

Evaluation and management of Arsenic contamination in agricultural soil and water - AgriAs

Market study of low-cost arsenic removal techniques

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Executive summary

Arsenic in drinking water and the food chain is a major environmental public health problem, known to affect more than 70 countries around the world. Other than health, chronic arsenic exposures also have profound social implications and consequences for the victims. The aim of this report was to outline the arsenic exposure through drinking and irrigation water and provide an overview of the technologies available for arsenic remediation in the aquatic environment. It was sought to determine the market drivers for arsenic removal technologies and which areas require further improvement in order to implement new techniques at commercial scale. The work reported in this document was carried out as part of the project “Evaluation and management of Arsenic contamination in agricultural soil and water” (AgriAs). This document has been produced under WP1 (Task 1.4) with the funding from the Academy of Finland.

This report is written to gather information about the technologies on arsenic removal from water and to collect information about the markets and economic aspects. The information for this report is obtained by literature review and from market reports. The report is comprised of mainly three chapters. The first chapter highlights the exposure and health impacts of arsenic exposure. The second chapter presents the findings from research field in terms of processes to mitigate the key issues. The third chapter provides an overview of the global market situation of different arsenic removal technologies.

Though the majority of the population exposed to arsenic live in South Asian countries, there has been growing evidence of arsenic occurrence in European soils and waters. Other than drinking water, arsenic can also enter into the food chain by irrigating the crops with arsenic-rich water. Irrigation water contaminated by arsenic can cause a gradual and continuous build-up of the arsenic layer in the soil, resulting in an exposure route through agriculture production. However, arsenic contamination poses much greater challenges in the developing countries due to the lack of infrastructure compared to the developed countries. The revised maximum contamination limit of arsenic from 50 µg/L to 10 µg/L in drinking water by WHO has been one of the main drivers to develop new technologies or improve the old techniques in order to comply with regulations. In the research field, the focus is on developing new materials for water treatment, which are cheap and generate minimum secondary waste. That is because secondary waste can also halt the permit process and handling of that waste can increase the cost of the overall processes. The current global arsenic removal market is valued at 698 million USD. Further investigations reveal that the market is expected to grow up to 1053 million USD by the end of 2022. Limited access to safe drinking water, increased population and health awareness are some of the factors appear to be the major cause of increased demand for arsenic removal technologies.

The report finds the prospects that technologies, which require a minimum amount of chemicals, are more favourable and the amount of resulted waste is a crucial part of the technology selection procedure. Adsorptive and precipitative methods are currently the most common methods used for arsenic removal from water at commercial scale. The regeneration of adsorbents can reduce the cost significantly and be utilizing the industrial/agricultural waste products as adsorption materials can increase the sustainability of the process. The nature and amount of co-existing pollutants in water are important to determine and they have a significant effect on the efficiency of arsenic removal method. The importance and issues related to arsenic removal from irrigation water have not attracted much attention among the scientific community as most of the activity and discourse have focused on the technical and scientific issues related to arsenic in drinking water. Collectively, this study suggests that low-cost arsenic removal system for arsenic removal from irrigation channel water require further investigation.

Abbreviations and symbols

AGMD	air gap membrane distillation
AM	adsorption media
As	arsenic
As(III)	arsenite
As(V)	arsenate
As(-III)	arsine
CAGR	compound annual growth rate
CaO	calcium oxide
Cl ⁻	chlorine ion
Cr(III)	chromium
DCMD	direct contact membrane distillation
DO	dissolved oxygen
EPA	Environmental Protection Agency
EU	European Union
Fe (VI)	Ferrate (VI)
Fe (III)	ferric oxide
Fe (II)	ferrous oxide
FeO	iron oxide
g/L	gram per liter
gpm	gallon per minute
gpd	gallon per day
HCO ₃ ⁻	bicarbonate ion
HPO ₄ ²⁻	hydrogen phosphate ion
H ₂ PO ₄	dihydrogen phosphate
H ₂ SO ₄	sulfuric acid
IR/CF	iron removal/coagulation-filtration
IX	ion exchange
KOH	potassium hydroxide
K ₂ S	potassium sulfide
kW	kilowatt
LEP	liquid entry pressure
MCL	maximum contamination limit
MD	membrane distillation

mg/L	milligram per liter
MGD	millions of gallons per day
MF	microfiltration
mM	millimole
Mn (II)	manganese
NF	nanofiltration
NOM	natural organic matter
NaOH	sodium hydroxide
NO ₃ ⁻	nitrate ion
O/M	operation and maintenance
POE	point of entry
POU	point of use
ppm	parts per million
RO	reverse osmosis
SiO ₃ ²⁻	silicate ion
SO ₄ ²⁻	sulfate ion
TC	toxicity characteristics
TDS	total dissolved solids
TiO ₂	titanium dioxide
UF	ultrafiltration
UNICEF	United Nations Children's Fund
USD	United States Dollar
USEPA	United States Environmental Protection Agency
UV	ultraviolet
VMD	vacuum membrane distillation
WHO	World Health Organization
ZVI	zero valent iron
ZnCl ₂	zinc chloride
µg/L	microgram per liter

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1 Background

Arsenic is a naturally occurring metalloid in the environment. According to United Nations (UN) report, arsenic poisoning is the second most important health hazard related to drinking water (Nicomel et al. 2015; Van Halem et al. 2009). Arsenic pollution of groundwater and, to a much lesser extent, surface water, is known to affect more than 70 countries. According to estimations, there are more than 200 million people worldwide exposed to arsenic in the drinking water at the concentration above 10 µg/L and a majority of them lives in southern Asian countries such as Bangladesh, India, Vietnam and Nepal (Nicomel et al. 2015; Ravenscroft et al. 2009). Inorganic contamination of groundwater is the most common form of arsenic exposure to humans, which is worst in Asian countries, especially in Bangladesh and India as a majority of the population depends on tube wells' water supply for daily needs.

Other than severely affected South Asian countries, there is evidence of As occurrence in European soils and waters (Jadhav et al. 2015; Tarvainen et al. 2013) as well. This may account, for example, the Po Basin in northern Italy, and the inland part of the Danube bounded by the Carpathian Mountains in Hungary, Croatia and western Romania (Ravenscroft 2007) and south of the province of Valladolid and the north of the province of Segovia, Spain, an agricultural region known for the presence of arsenic (between 38 and 136 µg/L) in its subterranean waters. More than half a million people living in small towns and villages of northern Serbia drink water with high levels of arsenic and in southern Hungary, drinking water in almost 400 settlements is contaminated (SAR/ADART 2015). Figure 1 shows the population at risk in the selected countries in Europe. These countries are predicted to have arsenic pollution in alluvial groundwater (Ravenscroft 2007).

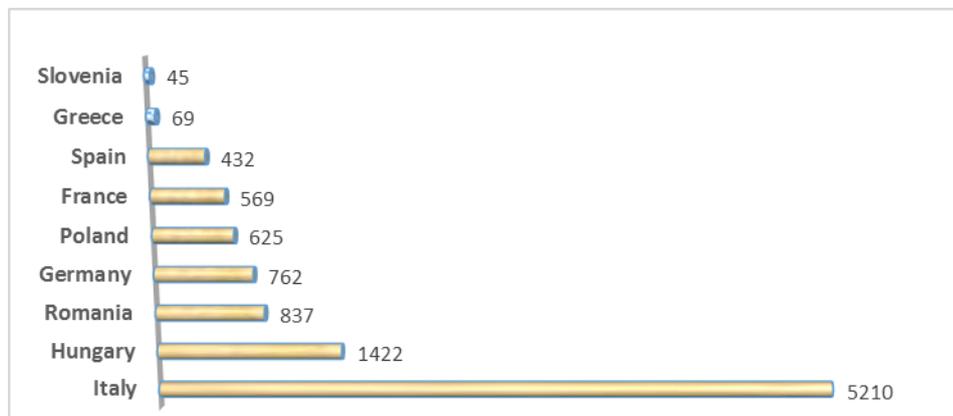


Figure 1. Estimated population at risk to As contamination in selected countries ($\times 10^3$).

The values shown in Figure 1 were taken from the UNICEF report prepared by Ravenscroft (2007) and these numbers are related to at-risk population and not to be confused with the exposed population. There is a fundamental difference between these two terms, at-risk population defines the number of people living in areas where there is a significant risk that groundwater contains hazardous concentrations of arsenic while exposed population defines the numbers of people drinking water containing arsenic more than maximum contamination limit MCL (10 µg/L) issued by the World Health Organization, WHO. Although, arsenic contamination poses much greater challenges in developing countries due to the lack of infrastructure compared to the industrialized/developed countries. Many of the developing

countries already have limited access to drinking water, which makes the matter even more complex in order to mitigate the problem. There is also a misconception among rural communities that water is clean when it does not have visible contaminants. In addition, boiling water to cooking temperature does not affect the chemical nature of arsenic compounds, which are generally found in contaminated water supplies.

While drinking water remains the major source of exposure, there has been a growing evidence that As in the food chain has a significant contribution to the overall exposure. It is also known that irrigation with As rich water causes a gradual and continuous buildup of As in the soil and can enter the food chain. According to one study focused on irrigation water of two Spanish provinces (Valladolid and Segovia), Moyano et al. (2009) reported the 35 times higher occurrence of arsenic in potatoes compared to the potatoes grown in arsenic-free water. However, the potential impact is especially severe in West Bengal, India, and Nepal Terai, where As-rich groundwater sources are widely used for rice production.

Origin of the arsenic concentrations found in drinking water and soil can be associated to both natural and man-made sources. Arsenic occurs naturally as a constituent in mineral species and subsequently introduced into groundwater sources by geochemical factors. Anthropogenic sources include mining, pesticides, fertilizers, metallurgy and wood preservation. (Singh et al. 2015; Nicomel et al. 2015; Frost & Sullivan 2007). According to World Health Organization (WHO), ingestion of arsenic can cause both cancer and non-cancer health effects. The immediate symptoms of acute arsenic poisoning include vomiting, diarrhea, and abdominal pain. The long-term exposure can cause cancer of skin, lungs, urinary bladder and kidneys. In addition, skin pigmentation is usually the first symptom of long-term exposure (WHO). Furthermore, different symptoms and signs can appear in different population and age groups. The tolerance towards arsenic poisoning can also vary among different regions, communities, and age-groups (Mazumder 2008).

