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Review

Iron-based subsurface arsenic removal technologies by aeration: A review of the current state and future prospects

Vu T. Luong [a], Edgardo E. Cañas Kurz [b], Ulrich Hellriegel [b], Tran L. Luu [a], Jan Hoinkis [b, *], Jochen Bundschuh [c]

[a] Vietnamese-German University, Le Lai Street, Hoa Phu Ward, Thu Dau Mot City 822096, Binh Duong Province, Viet Nam
[b] Center of Applied Research, Karlsruhe University of Applied Sciences, Moltkestr. 30, 76133 Karlsruhe, Germany
[c] Faculty of Health, Engineering and Sciences, University of Southern Queensland, West St, Darling Heights, 4350 Toowoomba, Australia

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ABSTRACT

Arsenic contamination in groundwater is a critical issue and one that raises great concern around the world as the cause of many negative health impacts on the human body, including internal and external cancers. There are many ways to remove or immobilize arsenic, including membrane technologies, adsorption, sand filtration, ion exchange, and capacitive deionization. These exhibit many different advantages and disadvantages. Among these methods, in-situ subsurface arsenic immobilization by aeration and the subsequent removal of arsenic from the aqueous phase has shown to be very a promising, convenient technology with high treatment efficiency. In contrast to most of other As remediation technologies, in-situ subsurface immobilization offers the advantage of negligible waste production and hence has the potential of being a sustainable treatment option. This paper reviews the application of subsurface arsenic removal (SAR) technologies as well as current modeling approaches. Unlike subsurface iron removal (SIR), which has proven to be technically feasible in a variety of hydrogeochemical settings for many years, SAR is not yet an established solution since it shows vulnerability to diverse geochemical conditions such as pH, Fe:As ratio, and the presence of co-ions. In some situations, this makes it difficult to comply with the stringent guideline value for drinking water recommended by the WHO ($10\,\mu g\,L^{-1}$). In order to overcome its limitations, more theoretical and experimental studies are needed to show long-term application achievements and help the development of SAR processes into state-of-the-art technology.

Contents

* Corresponding author.
E-mail address: jan.hoinkis@hs-karlsruhe.de (J. Hoinkis).

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1. Introduction

Arsenic (As) is considered to be one of the most serious inorganic contaminants in groundwater and it is recognized as a significant environmental cause of cancer mortality globally (Martinez et al., 2011; van Halem et al., 2009a; WHO, 2011a). Inorganic arsenic occurs naturally at high levels in groundwater in many countries around the world, including mostly South-America and Southeast Asia (Amini et al., 2008; Mukherjee et al., 2014). In reducing environments, arsenic exists in the natural pH range of groundwater primarily as an oxyanion of trivalent arsenite As(III) that is neutral in charge, H_3AsO_3. In oxidizing environments it exists as pentavalent arsenate As(V), which is negatively charged, $H_2AsO_4^-/HAsO_4^{2-}$ (Smedley et al., 2002). The current limit of arsenic in drinking water recommended by the World Health Organization (WHO) is 10 $\mu g\,L^{-1}$ (WHO, 2011b). The sources of exposure are drinking water, crops irrigated with contaminated water and food prepared with polluted water. After long-term exposure to high levels of inorganic arsenic, the first visible symptoms are usually observed in the skin, and include pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (hyperkeratosis). Generally, these occur after a minimum exposure of approximately five years and may be a precursor to skin cancer (James et al., 2017; WHO, 2012).

A variety of *ex-situ* and *in-situ* treatment technologies for arsenic removal from water (including immobilization) has been implemented over the last two decades. *Ex-situ* processes include precipitation/flocculation, ion exchange, membrane technologies (Figoli et al., 2016) and adsorption, with adsorption technologies using multiple materials being the most common (Jadhav et al., 2015; Jain and Singh, 2012; Mondal et al., 2013; Nicomel et al., 2015; Singh et al., 2015). *In-situ* treatment comprises an array of relatively novel methods typically including technologies such as chemical oxidation, arsenic immobilization by sorption and bioremediation techniques including arsenic biotransformation, phytostabilization and hyperaccumulation in plants (Bundschuh et al., 2014; Xie et al., 2015). Other alternative *in-situ* technologies (permeable reactive barriers (PRB), electrokinetics, nanoparticles/zero valent iron, natural attenuation, etc.) might be suitable for groundwater and/or soil treatment as they have the overall advantage of being environmental friendly and less expensive compared with conventional technologies but some disadvantages arise due to the novelty of these technologies and the overall lack of long-term experience using these techniques (Litter et al., 2014).

