VS media. It can be noted (Fig. 4-24) that the Mn concentration in the effluent of VS media was subsequently dropped below 0.01 mg/L. Contrary to VS media, the MOCS media did not show any increase or decrease in the effluent Mn levels after the new technology had been applied. It is shown (Figs. 4-24 and 4-25) that the dissolved influent Mn concentrations were reduced over time. This could be explained by the step-wise increase in KMnO₄ dose which resulted in the rapid oxidation of Mn(II) to solid MnO₂, completed even before the water entered the filter bed.

Figure 4-22: Effluent and influent Fe concentrations after the implementation of AOCF (VS Media).

Figure 23: Effluent and influent Fe concentrations after the implementation of AOCF (MOCS Media).
Effect on ammonium removal

The developments in NH$_4^+$ and NO$_3^-$ concentrations in the effluents of both the filter media after the AOCF had been implemented have been shown (Figs. 4-26 and 4-27). In previous studies related to KMnO$_4$ use in water treatment, the effect of permanganate on nitrifying bacteria has not been evaluated. In this study, within the range of 1 mg/L to 1.7 mg/L KMnO$_4$, no negative effect on ammonium removal was noticed which may suggest absence of detrimental effect on nitrifying bacterial groups.

Figure 24: Effluent and influent Mn concentrations after the implementation of AOCF (VS Media).

Figure 25: Effluent and influent Mn concentrations after the implementation of AOCF (MOCS Media).
4.3.3 Influence of AOCF on filter run times

After the AOCF technology had been implemented at the pilot scale model of WTP Dorst for the evaluation and optimisation, the Fe removal mechanism was slightly altered from the active mechanism before the dosing of chemicals started i.e., during the start-up phase. In the full-scale process of WTP Dorst and in the pilot filters during the ripening phase two mechanisms simultaneously removed Fe from the raw water. These included flocculation/filtration mechanism and adsorption/oxidation mechanism. Approximately 60 % of the total dissolved Fe was being removed through the flocculation/filtration mechanism and the rest 40 % entered the filter bed in dissolved form where the dissolved Fe(II) first adsorbed to the media grains and then oxidized on the surface. In contrast, after the application of the new
technology (AOCF) at the pilot scale, a significantly increased amount of Fe was removed by flocculation/filtration mechanism (more than 90 %) and only less than 10 % was removed by the adsorption/oxidation mechanism. The primary reason for this shift in Fe removal mode was the inclusion of increased concentration of Fe(III) in the influent water as FeCl₃. Secondary to it was the effect from the addition of KMnO₄ which rapidly oxidized the initially present dissolved Fe(II) in the raw water to contribute to flocculation. Due to this Fe removal mechanism shift, the most significant impact came on the filter run times, which were significantly reduced for both types of filter media. The voids in the filter beds started being clogged rapidly. For comparison, the unprocessed effluent quality data of both the filters has been provided (Appendix IV). It can be noticed that after 9-Sep-2013 (start of dosing) frequent Fe break-throughs (effluent Fe peaks in graphs) were encountered in both the filters. Further, with every Fe break-through event, an As break-through was also observed since Fe was the principle sorbent of As in AOCF technology. This situation produced an indispensable need to backwash the filters after approximately 24 hours of continuous filter operation. It should be noted that before the start of dosing, the headloss was the criteria for putting the filters on backwash and approximately 72 hours was the run time of both the pilot filters.

5. CONCLUSIONS

- The existing mechanism of As removal at WTP Dorst is co-precipitation and adsorption with iron oxyhydroxides which are formed after the dissolved iron in raw water come in contact with the atmospheric oxygen.
- Most of the As in the source water of WTP Dorst after the cascade aeration treatment remains in reduced As(III) form. However, after the water passes through the filter bed the entire fraction of As in the plant effluent becomes As(V). This rapid oxidation of As(III) in the full scale filter bed may be due to the oxides of Mn, deposited over time on the filtration media grains.
- Iron chloride (FeCl₃) was the most appropriate coagulant for use in As removal from the source water of Dorst according to bench scale tests. It showed an overall better As removal efficiency than its competitors, i.e., FeSO₄ and alum, at all the pH values between 5 and 8.5.
- When chemical oxidation with KMnO₄ was combined with the FeCl₃ coagulation treatment, significant increase in As removal was noticed and residual As levels lower than 1 µg/L were achieved with various KMnO₄-FeCl₃ combination dosings. This hybrid technique of As removal has been named as Advanced Oxidation – Coagulation – Filtration (AOCF).
- The AOCF technology has been found capable of consistently reducing effluent As concentrations to below 1 µg/L at pilot scale. The new technology could be easily implemented at the pilot scale physical model of WTP Dorst requiring only an addition of a chemical dosing setup.
- The natural pH of the source water of WTP Dorst is within the optimum range of achieving maximum As removal by AOCF.
- When a chemical dosing combination of 1.7 mg/L of KMnO₄ and 2 mg/L of Fe(III) was applied at pilot plant, consistent residual As
levels of lower than 1 µg/L were obtained in the effluent of virgin sand media (VS Media).