2 Remediation of arsenic contamination

The regulatory framework is one of the key factors, which determine the standards for water treatment technologies. Since WHO lowered maximum contamination limit (MCL) for arsenic from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$, the focus had been to find new methods for the removal of arsenic from water. Following the WHO standard, European Union (EU) set the acceptable limit of 10 $\mu\text{g/L}$ of arsenic in drinking water (DWD 98/83/EC) (D'Ippoliti et al. 2015). However, many developing countries are still using the previous WHO guideline of 50 $\mu\text{g/L}$ due to the fact that it requires a tremendous economic cost in order to achieve the current arsenic standard of 10 $\mu\text{g/L}$ in drinking water. Technologies meeting technical criteria have to be verified under socioeconomic aspects as well. Introducing arsenic mitigation technologies varies according to the infrastructure, from large centralized water treatment facilities in urban areas to small water treatment systems for rural communities (Frost & Sullivan 2007). There are varieties of different technologies, which can be used at large scale but some of these technologies can also be used for small systems at the household level. The basic principles of arsenic removal technologies are based on conventional techniques of oxidation, precipitation, and adsorption.

In areas where the drinking water contains unsafe levels of arsenic, the immediate concern is to find a safe alternative source for drinking water supply. It is not always possible, as many developing countries have presently very limited sources of drinking water. Nevertheless, it becomes necessary to apply arsenic removal technology for safe drinking water. Numerous technologies have been developed and refined to remove arsenic from water. On the basis of different processes, arsenic removal technologies can be classified into main categories as shown in Figure 2. (Ahmad et al. 2017; Singh et al. 2015; Nicomel et al. 2015)

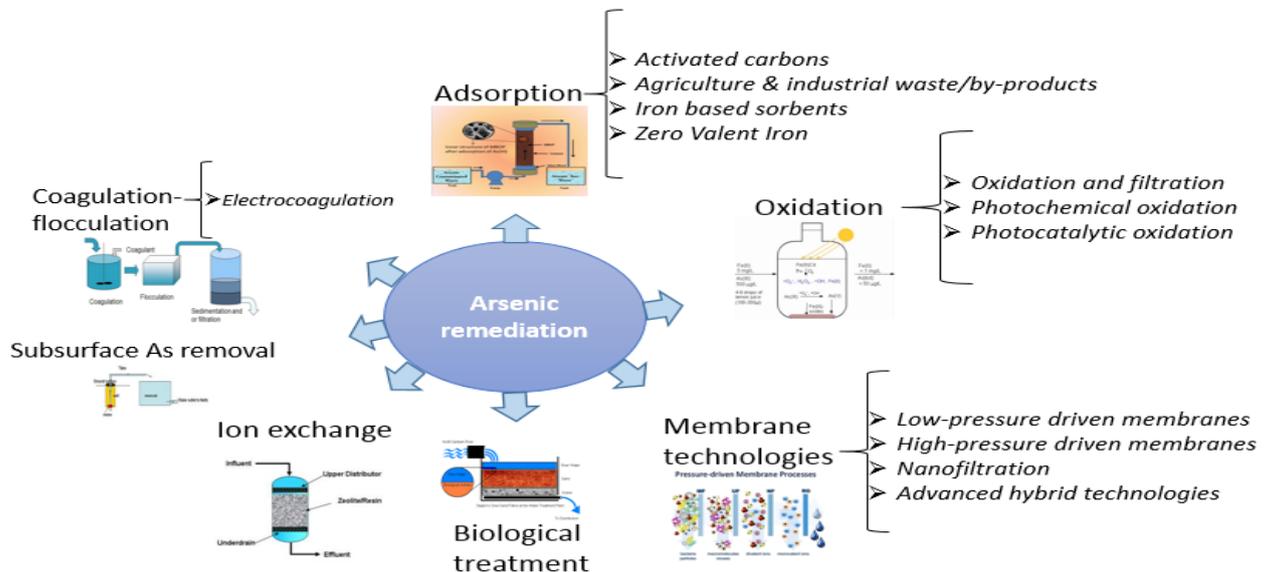


Figure 2. Various techniques used for the removal of arsenic from water. (Modified figure from Singh et al. 2015)

2.1 Oxidation

Arsenic occurs naturally in both organic (arsenic atoms bonded to carbon atom) and inorganic (no carbon atom) forms. In terms of oxidation state, arsenic can exist in four forms such as arsenite As(III), arsenate As(V), arsenic As(0) and arsine As(-III). Depending on the environmental conditions of groundwater sources, the most common arsenic forms in water are As(III) and As(V). As the chemical speciation of arsenic is an important element in water treatment process, the main purpose of oxidation technique is to convert arsenite As(III) to arsenate As(V). Because most of the treatment technologies have higher efficiency towards the removal of the negatively charged pentavalent form of arsenic (As(V)) compared to the neutrally charged trivalent form of arsenic (As(III)). Therefore, oxidation becomes a necessary pre-treatment step for the conversion of arsenite As(III) to arsenate As(V). The oxidation process is typically carried out by adding an oxidizing agent such as oxygen, chlorine, permanganate and hydrogen peroxide. In most cases, the process of oxidation is used as a pre-treatment step in combination with other treatment technologies. (CWQCD 2012; Frost & Sullivan 2007). Oxidation techniques use various processes, which are discussed further, in the following sections.

2.1.1 Chemical oxidation

Oxidation of As(III) carried out by pure oxygen or air can be considered as the most simple method (Lowry and Lowry 2001) but the oxidation rate is very slow as Kim & Nriagu (2000) reported that 54 to 57% of As(III) was oxidized to As(V) in 5 days period of time. Therefore, often the oxidation is achieved by using a chemical oxidant such as ozone, hydrogen peroxide, chlorine, chlorine dioxide, chloramine, permanganate, and ferrate (Criscuoli et al. 2009, Singh et al. 2015). Among these oxidants, ozone, chlorine, permanganate, and ferrate have higher oxidation rates compare to hydrogen peroxide and chloroamine (Bissen & Frimmel, 2003; Singh et al. 2015). Khuntia et al. (2014) observed that oxidation of As(III) to As(V) using ozone is fast due to the involvement of hydroxyl radicals generated under particular conditions such as low pH of the medium, and oxidation rate can further increase in the presence of carbonates and bicarbonates in water. However, oxidation of As(III) with ozone requires high energy input, which makes it a too expensive method, especially in developing countries (Jiang 2001). Whereas, oxidation carried out by chlorination can leave disinfectant byproducts such as trihalomethanes and halo acetic acid, which can form carcinogenic bromate ions by reacting with bromide present in water (Singh et al. 2015). While ferrate(VI) does not react with bromide ion, thus it will not produce harmful bromate ions in the treatment of bromide-containing water (Singh et al. 2015). Moreover, ferrate(VI) as an environmentally friendly powerful oxidant has multifunctional properties and the oxidation process of As(III) to As(V) occurs by an internal redox potential via direct oxygen transfer mechanism during the As(III)-Fe(VI) interaction. In this process, Fe(III), as a by-product of Fe(VI) is non-toxic and would act as a powerful coagulant in the same process. (Lee et al. 2003; Talaiekhosani et al. 2017)

2.1.2 Photochemical oxidation

Photochemical oxidation of As(III) can be referred to photolysis of naturally occurring iron Fe(III) complexes in water with the generation of highly oxidizing hydroxyl radicals in the presence of oxygen and photons (Emett & Khoe 2001). It is a Fenton-like reaction whereby photons from UV light are absorbed by the iron, producing reactive hydroxyl radicals, these free radicals take part in the oxidation of As(III) and reduction of Fe(II) to Fe(III). As a result, positively charged Fe(III) hydroxide adsorb As(V) particles and co-precipitation occurs in the form of flocs. (Gill & O'Farrell 2015; Singh et al. 2015) Utilizing the solar radiation instead of using UV lamps makes this oxidation process energy efficient and thus reduces the operational cost. O'Farrell et al. (2016) conducted a study to evaluate the full-scale continuous flow reactor in natural sunlight. The results showed that with the optimum Fe/As molar ratios of 13.4, 21.5 and 67.1, As with initial concentrations of 1000 µg/L, 500 µg/L and 100 µg/L was reduced to below MCL of 10 µg/L in over 4 hours of irradiation time. Nonetheless, iron was added in the form of Fe(III) instead of Fe(II), while Fe(II) is a common form of naturally occurring iron in groundwater (O'Farrell et al. 2016). In the case of Fe(II) in water, citrate such as lemon juice can increase the removal of arsenic (O'Farrell et al. 2016; Hug et al. 2001). When citrate is added, the Fe(III) formation is accelerated by forming stable Fe(III)CitOH⁻. Consequently, reduction of Fe(III) is accelerated which leads to arsenic removal (Gill and O'Farrell 2015).

It is noteworthy that the quality of groundwater can vary widely due to anthropogenic activities such as the use of fertilizers. Therefore, co-occurring negative ions in groundwater such as phosphates and silicates have a high affinity for the iron oxyhydroxide sites, which poses a negative effect on the arsenic removal (Voegelin et al. 2010). Moreover, in the presence of sulfates, the reaction mixture produces a Fe(III)-sulfate complex, which competes to absorb photons from near UV light at 310 nm but doubly charged sulfate does not produce reactive sulfate free-radicals (Emett & Khoe 2001).