Table 1 shows an overview of the most common *ex-situ* and *in-situ* arsenic removal techniques and their most prominent advantages and disadvantages.

Fe(III)-(hydr)oxides (also referred to as amorphous hydrous ferric oxides or HFO) are known as the most important arsenic sorption materials due to their high specific surface area and ability to adsorb total As in large capacities. It is well known that dissolved Fe(II) in groundwater that is exposed to air is oxidized to Fe(III) and subsequently forms sparingly dissolvable HFO (Appelo and De Vet, 2003; Omoregie et al., 2013; Welch et al., 2008). Through this process, some part of the total dissolved arsenic is also removed by co-precipitation with the oxidized Fe through different mechanisms such as surface ionization, surface complexation and ligand exchange (Buamah et al., 2008; Farrell and Chaudhary, 2013; Van Der Laan, 2009). In *ex-situ* treatment, this can be used as pretreatment for e.g. subsequent membrane filtration (Schmidt et al., 2016).

The most salient advantage of the SAR process over *ex-situ* and other *in-situ* technologies is its negligible waste production, low maintenance costs and simple operation without additives or chemicals, making it especially suitable for remote and undeveloped rural areas (Shan et al., 2013; van Halem et al., 2010a), with the potential to become a sustainable long-term treatment option.

It should be noted that arsenic-laden water is not eliminated by the SAR treatment of arsenic; the arsenic is just transferred from a soluble phase to a less readily immobile phase. Arsenic waste is hereby bound into the aquifer layer and no waste stream is produced for the user. In *ex-situ* processes, on the other hand, toxic sludge and/or arsenic-laden concentrate streams are produced, which may require costly methods for treating and proper disposal. For example, the disposal of used adsorption media from *ex-situ* processes poses a threat to the environment and specific recommendations for the arsenic waste disposal are often omitted or mentioned as an area for future research. Therefore, the proper disposal and stabilization of arsenic-laden waste remains a barrier to the successful and economic implementation of arsenic removal technologies (Clancy et al., 2013; Litter et al., 2014).

On a household level, several low-cost and easily applicable techniques have been applied using different arsenic removal technologies such as precipitation with aluminum or iron hydroxide flocs and subsequent filtration, adsorption on artificial and natural sorbents, water softening with lime, ion exchange and bioremediation (Berg et al., 2006; Pokhrel et al., 2009b). In aquifers with high ferrous iron concentrations(Fe(II)) the arsenic removal by using sand filters is also suitable (Berg et al., 2006). The *in-situ* chemical treatment is also an alternative involving the injection of oxidants into the soil and aquifer ($KMnO_4$, H_2O_2) to promote the oxidation of arsenic, and coagulants to enhance the sorption and coprecipitation ($FeCl_3$) (Litter et al., 2014). Recently, a few studies have also looked into *in-situ* immobilization of arsenic under reducing conditions by forming subsurface Fe-sulfides coatings (Kirk et al., 2004; Omoregie et al., 2013; Pi et al., 2017). The electrolytic oxidation and subsequent removal of arsenic through electrocoagulation has also been studied in detail recently (Nidheesh and Singh, 2017; Song et al., 2017). The purpose of this paper is to review subsurface arsenic removal (SAR) by aeration as a promising *in-situ* technology with the advantage of negligible waste production since the arsenic is kept subsurface in the aquifer. Furthermore, SAR technology has proven to be relatively simple and less expensive compared with conventional above-ground and *ex-situ* treatment methods. To date, this technology has been tested within a variety of small and large pilot trials mostly in India and Bangladesh. In this paper SAR technology will be evaluated for its application on a global scale.

2. Subsurface arsenic removal (SAR) technology based on subsurface iron removal (SIR)

Subsurface arsenic removal (SAR) is a simple *in-situ* technology that relies on subsurface removal by adsorption and co-precipitation with iron (hydr)oxides through mechanisms such as surface complexation and ligand exchange. In Europe, subsurface iron (SIR) and manganese removal has been successfully used for many decades; however, subsurface removal of arsenic is a relatively new technique (Rott et al., 2002).