- When a chemical dosing combination of 1.7 mg/L of KMnO₄ and 2 mg/L of Fe(III) was applied at pilot plant, consistent residual As levels of lower than 1.5 µg/L were obtained in the effluent of the metal oxide coated sand media (MOCS Media) which was extracted from the real filters of WTP Dorst.

- The application of AOCF do not disturb the pre-existing removal efficiencies of common groundwater undesirable constituents e.g. Fe, Mn and NH₄⁺. However, a decrease in filter run times was noticed due to earlier Fe breakthrough problems.

### 6. RECOMMENDATIONS

In order to reduce residual As concentrations to less than 1 µg/L, Advanced Oxidation - Coagulation - Filtration (AOCF) with a KMnO₄ dose of 1.7 mg/L and FeCl₃ dose of 2 mg/L can serve as the new groundwater treatment technology at WTP Dorst. Any adverse influence on the removal efficiencies of other principle contaminants should not be expected after the application of this technology at WTP Dorst. However, shorter filter run times due to earlier Fe breakthroughs may put forward some minor operational side-effects. Optimisation of filter run times at pilot setup is therefore recommended before the implementation of AOCF at the full scale treatment process of Dorst. The decrease in filter run times is a commonly encountered operational issue in water treatment, especially when FeCl₃ is used for treatment. Considerations should be given to evaluate at pilot scale the double-layer (dual media) filtration with anthracite and fine sand as top and bottom media layers respectively. Use of single media with smaller grain size can also be a solution since the sand in the filters of WTP Dorst and the pilot experiments was relatively coarser in grain diameter (1-1.6 mm). Generally, a grain size of 0.4 to 0.8 mm is recommended in case of silica sand for rapid sand filtration.

The use of FeSO₄ in place of FeCl₃ and putting more load on adsorptive Fe removal mechanism (instead of flocculative removal) should also be evaluated for achieving increased filter run times, however in that case an optimization of oxidant-coagulant combination dose and point of dosing the chemicals will be required to achieve residual As levels of less than 1 µg/L.

### REFERENCES


Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic


Casiot, C., Morin, G., Jullot, F., Burneel, O., Personne, J.C., Leblanc, M., Duquesne, K., Bonnefoy, V. and Poulichet, F.E. 2003. Bacterial
immobilization and oxidation of arsenic in acid mine drainage (Carnoules Creek, France). *Water Research* **37**: 2929-2936.


Criaud, A. and Fouillac, C. 1989. The distribution of arsenic(III) and arsenic(V) in geothermal waters: Examples from the Massif Central of France, the Island of Dominica in the Leeward Islands of the Carribean, the Valles Caldera of New Mexico, USA and southwest Bulgaria. *Chemical Geology* **76**: 259-269.


vibrational spectroscopy and surface complexation modeling. *Colloid Interface Science* **234**: 204-216.


Evaluation and Optimization of Advanced Oxidation Coagulation Filtration (AOCF) to Produce Drinking Water with Less than 1 µg/L of Arsenic


conference -Trace metals in water supplies: Occurrence, significance, and control. University Bulletin No. 71, University of Illinois.


Sherman, D.M. and Randall, S.R. 2003. Surface complexation of arsenic(V) to iron(III) (hydr)oxides: Structural mechanism from ab


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APPENDIX I - WATER COMPANIES OF NETHERLANDS AND THEIR AREAS OF BUSINESS
APPENDIX II - PROCESS SCHEME OF WTP DORST
### APPENDIX III - RAW AND EFFLUENT WATER QUALITY AT WTP DORST

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APPENDIX IV - PILOT PLANT EFFLUENT DATA (UNPROCESSED)

VS Media

MOCS Media