2.1.3 Photocatalytic oxidation

Photooxidation of As(III) to As(V) is possible within a few minutes by using photocatalysis technique (Bissen et al. 2001; Singh et al. 2015). Yang et al. (1999) demonstrated for the first time that a heterogeneous photocatalytic process can oxidize As(III) to As(V) in the aquatic environment. After that, several studies (Lee and Choi 2002; Jayaweera et al. 2003; Ryu and Choi 2004; Xu et al. 2005) have reported the promising results about the conversion of As(III) to As(V) by using a photocatalytic oxidation process (Guan et al. 2012). Depending on the band-gap of the catalytic material, photocatalysis can utilize visible/solar light instead of UV-light, which makes it a good candidate as a low-cost benign process for arsenic removal. Moreover, photocatalytic material such as titanium dioxide is highly chemically stable, non-toxic and a low-cost material and it has a high oxidizing power (Ohama & Van Gemert 2011).

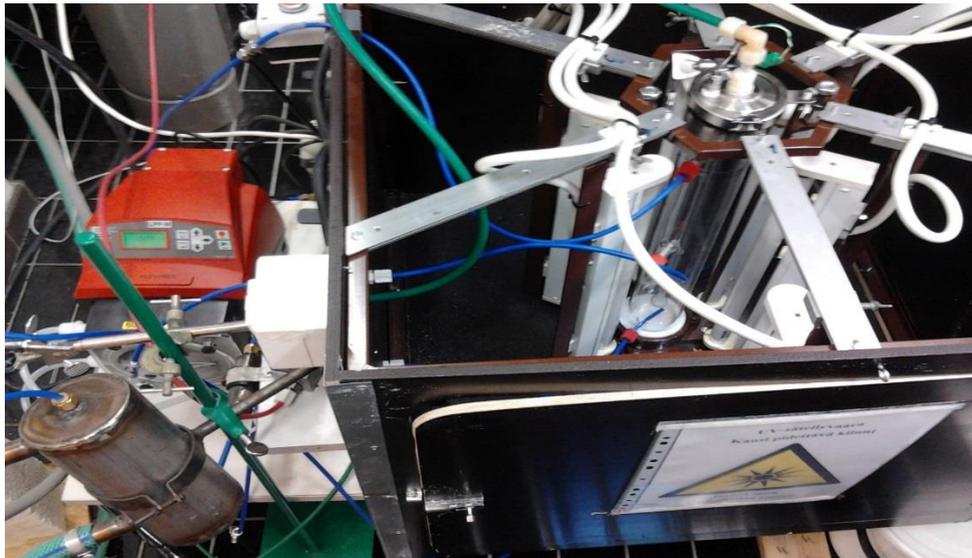


Figure 3. Laboratory scale equipment for photocatalytic oxidation (ECE, University of Oulu).

Photocatalytic oxidation of As(III) to As(V) is usually followed by the adsorption of arsenic species on the surface of photocatalyst as there exists an electrostatic attraction between the oxy-anionic forms of As(V) and the positively charged photocatalyst. This is favored in an acidic environment under pH less than zero point charge of the photocatalyst, usually in the range of 6.2-6.9 in the case of titanium dioxide (Mondal et al. 2013). Nonetheless, other anions such as silicate, fluoride, and phosphate in groundwater also compete for adsorption on the surface of a photocatalyst (Yan et al. 2016; Mondal et al. 2013). Bicarbonates and humic acid affect the photocatalyzed oxidation of As(III). Deng et al. (2010) determined the influence of anions in groundwater on the adsorption of As(V) on the surface of Ce-TiO₂; the results showed the order of adsorption to be as follows: $\text{HPO}_4^{2-} > \text{HCO}_3^- > \text{SiO}_3^{2-} > \text{SO}_4^{2-} \approx \text{NO}_3^- > \text{Cl}^-$.

2.2 Adsorption

Adsorption is the primary mechanism in adsorptive media processes. For adsorption treatment, media has an affinity to attract and retain the arsenic particles on the surface of an adsorptive media (CWQCD 2012). Adsorption processes have been used widely because of their easy operation, handling, and low-cost. According to the report published on Water Online (Reinsel 2015), it is estimated that 80% of drinking water treatment facilities utilize adsorption based treatment methods for the removal of arsenic. Several adsorptive media like activated alumina, activated carbon, iron, and manganese coated sand, hydrated ferric oxide, titanium oxide and many natural and synthetic media have been reported to remove arsenic from water (Singh et al. 2015).



Figure 4. Laboratory scale adsorption columns (ECE, University of Oulu).

Over the course of several years, Environmental Protection Agency (EPA) has carried out 28 full-scale adsorptive media demonstration projects ranging from 45 liters per minute to 3000 liters per minute. According to the collected data, the overall average influent arsenic concentration of 33 $\mu\text{g/L}$ was reduced successfully to the average effluent arsenic concentration of 1.3 $\mu\text{g/L}$ (Gutierrez 2016). However, the exhausted adsorptive media replacement is a major part of the operational cost and the disposal of the spent arsenic-laden media requires solid waste management. Some of the important adsorption materials are discussed further in the following segments.

2.2.1 Iron based sorbents

Among all adsorbents, iron based adsorption is the most commonly used treatment method for arsenic removal from groundwater. Depending on the chemistry of the remediation process, iron based technologies can be divided into two overlapping groups; one is when iron acts as a sorbent, co-precipitant or contaminant immobilizing agent and the other is when iron behaves as a reductant (convert contaminants into lower oxidizing state or used as an electron donor). Goethite ($\alpha\text{-FeOOH}$) and hydrous ferric oxide (HFO) are two important iron based materials that are used as sorbents but goethite is less reactive than HFO due to the lack of sufficient surface area. (Mondal et al. 2013) Moreover, environmental Fe(III) biominerals produced as a result of iron mineral deposition by iron-oxidizing bacteria have been described as good adsorbents for As(V) (Mitsunobu et al. 2012). Zeta potential analysis revealed that synthetic Fe(III) mineral samples had a negative charge at pH 7, and environmental Fe(III) biominerals having more negative charge and there are morphological differences between synthetic Fe(III) minerals and environmental Fe(III) biominerals. In terms of reactivity, environmental Fe (III) biominerals sorb As (III) to the same extent as synthetic ferrihydrite, however, environmental Fe minerals sorb three times more As(V) than ferrihydrite. (Sowers et al. 2017)

Generally, iron based adsorbents available in the market are granular ferric hydroxide (GFH), iron coated sand, modified iron and iron-oxide based adsorbents (Singh et al. 2015); for

example, commercially available, granular iron oxide based arsenic removal media (Bayoxide E33) was developed, which can remove arsenic below four parts per billion (“Severn Trent Services”, n.d.). This media was designed with a high capacity for arsenic and long operating cycles and low operating costs are claimed. In the same context, EaglePicher Filtration & Minerals, Inc. developed a nanocrystalline media, which removes both arsenite and arsenate without any chemical pretreatment. The media is a ferric/lanthanum hydroxide compound deposited onto a diatomaceous earth substrate to provide a high surface area and more efficient removal.

Although the commonly used iron-based media products are reasonable in price, the cost for the replacement of spent media accounts for around 80% of the total operational costs. One option to media replacement is on-site regeneration and reuse of the exhausted media. During the EPA project (Chen et al. 2015), laboratory-scale batch and column regeneration tests were conducted on six exhausted iron-based media products obtained from six full-scale arsenic removal treatment systems. The results indicated that 4% caustic (NaOH) solution can strip as high as 80% or more of the arsenic from some iron-based exhausted media. Regeneration of an iron-based media to remove arsenic can restore some of its arsenic removal capability providing the possibility of media reuse and lower O/M costs. After the pilot studies, the same process has been applied to a full-scale water utility at Twentynine Palms, California with just 20% of the cost of a new adsorbent media.

2.2.2 Zero valent iron

Elemental metallic iron Fe(0) as zero valent iron (ZVI) is non-toxic, cheap and abundant material, which has been used for the treatment of groundwater. When the oxygenated water contacts with ZVI, it results in corrosion of ZVI and form by-products like Fe(II) and Fe(III) oxides/hydroxides, and arsenic species tend to form inner-sphere complexes with the corrosion products (Mondal et al. 2013). Dissolved oxygen (DO) and pH of the medium are important factors for arsenic removal by zero valent iron (ZVI) and it is desirable to analyze these variables. Arsenic removal was dramatically affected (Bang et al. 2005) by the DO content and the pH of the solution. One possible mechanism is that dissolved oxygen reacts with ZVI and generates reactive intermediates, such as hydroxyl radicals, which further take part in iron oxidation to form iron hydroxide ions. Under oxic conditions, 99% of As(V) and 82% of As(III) were removed at pH 6 whereas, after purging nitrogen gas to removing DO, arsenic removal efficiency decreased and only 10% of arsenic was removed. Hence, high dissolved oxygen and low pH increased the oxic corrosion of Fe(0) resulting in an increased number of iron hydroxide ions available for arsenic adsorption. Moreover, studies (C and Plus 2001; Singh et al. 2015) also demonstrated that reduction of As(V) to As(III) and As(III) to metallic As takes place upon reaction with ZVI in the absence of O₂. Thus, different reaction mechanisms of As with ZVI predominate in aerobic and anaerobic environments.

Based on the zero valent iron, approximately 350,000 filters are in use in Bangladesh, India, Pakistan, Nepal, and Egypt (Singh et al. 2015). The Kanchan Arsenic Filter (Ngai et al. 2005) is a household drinking water treatment device based on slow sand filtration and iron hydroxide adsorption principles. The small cross-section of Kanchan Arsenic Filter comprised of rusted iron nails which exhibits the working principle of zero valent iron technique. Wenk. C (2008) at ETHZ, Swiss Federal Institute of Technology studied the household scale arsenic removal from drinking water and reported that commercially available iron nails show similar

corrosion rates per unit surface area as the ZVI-powders. An in-field study for arsenic removal from natural water (Camarones River, Chile) by using solar radiation assisted zero-valent iron technique has shown interesting results (Cornejo et al. 2008). The study proposed the use of citrate and solar radiation to improve the efficiency of zero-valent iron method for arsenic removal. The combination of citrate (CIT) and Fe(III) forms a Fe-CIT complex that absorbs solar radiation, generating highly oxidant species. These oxidants in solution favor the oxidation process of Fe(0) to Fe(III), eventually accelerating the arsenic removal from water. The arsenic reduction from the concentration of 1040 $\mu\text{g/L}$ to 4.8 $\mu\text{g/L}$ was achieved by using 1.3 g of zero-valent iron and 4.5 mg of citrate per liter of contaminated water under 6h of irradiation time.