The *in-situ* remediation of arsenic is based on the underground precipitation and adsorption onto ferric oxides, and consists primarily of three main steps: 1) Water is extracted from the aquifer and oxygenated via an aeration system; 2) The oxygen-enriched water is infiltrated back into the aquifer through an infiltration well forming large oxidation zones in the aquifer. Aqueous Fe(II) is oxidized to solid Fe(III)-hydroxides fomenting the removal of aqueous arsenic onto/into solid phases; finally 3) Water around the well with low iron and arsenic can be extracted from the aquifer.

By periodically extracting anoxic groundwater and injecting

Table 1
Advantages and disadvantages of common arsenic removal technologies.

	Advantages	Disadvantages
Ex-Situ (Berg et al., 2007; Litter et al., 2010; Mohan and Pittman, 2007; Mondal et al., 2006; Pokhrel et al., 2009a; Sarkar and Paul, 2016)		
Oxidation	+ Simple and low cost operation	+ Highly contaminated with As sludge
(air, UV, ozone, ox. agents)	+ Chemical oxidation relatively simple and rapidly oxidizes other impurities	+ Dose of oxidizing agents: Extra costs and chemical waste
+ **Precipitation**		
(Alum/iron coagulants)	+ kills microbes	+ Some oxidants produce toxic and carcinogenic by-products.
+ **Filtration**	+ Lime softening: efficient As removal and reduces corrosion	+ Efficiency reduced by competing ions
Adsorption	+ Well established and commercially available	+ Produces toxic solid waste
(active carbon, activated alumina, ferric hydroxides)	+ High removal efficiency	+ Regeneration/replacement of adsorbent
	+ Improves taste and odor	+ Optimum pH conditions required
	+ Suitable for home use with simple replacement requirements	+ Suspended solids and other salts affect adsorption efficiency
Ion exchange	+ High efficiency and versatile process	+ Not suitable for As(III) removal
(synthetic resins, zeolites)	+ Ion-exchange resin: well-defined medium and high capacity	+ High investment and maintenance costs
		+ Toxic sludge disposal problem
		+ Replacement and regeneration of resins
Membrane filtration	+ Well established process useful at households level	+ High investment, operation and maintenance costs
(NF, RO)	+ Removes dissolved salts, turbidity and other contaminants	+ Produces highly contaminated waste water
		+ Membranes are prone to scaling and fouling
	+ No solid waste is produced	+ Low water recovery rates (10–20%)
	+ Highly effective towards As, also with high TDS	
In-Situ (Bundschuh et al., 2014; Litter et al., 2014; van Halem et al., 2010a; Xie et al., 2015)		
SAR:	+ No solid or liquid waste production	+ High dependency on hydrogeological and geochemical conditions (e.g. pH, redox)
+**Oxidation** (air)	+ Low cost and low maintenance	
+**Sorption/Co- precipitation**	+ Protects well and pumps from clogging	+ Competing ions can reduce As adsorption
	+ Adsorption (Fe, Mn) and oxidation of other substances (organic matter)	+ Addition of iron sometimes needed
		+ As immobilization in long-term uncertain
	+ If ox. with air: no use of chemicals	+ Air oxidation slow process especially for manganese
Permeable Reactive Barrier	+ No waste production in the surface	+ Higher initial costs
(ZVI, iron slag, Fe/Al-oxides, multifunctional barriers)	+ Low operational and maintenance costs	+ Involves complicated drilling
	+ No large installations or equipment on the surface	+ High permeable and reactive/adsorbent materials needed
		+ Dependency on physical and geochemical conditions
		+ Long-term effectiveness uncertain
Bioremediation	+ Cost effective	+ High dependence on soil chemistry, climate, hydro-geo dynamics, environ. conditions etc.
(Biosorption/-transformation;	+ Plants/microbes reduce pollutant leaching into soil and groundwater	
Phytoextraction/-stabilization;		+ Disposal of As bearing waste
Hyperaccumulation, etc.)	+ Combination for bioenergy production from biowaste possible	+ Use of soil amendments (iron, organic matter, phosphorous) sometimes needed
	+ Growth of microorganisms have positive effects on soil and groundwater	+ As mobility increased by some soil nutrients/ competing ions

aerated water into the aquifer through the tube well, alternate oxidizing and adsorbing phases of iron and arsenic are induced so that larger water volumes with reduced arsenic levels can be subsequently extracted (Grischek et al., 2015).

Two types of technological SAR systems can be differentiated: 1) One or two wells being operated alternately by injection-extraction for small-scale application; and 2) Extraction well surrounded by infiltration wells for large-scale application.