2.2.3 Agricultural and industrial waste/by-products

Agricultural waste/by-products such as rice husk in its raw form have potential to be used as an adsorbent for the removal of As(V) from drinking water. For the influent As(V) concentrations of 30 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$, the maximum average removal of 80.7% was achieved in a 5 cm diameter column at a bed height of 28 cm by using 47.5 g of adsorbent (Asif and Chen 2017). However, once the rice husk becomes exhausted, the problem of disposal of arsenic-bearing waste must be addressed, because regeneration of rice husk is not cost effective.

The wastes of extracted olive pulp and olive stones were also utilized to remove As(III) from water (Budinova et al. 2006). By using different activation procedures, olive waste was converted to activated carbon and utilized to remove As(III) from water in the concentration range of 5-20 mg/L. In another study (Hossain et al. 2016), tea wastes were investigated for the removal of arsenic from contaminated water and results showed the effectiveness by removing arsenic at acceptable capacities overextended operative times such as 4-6 h. Spent coffee powder coated with polyethylenimine (PEI) and ferric ions were also used as an adsorbent for As(V) from water (Hao et al. 2017).

Industrial by-products/wastes, such as blast furnace slag (generated in steel plants), red mud (waste formed during production of alumina), fly ash (residue from coal power-stations) and Fe(III)/Cr(III) hydroxide (sludge from cooling water systems in industries) have been studied as adsorbent materials for aqueous arsenic remediation (Mohan & Pittman Jr. 2007).

Blast furnace slag (BFS) is one of the cheapest and widely available material, having FeO and CaO as the main components (Kanel et al. 2006). Because of its compositional properties, it can be utilized as an adsorbent for the removal of arsenic from water. Iron oxide and calcium oxide tend to project strong binding capacity towards arsenic ions and their ability to produce stabilized sludge after arsenic adsorption make them good candidates as adsorbents for water treatment (Kanel & Choi 2016). In this context, Kanel et al. (2006) used blast furnace slag (BFS) for aqueous As(III) remediation. The maximum As(III) adsorption capacity by BFS was 1.40 mg As(III) per grams of BFS at 1 mg/L As(III) initial concentration. Oxidation of As(III) to As(V) and its adsorption/precipitation onto BFS was the dominating mechanism. Although during tests with real groundwater, the effects of competing anions showed that bicarbonates, nitrates, sulfates, silicates, and phosphates (>10 mM) are potential interferences in the As(III) adsorption reaction. Similar findings were reported by Kanel and Choi (2016)

and results were promising in terms of adsorption efficiency by comparison with commercially available zero-valent iron (ZVI).

Red mud is generated as waste during the refining of bauxite ore for the production of alumina. It is estimated that 1-2 tonnes of red mud can be generated during typical Bayer process for the production of 1 ton of alumina (Mohan & Pittman Jr. 2007). Red mud can be used as an adsorbent for arsenic in aqueous solutions and its adsorption capacity can be enhanced by acid treatment. Altundoğan et al. (2002) conducted the study by using red mud and adsorption data showed that the process was pH dependent, optimum pH range of 5.8–7.5 in the case of As(III) and 1.8–3.5 for As(V). The maximum removals were 96.52% for As(V) and 87.54% for As(III) for solutions with the final pH values of 7.25 and 3.50, respectively, and for the initial arsenic concentration of 10 mg/L, activated red mud dosage of 20 g/L, contact time of 60 min and temperature of 25 °C. Another study conducted by Li et al. (2010) suggested FeCl₂ mixing with red mud in order to increase the arsenic removal efficiency.

Another abundant industrial-waste is fly ash, which is produced in large quantities by coal combustion in power plants. From a coal utilization perspective, fly ash is a resource yet to be fully utilized and one interesting possibility might be to use it as a low-cost adsorbent for water treatment (Ahmaruzzaman 2010). A novel adsorbent was developed by mounting amorphous FeOOH on the surface of fly ash (Li et al. 2009) and it was applied successfully for the removal of As(V) in 50 mg/L concentration during the time of 8 hours. While Rahman et al. (2004) have reported a significant removal of both As(III) and As(V) at low concentrations by using Maple wood ash without any chemical treatment.

The sludge based adsorbents have been used for the removal of heavy metals, dyes, phenols and phenolic compounds, phosphate anions and other miscellaneous compounds (Devi & Saroha 2017). In the same manner, Fe(III)/Cr(III) hydroxide waste and chrome sludge have potential to be utilized as adsorbents for the As(V) removal. Wastewater containing chromium(VI) can be treated with electrolytically generated Fe(II) under acidic conditions. The resulting sludge containing Fe(III)/Cr(III) ions has shown adsorption properties for the removal of As(V) from the water. Moreover, chrome sludge, a waste material produced during an electroplating process was also tested and the results obtained showed 21 mg/g as the sorption capacity. (Mohan & Pittman Jr. 2007)

2.2.4 Activated carbon based sorbents

The use of carbon for water purification extends far back to 400 B.C. when ancient Hindus and Phoenicians had started using charcoal because of its antiseptic properties (The history of activated carbon, 2014). Modern activated carbon was industrially produced for use in the sugar industry during the 19th century and the first reported application for water treatment was documented in the United States during 1930. Activated carbon can be obtained from a variety of carbon-containing materials, but the most common sources of activated carbon are wood, coal, lignite, coconut shell and peat. (Mohan & Pittman Jr. 2007) A large number of processes for making activated carbon have been developed over the past century. However, generally, the synthesis process consists of pyrolysis of the starting material, followed by a stage of controlled oxidation or vice versa (Al-Swaidan & Ahmad 2011). During the pyrolysis step, carbon containing substrate is heated in the absence of air below 600 °C and the activation stage involves treatment with oxidizing agents (steam, carbon dioxide, or oxygen)

or with chemical activators (ZnCl_2 , H_2PO_4 , H_2SO_4 , KOH , K_2S , KCNS , etc.) (Mohan and Pittman Jr. 2007).

Activated carbons, despite their wide application for water purification, are highly dependent on the pH and at high pH levels, the adsorption capacity decreases significantly (Muñiz et al. 2009). Deng et al. (2005) carried out a comparative study of eight different AC-based household filtration systems and observed the highest removal efficiency with modified-activated carbon materials. Such modification of activated carbon materials was also recommended by Daus et al. (2004), who observed the arsenic removal efficiency of the studied materials to be in the following order: zirconium-loaded activated carbon > iron hydroxide granulates > zero-valent iron > activated carbon. However, other than surface properties of activated carbon, adsorption capacity also depends on chemical properties of the adsorbate, temperature, ionic strength and pH of the solution (Mohan & Pittman Jr. 2007).

2.3 Coagulation-Flocculation

Coagulation-flocculation with metal salts and lime followed by filtration is one of the most commonly used methods for arsenic removal from water (Singh et al. 2015). The most commonly used coagulants such as aluminum salts and ferric salts cause destabilization of surface charges on the colloidal and suspended matter, which results in flocs formation, arsenic adsorbs to floc particles which can be removed by filtration (CWQCD 2012). The efficiency of the process is affected by the coagulant-type, pH level and presence of competing anions in water. Multiple steps involved in this method of arsenic treatment make it a complex system, however, this is the most common method adopted by municipal wastewater treatment units in USA (Ravenscroft et al. 2009). In general coagulation/flocculation system in arsenic removal is well suited at large scale water treatment plants such as municipal water treatment facilities where the inflow of water is in the range of 2 million gallons per day (CWQCD 2012). However, The Bucket Treatment Unit (BTU), developed by DANIDA (Ministry of Foreign Affairs of Denmark) project in Bangladesh is based on the coagulation/flocculation process. It uses two buckets, each 20 L, placed one above the other. Chemicals are mixed manually in upper bucket and water is allowed to flow downward and pass through the sand filter installed in the lower bucket (Ali et al. 2001).

Lime precipitation is typically used as a pre-treatment, as it can reduce arsenic concentration from high levels (e.g., hundreds of mg/L) to medium levels (e.g., 1 to 5 mg/L). It has been observed that arsenic removal by lime is usually between 40-70%. However, an additional process would be required in order to achieve arsenic concentration down to drinking water standards. (Reinsel 2015)

Among the chemical coagulation, Fe based coagulants such as ferric chloride or ferric sulfate are more effective for water treatment than Al-based coagulants (Mondal et al. 2013). This must be taken into consideration since many aquifers where arsenic contamination is present also contain phosphates or silicates, which reduces the efficiency of arsenic removal. However, the major limitation of the coagulation/flocculation process is the production of a large amount of arsenic-containing sludge. The management of the produced secondary pollution is important and adds cost to the overall process.

2.3.1 Electrocoagulation

Electrocoagulation is an alternative process to coagulation/flocculation. In this process, instead of adding chemical reagent, metallic cations are directly generated in the effluent by electrolytic oxidation of an appropriate anode material (Wan et al. 2011). The generated metallic cations work as coagulants and the amount of generation of metallic ions is based on the applied current density. Typically, with iron electrodes, Fe(II) released can subsequently be oxidized in solution to produce Fe(III) hydroxide or oxyhydroxide, which make bonds with pollutants such as arsenic and form flocs. The metallic flocs enlarge the size from micro flocs to macro flocs attaining the self-settling size.

Based on that process, arsenic remediation method called ElectroChemical Arsenic Remediation (ECAR) has been developed at Lawrence Berkley National Labs. This method uses a small amount of electricity to create rust in the contaminated water. The rust binds to arsenic, which can then be removed from water through settling and/or filtration (ECAR 2016). By using solar energy for electricity, the operating cost can be very low compared to many other technologies. The amount of sludge produced is minimum and it was found to lower the initial As concentration from as high as 3000 $\mu\text{g/L}$ to below the WHO-MCL of 10 $\mu\text{g/L}$ (Singh et al. 2015).

2.4 Ion exchange

Ion exchange is a physicochemical process and the working principle is based on the exchange of ions between solid phase resin and the feed water (Lee et al. 2017). Ion exchange resins can be anion exchangers or cation exchangers, generally, strong-base resins are selected for the removal of arsenate or arsenite with chloride ions (Ravenscroft et al. 2009). Due to stronger affinity of charged ions for the resin, oxidation of As(III) to As(V) is required as a pre-treatment step. However, oxidizing agents can degrade the performance of resins, therefore an excessive oxidant is necessary to be removed prior to the ion exchange process (CWQCD 2012). According to consecutive studies (EPA 2000; EPA 2002, EPA 2003) conducted by EPA, four full-scale ion exchange treatment plants and 2 pilot treatment plants demonstrated the performance by removing up to 95 percent of incoming arsenic (22-55 $\mu\text{g/L}$) in the feed water.

The presence of other competing ions such as sulfates can impact the performance of the ion exchange process, it is not economical to use the ion exchange process for arsenic removal when sulfates exceed 150 ppm and TDS exceeds 500 ppm in the feed water (Ravenscroft et al. 2009). Moreover, when ion exchange resin is saturated with arsenic, it must be regenerated with a strong solution of HCl or NaCl or the exhausted resin has to be replaced. In both cases, the produced waste stream requires proper waste management.

2.5 Membrane Techniques

In view of drinking water treatment, membrane filtration relies on the synthetic membrane containing billions of pores acting as selective barriers, which allow some constituents of

water to pass through while others are rejected (Johnston et al. 2001). Generally, there are two categories of pressure-driven membrane filtrations: low-pressure membrane processes such as microfiltration (MF) and ultrafiltration (UF); high-pressure membrane processes such as nanofiltration (NF) and reverse osmosis (RO). Using microfiltration (MF) and ultrafiltration (UF) alone is not an effective technique for the removal of arsenic from water due to their large pore size (Nicomel 2015). Therefore, the particle size of arsenic-bearing species must be increased by using a coagulation-flocculation process prior to the filtration. On the other hand, nanofiltration (NF) and reverse osmosis (RO) techniques are suitable for the removal of dissolved arsenic in water given that the feed is free from suspended solids. Hence, a low amount of water rejection may be an issue in water-scarce regions (Johnston et al. 2001).

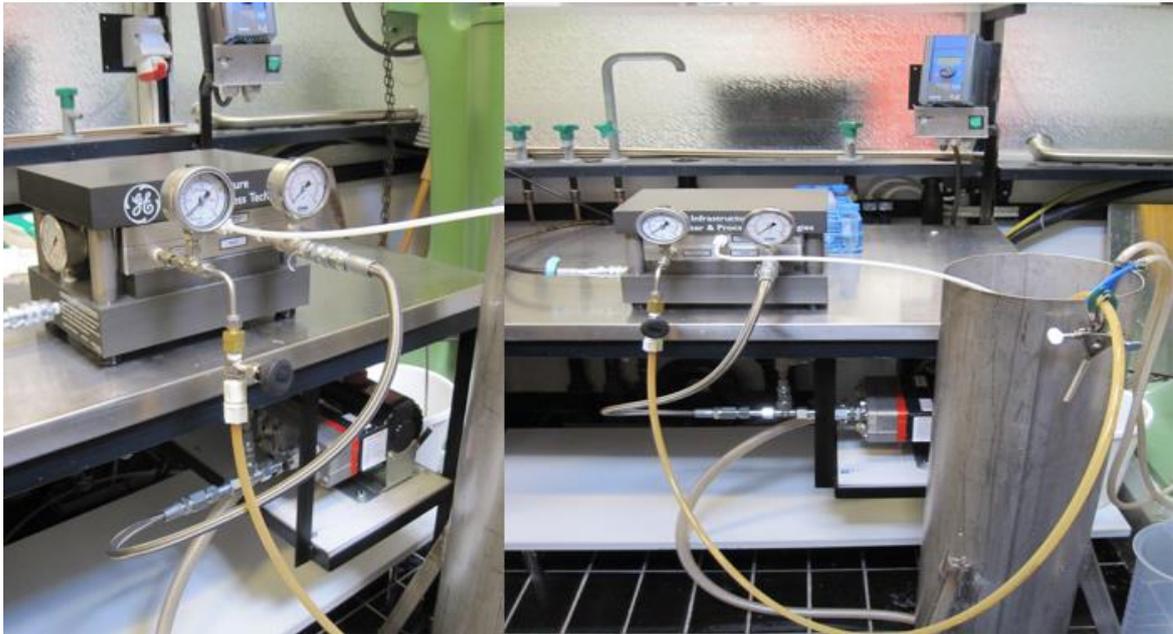


Figure 5. Laboratory scale membrane filtration equipment (ECE, University of Oulu).

2.5.1 Arsenic removal by using low-pressure driven membrane processes

Low-pressure membranes such as MF and UF, normally require low pressure from 0.35 to 6.8 bar and primarily remove contaminants through physical sieving (Shih 2005). Microfiltration (MF) membranes are only able to remove colloidal and suspended particles in the range of 0.1-10 μm . The size of the dissolved As are small enough to pass through the pores of an MF membrane. Thus, the efficiency of As removal is highly dependent on the size distribution of As bearing particles. Therefore, the As removal by an MF membrane can only be achieved by increasing particle size of As bearing species prior to MF (Singh et al. 2015). For example, coagulation and flocculation processes can be effective to increase the particle size of As bearing species in water. Microfiltration (MF) membranes with pore size of 0.22 and 1.22 μm combined with either ferric chloride or ferric sulfate and cationic polymeric flocculants were used to investigate the arsenic removal efficiency (Shih 2005). The results showed that the arsenic removal efficiency by using combined flocculation and MF technique is higher than using MF only. However, the effectiveness of As adsorption onto Fe(III) complex is an important factor, which can be affected by pH of the solution and the state of arsenic species.

Therefore, oxidation of As(III) to As(V) is recommended prior to the coagulation-microfiltration process.

Ultrafiltration (UF) is another low-pressure driven membrane process. UF membranes have pore sizes in the range from 0.01 μm to 0.1 μm and are capable of retaining species in the molecular weight ranging from 1000 to 100,000 Da (Madsen 2014). Similar to MF, the pores of the UF membrane are not small enough to reject the dissolved arsenic in contaminated water. Thus, UF with surface modification may have higher arsenic removal efficiency compared to the UF with only pore size dependent sieving. Arsenic removal by negatively charged composite sulfonated polysulphone UF membrane was investigated and results indicated the influence of co-occurring ions and natural organic matter (Uddin et al. 2007a). The mechanism of As removal was mainly due to the electrostatic interaction but in the presence of divalent cations such as Ca^{2+} and Mg^{2+} , the As(V) rejection reduced to almost zero. The presence of natural organic matter (NOM) improved As(V) rejection in the presence of divalent cations. In another study by Iqbal et al. (2007), the effect of co-occurring inorganic solutes (such as carbonates, phosphates, and sulfates) on the removal of As(V) was investigated by using a flat sheet hydrophilic polyethersulfone (PES) ultrafiltration membrane. The results indicated the effectiveness of adding the surfactant micelles but, at the same time, co-occurring inorganic solutes reduced the arsenic removal significantly.

2.5.2 Arsenic removal by using high-pressure driven membrane processes

High pressure driven membranes such as reverse osmosis (RO) and nanofiltration (NF) normally require high pressure from 3.5 bar to 68 bar. Reverse osmosis (RO) is a well-established technology and identified as the best available technology for the small water treatment systems to remove arsenic from water (Singh et al. 2015). Due to extremely small pores of the membrane ($<0.001 \mu\text{m}$), a very high rejection of low-molecular-mass compounds and ions can be achieved. The Environmental Verification Programme operated by USEPA used the (TFC-ULP) RO membrane from Koch Membrane Systems to test the removal of arsenic from drinking water. During the 34 day trials, the results showed 99% removal of As from feed water containing 60 $\mu\text{g/L}$ of arsenic. However, pH of the solution and dissolved organic carbon had a significant effect on the removal efficiency and the removal of As(V) was higher than As(III) (Shih 2005). Nevertheless, a high osmotic pressure is required and the water flux through RO membrane is very low. Considering the developing countries, traditional RO technology seems difficult to apply due to its high-energy consumption and high maintenance cost.

On the contrary, nanofiltration (NF) membranes provide higher water fluxes at relatively lower trans-membrane pressures. This is probably because they are asymmetric and negatively charged at neutral and alkaline pH. Therefore, in addition to the difference in diffusion rates, the separation is supplement by repulsion mechanism between anions in solution and surface groups. As a result, high ion rejections similar to those in RO can be achieved but at a higher water flux through the membrane (Uddin et al. 2007a). However, NF is effective for the removal of multivalent ions but fails to be effective in the removal of monovalent and neutral molecules (Uddin et al. 2007b). Because arsenic can exist in water in both neutral and monovalent or divalent forms, it might be required to regulate the water chemistry in order to achieve efficient removal of arsenic by NF membranes. In addition, a study conducted by Wang et al. (2009) suggested that co-existing ions of Cl^- , Na^+ , SO_4^{2-} and

Ca^{2+} in the feed groundwater had a negative impact on the As(V) removal efficiency. Arsenic removal by a NF membrane in the form of As(III) is lower than As(V), therefore groundwater containing As(III) must undergo a pre-oxidation step prior to the NF process.