Fig. 1 shows a schematic diagram of a typical SAR unit consisting of an aeration system, with storage tank, and one tube well for the infiltration and the extraction of the groundwater. Under natural reducing conditions of an aquifer ($Eh < 0$) iron(II), manganese(II) and arsenic(III) can be found in dissolved form. With the input of oxygen during the infiltration/oxidation phase (Fig. 1, left), the redox potential of the aquifer increases ($Eh > 0$) and aqueous Fe(II) will be oxidized to solid iron hydroxide. The oxidation of manganese takes place after iron(II) oxidation is completed. In the course of time, solid iron and manganese oxidation products will build up a coating around the soil grains in groundwater enhancing adsorptive places (Henning and Rott, 2003).

During the adsorption or delivery phase (Fig. 1, right) contaminated groundwater flows through the formed adsorption zones where iron, manganese and arsenic species can be adsorbed and then co-precipitated through different mechanisms. When more water is extracted, dissolved Fe(II) is adsorbed onto the Fe(III) coated soil grains (Jeon et al., 2003). The adsorbed Fe(II) will be oxidized during the next oxidation phase resulting in an enhanced adsorptive surface area of HFO, which has the ability to adsorb both As(III) (Dzombak and Morel, 1990) and As(V) (Suthersan et al., 2017).

The main chemical oxidation reactions occurring can be written as:

$$2Fe^{2+} + ½O_2 + (x+2)H_2O \rightarrow Fe_2O_3 \cdot xH_2O + 4H^+ \quad (1)$$

$$2Fe^{2+} + ½O_2 + 3H_2O \rightarrow 2FeO(OH) + 4H^+ \quad (2)$$

$$Mn^{2+} + ½O_2 + H_2O \rightarrow MnO_2 + 2H^+ \quad (3)$$

$$H_3AsO_3 + {}^1\!/_2O_2 \rightarrow H_2AsO_4^- + H^+ \quad (4)$$

In general, the oxidation of Mn^{2+} requires a redox potential $Eh > 800$ mV as shown in Fig. 2 which is higher than those needed for the oxidation of iron. Hence oxidation of manganese takes place after the oxidation of iron (Kim and Nriagu, 2000).

Despite the lower redox potential compared to Fe and Mn required for the oxidation of As(III) to As(V) (Fig. 2), oxidation by oxygen in water occurs very slowly making it generally not relevant for *in-situ* As removal. Some studies, e.g. Kim and Nriagu (2000), showed that the half-lifetime of naturally occurring As(III) was four

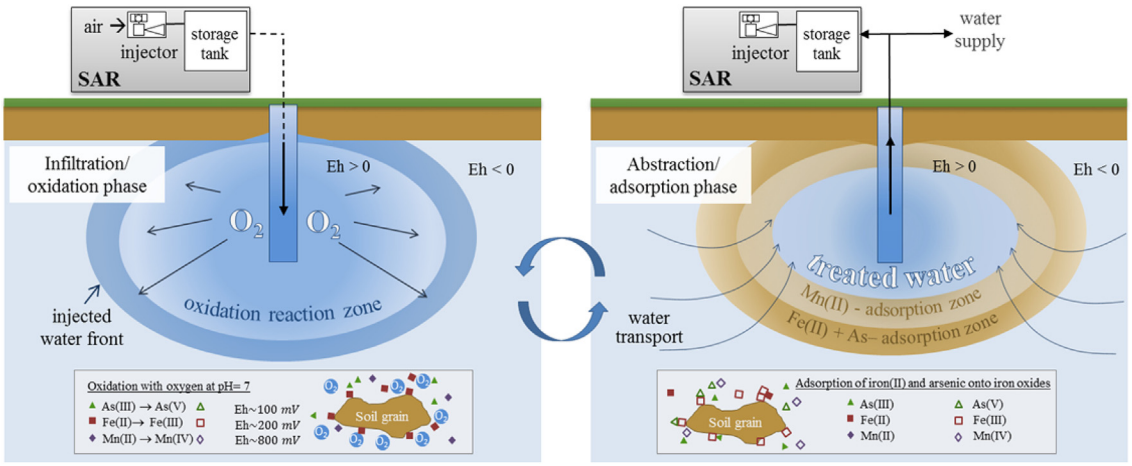

Fig. 1. Scheme of a subsurface arsenic removal system (SAR) consisting of an aeration unit and storage tank. Left: Infiltration of oxygen into the aquifer and relevant oxidation reactions. Right: Transport and adsorption scheme for the abstraction of treated water.