2.5.3 Advanced hybrid technologies

Membrane distillation (MD) is a relatively recent development for water treatment (Manna & Pal 2016). MD is a thermally driven non-isothermal process in which a hot aqueous feed solution is brought in contact with one side of a microporous hydrophobic membrane and water vapor diffuses through the membrane due to vapor pressure as the driving force provided by a temperature difference across the membrane. Membranes with pore sizes ranging from 0.01 μm to 1 μm can be generally used in the MD process. (Pal & Manna 2010)

MD technologies include 1) direct contact membrane distillation (DCMD) where a cold liquid is in direct contact with the membrane at the permeate side, 2) air gap membrane distillation (AGMD) where an air gap acts as the condensing surface at the permeate side, 3) sweep gas membrane distillation (SGMD) where a gas is forced through the gap at the permeate side to aid the evaporation of less volatile substances of interest, and 4) vacuum membrane distillation (VMD) where the gap channel configuration is subjected to vacuum. DCMD has received greater attention because it does not require an external condenser and it is more suitable for water-based applications. DCMD has the simplest MD configuration. The operation of DCMD is relatively easy and high flux can be obtained at the right operating conditions. (Ashoor et al. 2016)

The main requirements for the MD process are that the membrane should not be wetted and only vapors and non-condensable gases should be present within its pores. Because the membrane is not wetted by water, it is less prone to membrane fouling, it exhibits higher rejection of solutes when compared with conventional membrane technologies such as RO. Pore wetting occurs when the pressure of the liquid feed is able to propel the liquid through the membrane pores and this pressure is known as Liquid Entry Pressure (LEP) (Ashoor et al. 2016). Recently, there have been studies to remove arsenic by using the direct contact membrane distillation (DCMD) process and the results showed up to 100% removal of As(III) and As(V) from groundwater (Singh et al. 2015). The main cost-effective benefit is the possibility of utilizing solar energy for heating the feed which has been experimentally demonstrated by Pal and Manna (2010) in their study of using three different commercial membranes in the MD process. Membrane distillation process can be a potential option for arsenic removal from contaminated water to meet the maximum contamination level of 10 $\mu\text{g/L}$ as set by WHO (Manna & Pal 2016). However, there are some limitations such as the hydrophobic nature of the membrane. Pores of the membrane are wetted by the feed above liquid entry pressure (LEP) and the presence of organic matter in the feed can reduce the value of LEP, higher the organic matter the lower the LEP value. In addition to that, the presence of volatile components other than water can also affect the MD process.

2.6 Subsurface arsenic removal technique

Subsurface arsenic removal technique has potential to remove arsenic at low-cost without any waste stream (van Halem et al. 2010). The principle of this technique is based on in-situ oxidation of arsenic and iron present in groundwater. The in-situ oxidation process can be divided into two steps. In the first step, above-ground aeration is achieved and in the second step, aerated water is periodically injected into a groundwater aquifer. The injected water oxidizes adsorbed ferrous iron on the soil grains, resulting in hydrous ferric oxides (HFO). The surface area of hydrous ferric oxides (HFO) provides adsorption sites for the adsorption of soluble ferrous iron and arsenic from groundwater. (van Halem et al. 2010)

A similar approach was successfully applied in the field by Sen Gupta et al. (2009). The team has installed six plants in West Bengal, India. In all cases, total As in water samples after treatment was less than MCL 10 µg/L. The plant produces no sludge and the operation cost is very low. (Sen Gupta et al. 2009). Other trace elements such as silica, carbonates/bicarbonates and phosphates can be found in groundwater as well and may compete with As(III) for hydrous ferric oxides (HFO) sorption sites. Holm (2002) has conducted an experimental study in order to simulate the effects of bicarbonates, silica, and phosphates on the concurrent iron and arsenic removal from groundwater. The results indicated that for pH between 7-9, carbonates/bicarbonates, silica and phosphates had a negative impact on the arsenic sorption to HFO. Decreasing the pH to 7, improved the results in the case of carbonates/bicarbonates and silica but only modest improvements were seen in the case of phosphates.

2.7 Biological Treatment Technologies

Biological treatment methods are solely based on introducing bacteria as a reactive component in the aquatic environment. In particular, iron-oxidizing bacteria involved in the precipitation of ferrous ions have been applied in drinking water treatment processes in order to accelerate the removal of ferrous ions from groundwater. Under the optimum conditions, oxidation of As (III) to As(V) can also be catalyzed by the bacteria. As a result, intermixing of iron oxides, organic material, and bacterial species produces a complex sorbing material, which can immobilize arsenic by adsorption or by co-precipitation (Katsoyiannis & Zouboulis 2004). In view of this process, a Dutch company named as PAQUES is using patented THIOTEQ™ Scorodite process for arsenic removal. The process is based on in-situ-oxidation of iron and arsenic with the help of bacteria and plain air in order to form stable bioscorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Paques, 2017). Moreover, according to the report published by Water Online (Reinsel 2015), the ABMet process developed by Applied Biosciences of Salt Lake City uses biological sulfate reduction to precipitate arsenic and heavy metals.

2.7.1 Biological oxidation

Biological treatment methods are solely based on introducing bacteria as reactive components, which exploit natural biological processes. There are more than 30 bacterial strains, reported to be involved in the biological oxidation of arsenite As(III) in soil and groundwater (Fazi et al. 2016). The isolated bacterial strains described as chemolithoautotrophic arsenite oxidizers (CAO) use oxygen or, in some cases, nitrates and nitrites. Wang et al. (2017) have reported the feasibility of As(III) oxidation coupled with the

reduction of nitrates by using activated sludge containing nitrates, nitrites, and oxygen as the source of electron acceptors.

The simultaneous oxidation-removal process, by promoting biotic As(III) and Fe(II)/Mn(II) oxidation is based on the fact that As-contaminated groundwater is usually in reducing conditions and contains iron and magnesium concentrations (Fazi et al. 2016). Katsoyiannis and Zouboulis (2004) reported the microorganisms found to support biotic oxidation of iron, offering a favorable environment for the oxidation of As(III) to As(V) and adsorption on the obtained iron oxides resulting in the overall arsenic removal of 95% at the initial concentration of 200 mg/L of arsenic in the water sample. Similarly, bacteria can play an important role in the oxidation and removal of arsenic by generating reactive magnesium oxides (Singh et al. 2015). The main product of biological iron oxidation is usually a mixture of iron oxides, organic material, and bacteria, producing complex multiple sorbing solids, which can immobilize arsenic by adsorption or by co-precipitation (Katsoyiannis & Zouboulis 2004). Apparently, by the same principle, a Dutch company named as PAQUES is using patented THIOTEQ™ Scorodite process for arsenic removal. The process is based on in-situ-oxidation of iron and arsenic with the help of bacteria and plain air in order to form stable bioscorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Paques 2017). Nevertheless, the resulting produced As-bearing sludge requires solid waste management. In a review study conducted by Hayat et al. (2017), fungal remediation of As was also reported as a potential method for converting the dissolved arsenic (As(III) and As(V)) into volatile arsine (As(-III)) gas in order to avoid solid waste management.

3 Market analysis of arsenic removal technologies: An overview

The global Arsenic Removal market is valued at 698 million USD in 2016 and is expected to reach 1053 million USD by the end of 2022, growing at a CAGR of 7% between 2016 and 2022 (QYResearch 2017). The market for arsenic removal can be simplified into three major categories such as precipitative processes, sorption processes, and membrane processes. Generally, each method of arsenic removal from water consists of more than one step and it is important to consider all the available technologies to comply with maximum contamination limit for arsenic. The main considerations when selecting a treatment technology include:

- Water quality characteristics (including pH levels, initial concentrations of As(III) and As(V), co-existing pollutants and iron in water)
- Ease of implementation with current system
- Quantity of water to be treated
- Residual management and cost of disposing of the waste produced
- Cost of the equipment

Given various regional water quality parameters, the presence of iron plays a very important role in order to determine the criteria for technology selection. The amount of iron in the source water plays an important role in the selection of optimal treatment technology. Figure 3 illustrates the iron concentrations relative to arsenic concentrations in feed water and how the Fe:As ratio can influence the selection of the arsenic removal method.

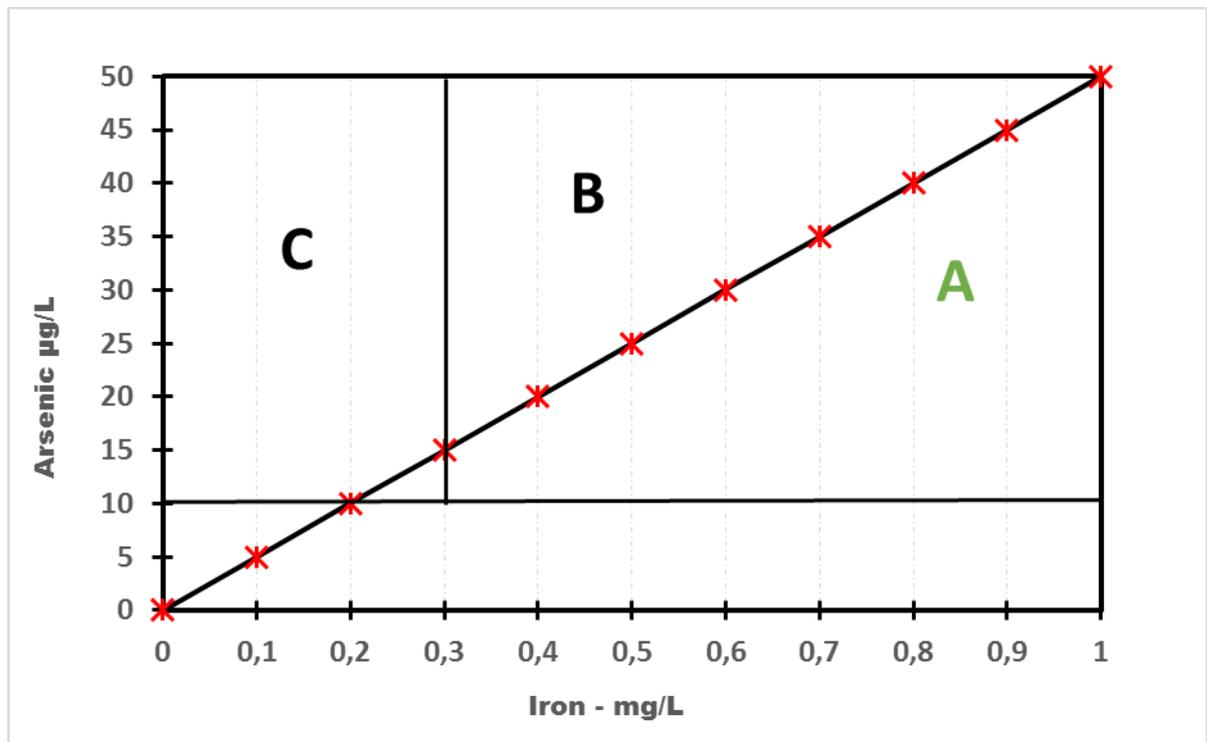


Figure 6. Iron to the arsenic ratio for arsenic treatment basic selection guide (Modified figure from Sorg & Lytle, n.d).