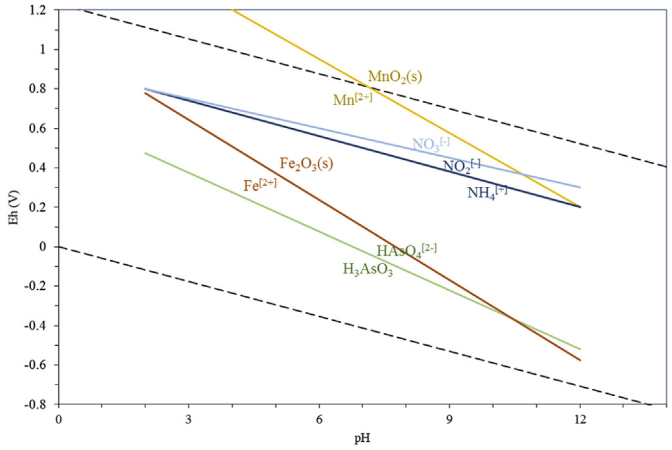

Fig. 2. Eh-pH diagram of relevant water parameters for aquatic systems (in between dotted lines). Based on Eh-pH diagrams from FACT database, (Smedley et al., 2002; Takeno, 2005), N-O-H system mod. from (Rott and Friedle, 2000).

to nine days when saturated with air and two to five days with pure oxygen. However, the oxidation process can be accelerated, for example by the presence of manganese oxides (MnO_2), which act under various conditions as a solid oxidizing media for both As(III) (as shown in Eq. (5)) and Fe(II) (Driehaus et al., 1995; Wu et al., 2015).

$$MnO_2 + H_3AsO_3 \rightarrow Mn^{2+} + HAsO_4^{2-} + H_2O \quad (5)$$

This process contributes to the abiotic As(III) oxidation what, on the one side, reduces the concentrations of the more toxic arsenite species (compared to arsenate). On the other side, the formation of manganese oxides also enhances the immobilization of As(V) by sorption onto Fe oxides and its precipitation as manganese arsenate compounds (Cheng et al., 2008; Huang and Kretzschmar, 2010; Nitzsche et al., 2015b).

If ammonium (NH_4^+), nitrite (NO_2^-), methane (CH_4) or other oxygen-demanding substances are present in the groundwater, the economic efficiency of the SAR process can be significantly lowered as more oxygen needs to be delivered by the system. The oxidation of NH_4^+ to nitrate (NO_3^-) over NO_2^- can be summarized according to following equation:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (6)$$

Although the oxidation processes occurring in the groundwater are both chemical and microbial-driven, Mn oxidation does not occur in the presence of NH_4^+ and NO_2: The chemical oxidation of Mn^{2+} by oxygen at neutral pH is rather slow as it occurs optimally at a very high redox-potential (cf. Fig. 2) so that microbial catalysis is needed for the effective manganese removal with SAR (Farnsworth et al., 2012; Nitzsche et al., 2015a). However, the oxidation of NH_4^+ and NO_2^- through nitrification is energetically more favorable than Mn oxidation, so that manganese removal through SAR will take place only after ammonium is completely oxidized (Gouzinis et al., 1998; Nitzsche et al., 2015b; Vandenabeele et al., 1995). Furthermore, processes with high oxygen demand such as the oxidation of ammonium or methane can lower the oxygen availability and thus slow the microbial activity for the manganese oxidation. It is therefore important to assess the quality of the raw water for each SAR application, i.e. when NH_4^+ might be present. Nonetheless, the successful removal of both manganese in the presence of ammonium has been observed in different case studies (Kellner et al., 2016; Rott et al., 2002). It must also be considered that seasonal fluctuations in the concentrations of ammonium might occur in places close to surface water sources. This indicates that the interaction between groundwater and surface waters have an effect on redox conditions throughout seasonal changes, which might have an impact on the SAR process throughout the year (Richards et al., 2017).

Changes in redox potential also have an influence on arsenic remobilization in the aquifer due to reductive dissolution of Fe(III) oxides. The key factors controlling this process are still poorly understood (Zhang et al., 2017b). The transformation of the Fe-oxides under reducing conditions is presumably controlled by biochemical processes and may cause pronounced changes in the As adsorption potential over time (Neidhardt et al., 2014). Generally, the transformation of less crystalline phases into more crystalline ones increases the potential for arsenic mobilization, and it can occur spontaneously or can be driven by changing redox conditions (Campbell and Nordstrom, 2014). Reductive conditions within the aquifer can be caused by the biogenic decomposition of buried organic material, and leads to the microbial reduction of iron (hydr) oxides and the subsequent release of the adsorbed arsenic (Berg et al., 2007, 2001; Frising, 2014; Zhang et al., 2017a).