Section A in Figure 3 indicates high iron levels (>0.3 mg/L) and high iron to the arsenic ratio (20:1). In that case, iron removal processes can be utilized to promote arsenic removal from water, usually by adsorption and co-precipitation. In section B in the figure, high iron levels (>0.3 mg/L) and low iron to the arsenic ratio (less than 20:1), favor a modified treatment process with the addition of iron salts. When the feed water contains low levels of iron (<0.3 mg/L) as indicated in section C, technologies such as adsorptive media and ion exchange are well suited. In addition, when selecting the arsenic removal treatment method, it is important to consider that liquid waste streams produced by the treatment method must have lower arsenic concentrations than the toxicity characteristics (TC) value in order to classify the waste as non-hazardous. The arsenic toxicity characteristic (TC) value is 5 mg/L. Those liquid waste streams that contain more than 5 mg/L of arsenic would, therefore, be classified as a hazardous waste and then require special methods for disposal with additional costs.

Other than process-based, arsenic removal market can also be divided into the following main two groups on the basis of the application. These are centralized community-based water treatment plants and the point of use (POU)/point of entry (POE) equipment for household use. According to a market report (Frost & Sullivan 2014), global residential and light commercial water treatment equipment market will grow to 19 million USD by 2020. It is important to consider that more than half of world's population use water coming from piped household water connection located inside the user's dwelling, plot or yard (Frost & Sullivan 2014), which makes the POU treatment system an important segment of the arsenic removal market. The primary advantage of employing POU treatment in a small system is reduced capital and treatment costs. However, most POU devices do not address the issue of pre-oxidation and such devices with the adsorptive process may not remove As(III). While reverse osmosis (RO) based POU devices may remove As(III) to acceptable standards.

Within the European Union (EU), agriculture represents around 30% of the total water abstraction. In fact, the major part of the irrigated land in Europe is located in the South in Spain, Italy, France, Greece, and Portugal accounting for 85% of the total irrigated area in EU. For example, in Spain irrigated agriculture accounts for 56% of total agricultural production (Lenntech 2017). Removal of arsenic as a mitigation option is not suitable for open channel irrigation purposes except when the iron is present naturally, which favor precipitations of oxides/hydroxides for removing arsenic from water under aerobic conditions using open irrigation channels. The crop uptake of arsenic can also be reduced by adding iron to aerated and sandy soils low in iron (Chakrabarty 2015). Other than natural sources, reuse of municipal wastewater and drainage water can be used as irrigation water. In Europe, for example, there is a large project in Clermont-Ferrand, France since 1997 where more than 10.000 m³/day of tertiary treated urban wastewater is reused for irrigation of 700 Ha of maize. In Italy, more than 4000 Ha of various crops are irrigated with recycled water. Spain also counts on several similar projects. However, the use of recycled water for irrigation may have some adverse impacts on the public health and the environment. The toxicity of arsenic in irrigation water varies widely for different crops. (Ali et al. 2012)

The major players in global arsenic removal market include Lenntech, Severn Trent Service, Tonka Water, AdEdge Water Technologies, Layne, RWL Water, Blue Water Technologies, Outotec, BioteQ Environmental Technologies, Everfilt, Harbauer, Hungerford Terry, Culligan, P2W, Kinetico Water Systems, HIDROFILT, Membrane Group, EconomyWater, Kent, Water Systems India. These companies are described in more details in the following sections.

3.1 Precipitative Processes

Precipitative processes account for a large portion of arsenic removal market and include conventional treatment methods such as coagulation assisted microfiltration, enhanced coagulation/filtration, and lime precipitation etc. It is a cost-effective approach for arsenic removal and, generally, requires large treatment and retention tanks for the precipitation reaction and settling to occur. The most commonly used method for removing arsenic in water treatment plants involves precipitation using iron and aluminum salts. Precipitative processes such as lime precipitation are typically used to bring high levels (e.g., hundreds of mg/L) of arsenic to moderate levels (e.g., 1 to 5 mg/L) in industrial effluents, however, an additional process would be required to bring arsenic concentrations down to drinking water standards. Table 1 provides information about the major manufacturers in the field of precipitative production processes.

Table 1. Major manufacturers of precipitation processes.

Manufacturer	Location of manufacturer	Description of product	Features
Tonka Water	Plymouth, Minnesota. USA	Aeration and precipitation followed by filtration by using multi-cell gravity filters.	Capacity 80 gpm to 2 MGD
AdEdge Water Technologies	Duluth, Georgia. USA	Coagulation by using Ferric chloride + filtration by using black filter media	Can also remove soluble iron, manganese, and sulfides. Creates less backwash water.
Layne	The Woodlands, Texas. USA	LayneOx is a catalytic media works with chlorine to oxidize and precipitate arsenic in water.	Iron, manganese, hydrogen sulfide and suspended solids can also be removed.
Outotec	Espoo, Finland.	The process consists of ferric arsenate precipitation stage followed by neutralization using lime milk.	This process is particular for the treatment of industrial effluents in order to meet the environmental regulations.
Everfilt	Mira Loma, CA. USA	Coagulants used are aluminum sulfate, ferric chloride or ferric sulfate.	Industrial and commercial application. Various application for treatment of irrigation water
Harbauer	Kolkata, India.	The process involves Manganese Dioxide media to precipitate naturally occurring iron in water which results as ferric hydroxide and then filtration through the sand filter.	It removes suspended solids, iron, arsenic and bacteria from raw water. Easily operated plant designed for rural communities mainly for developing countries.

Hungerford Terry	New Jersey, USA.	Chlorine is used to oxidize and precipitate naturally occurring iron in water which combines with arsenic followed by filtration using Greensand Plus filter.	As(III) needs to be oxidized to As(V) by oxidation process for the efficient removal of arsenic.
P2W	Rishon LeZion, Israel.	Arsenic removal along with other co-existing heavy metals in the industrial effluent by using electrocoagulation.	The average power consumption per cubic meter of water is around 0.1-0.5 kW. The electrodes replacement period varies between 6 to 12 months.
Hidrofilt	Nagykanizsa, Hungary.	Using Iron hydroxide for precipitation.	Application for municipal water, industrial wastewater, irrigation water, and small-scale mobile treatment unit for drinking water.

3.2 Sorption Processes

Sorption processes cover a part of the arsenic removal market based on adsorption and ion exchange systems. Arsenic removal by adsorptive media is the most common method utilized in municipal drinking water treatment facilities. As with coagulants, most adsorptive media are iron-based, once the adsorptive media is exhausted it requires to be replaced with new one or regenerated by using chemicals. The ion exchange process differs from the adsorptive media process in that ion exchange resins require regeneration periodically and reused. Ion exchange resins are typically regenerated with sodium hydroxide and sodium chloride, which create a liquid waste containing a high concentration of arsenic. However, sorption processes are better suited to medium to small-scale treatment operation than co-precipitation. Sorptive processes are the most common application at the point-of-use (POU)-treating water systems for household use.

Table 2 provides information about some of the companies providing sportive media systems and are part of the global arsenic removal market.

Table 2. Major manufacturers of sorption process.

Manufacturer	Location of manufacturer	Description of product	Features
Lenntech	Delft, Netherlands	Granular Ferric Hydroxide adsorptive media and Ion exchange resin (polystyrene-divinylbenzene-copolymer)	Adsorptive media removes both As(III) and As(V). Large-scale as well as POU systems. Ion exchange resin can also remove antimony, phosphates, and silica from the water.
Severn Trent Services	Coventry, UK	SORB 33(r) arsenic removal technology and Bayoxide(r) E33 arsenic removal media.	Standard system capacity 8 gpm to 2 MGD. Spent media requires disposal by landfilling.
AdEdge Water Technologies	Duluth, Georgia, USA	Adsorption by using granular ferric oxide media.	Capacity 10 gpm to 12 MGD. Spent media can be discarded as non-hazardous waste.
Layne	The Woodlands, Texas, USA	Granular Ferric Oxide adsorptive media. Ion exchange resin.	Capacity 2000 gpm. Adsorptive media is regeneratable. Low-waste Ion exchange system.
RWL Water	New York, USA	Iron hydroxide based adsorptive media. Ion exchange resin.	As(III), As(V), antimony, molybdenum, copper, phosphates, and lead can be removed with the same adsorptive media. Media is non-regeneratable.
Everlift	Mira Loma, CA, USA	Activated alumina and granular ferric hydroxide based adsorptive media. Greensand filters (Silica sand with manganese dioxide fused to the granules operate in pressure filters).	Industrial and commercial application. Various applications for the treatment of irrigation water for agriculture and landscape.
Culligan	Wycombe, UK	Multi-media filtration method. The capacity from household to large-scale municipal plants. The exhausted media needs to be replaced.	One of the biggest arsenic removal plants in Europe (600 liters/second). Arsenic, vanadium, and fluoride can be removed at the same time.

Kinetico Water Systems	Newbury, Ohio, USA	Cartridge filter media	Small-scale POU water systems. Spent media requires being replaced.
Hidrofilt	Nagykanizsa, Hungary	Activated carbon-based filters.	Municipal water, industrial wastewater, irrigation water treatment and small-scale mobile treatment systems for drinking water.
Matrix Eco Solution	New Delhi, India	Activated alumina and activated carbon based adsorptive media.	Fluoride and arsenic removal water treatment plants.
Water Doctor	New Jersey, USA	Five-stage filtration media. Micropore activated carbon used as adsorbents.	Small-scale water treatment system. Arsenic is removed along with iron and magnesium.
Zeolite (India)	Kolkata, India	Zeofil-oxidizing catalytic media for arsenic removal.	Capacity 20 gallons per hour to 20,000 gallons per hour.

3.3 Membrane Processes

Although membrane processes are also well suited for small-scale treatment operations, their applicability for arsenic removal appears to be limited. A major drawback to membrane methods is that many water sources require pretreatment to remove organics, particulates, iron, manganese, and scale-forming compounds in order to prevent membrane fouling. Reverse osmosis (RO) is capable of removing dissolved arsenic species to the level below 10 ppb. However, the process generates large volumes of brines that require disposal. In some cases, co-precipitation with iron salts is combined with microfiltration in order to decrease the operating pressures and the brine volume generated. Nevertheless, membrane technologies are attractive arsenic treatment processes for small water systems such as the point of use (POU) water treatment units for the household use.

Table 3 presents some of the major manufacturers of membrane processes as a part of the global arsenic removal market.

Table 3. Major manufacturers of membrane process.

Manufacturer	Location of manufacturer	Description of product	Features
Hidrofilt	Nagykanizsa, Hungary	Reverse osmosis, nanofiltration and ultrafiltration membranes.	Irrigation and drinking water treatment.
GE Power. Water & Process Technologies	Treose, Pennsylvania, USA	ZeeWeed-Ultrafiltration membranes.	Containerized system for groundwater treatment. Capacity 150,000 gpd.

Membrane Group	New Delhi, India	Reverse osmosis and ultrafiltration membranes.	Arsenic removal from groundwater and surface water.
Lenntech	Delft, Netherlands	Nanofiltration and reverse osmosis membranes.	Capacity-730 gpd to 2200 gpd. Point of use system (35 gpd).

3.4 Alternative treatment methods

The task of navigating through the alternative arsenic treatment technologies involves several technical considerations. Although nearly all of the unit processes previously presented could be used for arsenic reduction, some are economically more viable under specific circumstances. Optimization of existing processes is a realistic option and in recent years the focus has been to develop such methods, which are cost effective and eco-friendly. This has been accomplished by minimizing the input of chemicals and waste production as well as simplicity of the overall procedure. Table 4 address some of the treatment methods resulted as low-cost options especially for developing countries under various projects.

Table 4. Alternative treatment methods.

Title	Description
Subterranean Arsenic Removal Technology (SAR)	<p>In the in-situ treatment method, the aerated tube well water is stored in feed water tanks and released back into the aquifers through the tube well by opening a valve in a pipe connecting the water tank to the tube well pipe under the pump head. The dissolved oxygen in aerated water oxidizes arsenite to less-mobile arsenate, the ferrous iron to ferric iron and Manganese(II) to Manganese(III), followed by adsorption of arsenate on Fe(III) and Manganese(III) resulting in a reduction of the arsenic content in tubewell water.</p> <p>The in situ method is a very cost-effective and eco-friendly process for arsenic removal. The greatest advantage of this process is that there is no need for sludge handling.</p> <p>7 SAR plants were initially installed in West Bengal, India. Each plant is delivering 3000-4000 liters of water every day to around 100 families.</p>
Electro-Chemical Arsenic Remediation (ECAR)	<p>In ECAR, electricity is used to continuously dissolve an iron electrode, forming a type of rust in the water. Arsenic in the water binds to the rust particles, which can then be removed.</p> <p>ECAR operates at low voltages (< 3V in real groundwater with steel plates spaced 2 cm apart) and power can be supplied using a grid, battery, or solar photovoltaic sources.</p> <p>The first full-scale ECAR pilot plant in Paraganas district of India.</p>
SONO Filter	<p>It is a small-scale point-of-use filter system.</p> <p>The SONO filter consists of two buckets, one above the other. The upper bucket contains layers of coarse river sand, a composite iron matrix, and brick chips. The water passes through these layers and then passes onto the lower bucket where it passes through layers of coarse sand, wood charcoal, and fine sand. The water can then be collected from the lower bucket through a tap.</p>

	<p>This is a low-cost technology and can be applied locally. The disadvantage from the user's point of view is that it has a slow rate of delivery.</p>
Kanchan Arsenic Filter	<p>It is a household drinking water treatment device. The water poured slowly in a bucket passes over the brick chips, then the rusty iron nails, through the sand and comes out of the spout. The design flow rate of the Gem505 version is 15-20 liters per hour.</p>

4 Economic aspects

Generally, the cost of arsenic removal technology is case specific which is affected by several factors such as arsenic concentration in the feed, limit in arsenic concentration to be achieved, nature and amount of other compounds present in water, amount of waste produced and as well as the local infrastructure where technology needs to be applied. Nonetheless, there are certain parameters which are comparable in any case in order to determine the feasible choice of the treatment method. In this context, recommendations which resulted after a demonstration project done by U.S. EPA (Wang and Chen, 2011) can provide guidelines for the cost estimation of arsenic removal technologies. Certain key features about the cost comparison between conventional treatment technologies for arsenic removal are as follows:

- Equipment is a major cost component (2/3) of the total capital cost of a treatment system.
- The total capital costs varied widely according to the capacity of the treatment plant within particular technology.
- The cost of treatment system impacted by the design feature including tank material, type of media, valves and the level of instrumentation.
- For small capacity systems (< 100 gpm), the capital investment costs were higher for adsorptive media systems compare to co-precipitative/precipitative and ion exchange (IX) systems.
- The large (>100 gpm) co-precipitative/precipitative and ion exchange (IX) systems were more expensive than the large adsorptive media systems.
- The adsorptive media systems had higher operation and maintenance costs than the co-precipitative/precipitative and ion exchange (IX) systems, mainly due to the media replacement, which accounted for 79% of the total O&M costs. The lower maintenance cost is an advantage for the precipitative/precipitative and ion exchange (IX) systems over adsorptive media as long as the facility can handle residuals at low cost.
- Regeneration of adsorptive media has potential to lower O&M costs for large systems.

As a part of the Arsenic Rule Implementation Research Program, between July 2003 and July 2011, the U.S. Environmental Protection Agency (EPA) conducted 50 full-scale demonstration projects on treatment systems removing arsenic from drinking water in 26 states throughout the U.S. A key objective was to collect cost and performance data that might be used by small water systems, engineering firms, and state agencies to make informed decisions on selecting appropriate arsenic treatment technologies to achieve the revised arsenic maximum contaminant level (MCL) of 10 µg/L. The summary of the capital cost of each treatment system broken down into three components (equipment, site engineering, and installation) is provided in Table 5 (Wang and Chen, 2011).

Table 5. Summary of total capital investment costs (Wang and Chen, 2011).

Treatment Technology	No. of Systems	Design Flow rate range (Liter/minute)	Total Capital Cost (\$)	(% of Total Capital Costs)		
				Equipment	Site Engineering	Installation
Systems < 450 L/m						
AM	17	37 - 283	14,000 – 228,309	38 – 75	10 – 40	12 – 34
IR/CF	6	75 - 363	554,23 – 161,560	33 – 80	6 – 34	14 – 33
Systems > 450 L/m						
AM	11	378 - 2422	74,840 – 305,000	61 – 82	4 – 17	13 – 25
IR/CF	12	530 - 2914	216,876 – 427,407	55 – 75	4 – 17	15 – 36
IX	2	946 - 2044	286,388 – 395,434	61 – 66	12 – 13	22 – 27

* AM=Adsorptive media, IR/CF=Iron removal/coagulation-filtration, IX=Ion exchange

The costs provided in Table 5 do not include operation and maintenance costs and laboratory costs among different technologies. It is also noteworthy that the cost of any treatment technology may vary according to the geographical location as these values were calculated according to the local prices in the United States.

5 Conclusions

Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment. People are exposed to elevated levels of inorganic arsenic mainly through contaminated drinking water, using contaminated water in food preparation and crops irrigated with arsenic-rich water. The most important action in communities affected by arsenic is the prevention of further exposure to arsenic by the provision of a safe water supply. As a result of this study, the following conclusions can be withdrawn.

- The nature and amount of co-existing elements along with arsenic are crucial in order to determine the well suited treatment method for a given case. For example, co-existing iron plays an important role in the removal of arsenic from water.
- Numerous remediation methods based on conventional, modern and hybrid technologies are applied for the remediation of arsenic in several parts of the world. Most of the existing technologies for the removal of arsenic involve the direct removal of As(V) or converting As(III) to As(V) followed by the removal of As(V). Thus, the underlying problem of using these physicochemical treatment processes is the poor removal of As(III) and that it requires a pretreatment step.
- It is important to consider the nature and amount of final waste generated by applying any treatment method for arsenic removal. The cost of waste management impacts the overall cost analysis of any given technology.
- The concept of the circular economy can reduce the overall cost and environmental impact of the arsenic removal process. There are possibilities to develop adsorption materials by using the waste and other side streams generated by various industrial and agricultural activities.
- Irrigation water for small-scale farming and landscape use can be treated by using portable equipment available in the market but extensive research is required in order to remove arsenic from open channels' irrigation water at large scale.
- Since more than half of world's population use groundwater connected into dwelling plot or yard at home, it is important to develop more economic and efficient residential treatment equipment.

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