However, adsorbed arsenic can also retard or inhibit the

transformation of ferrihydrites by blocking surface sites and thus preventing its reductive dissolution and recrystallization, stabilizing the less-crystalline phases with higher adsorptive capacity (Campbell and Nordstrom, 2014).

Unstable redox conditions may also increase the remobilization of arsenic so that maintaining controlled redox conditions is crucial to avoid the long-term arsenic mobility (Bissacot and Ciminelli, 2014). Overall, the long term study of the adsorption-desorption process on the sediment surface is a key aspect needed for the understanding of the migration and transformation of arsenic (Zhang et al., 2017b).

Besides redox condition the chemical stability over time of the different mineral complexes and desorption kinetics of arsenic are affected by various geochemical factors including most importantly pH, natural organic matter content and microbial oxidation reactions (Datta et al., 2014; Leiva et al., 2014; Zhang et al., 2017b). Studies also show the effect of surface site competition e.g. HCO_3^-, phosphates, silicates etc. (Gao et al., 2013; Jeon et al., 2003; Kanematsu et al., 2013; Norrman et al., 2008; Thi Hoa Mai et al., 2014) on arsenic mobilization. The type of mineral deposits plays also an important role. Iron(III)arsenate minerals (e. g. scorodite; eq. (7)) shows a release of As under acidic and reducing conditions, whereas the stability of Fe-S-As minerals (e.g. arsenopyrite) is favored for example in reduced aquifers (Ciminelli, 2014). At higher pH other mechanisms might contribute to As release for example from desorption from iron-(hydr)oxides coatings and dissolution of arsenopyrite (Bia et al., 2014; Ciminelli, 2014).

Under most natural pH conditions in groundwater, As(V) adsorbs more strongly on Fe(III)-(hydr)oxides than As(III) (Pierce and Moore, 1982). The dominant mechanism for the proposed arsenic removal is an adsorption-oxidation reaction. Non-ionic arsenite As(III) can be adsorbed by HFO through Lewis acid-base interactions, whereas ionic arsenate As(V) is adsorbed by both Lewis acid-base and Coulombic (electrostatic) interactions (Huling et al., 2017) at lower pH conditions where amphoteric HFO is positively charged, and hence can be more readily adsorbed (Suthersan et al., 2017). Thus arsenite has a weaker adsorption on mineral phases as it is uncharged below pH < 9.2 (Ladeira and Ciminelli, 2004). Yet, some studies state that process regarding adsorption onto iron minerals are much more complex (Dixit and Hering, 2003) and that adsorbed arsenite can oxidize in a variety of minerals and natural soils (Campbell and Nordstrom, 2014).

The primary mechanism for removal of As(V) and As(III) from groundwater is likely to be the adsorption by oxidized sediments containing Fe(III) (Stollenwerk et al., 2007). Arsenate can react with $Fe(OH)_3$ to $FeAsO_4$ as shown in (Eq. (7)):

$$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4 \cdot 2H_2O + H_2O \quad (7)$$

The strongest adsorption of both arsenic species on the iron oxides is formed via inner-sphere complexation through direct coordination with the hydroxyl groups on the surface of HFOs (Cheng et al., 2008; Loring et al., 2009), mainly by way of monodentate, mononuclear complex as well as bidentate complexes with lower adsorption rate through ligand exchange (Grossl et al., 1997; Yoon et al., 2016), as shown in Fig. 3.

Besides the oxidation state of As, adsorption efficiency also depends on other solutes that compete with As for adsorption sites through similar mechanisms. Phosphate, bicarbonate and silicate have similar, strong ligand properties to arsenate and arsenite, and can compete with arsenic through Lewis acid-base interactions for the adsorption on iron (Stollenwerk et al., 2003; Suthersan et al., 2017).

The decreasing arsenic removal efficiency by these ions is also linked to the sequestering properties that hinder the formation of ferric(III)-hydroxide from Fe(II). Furthermore, the effects of competing anions on the As(III) removal in oxidation/adsorption processes have been proven to have a strong dependence on pH changes, showing higher competitive adsorption with increasing pH values (Guan et al., 2009).

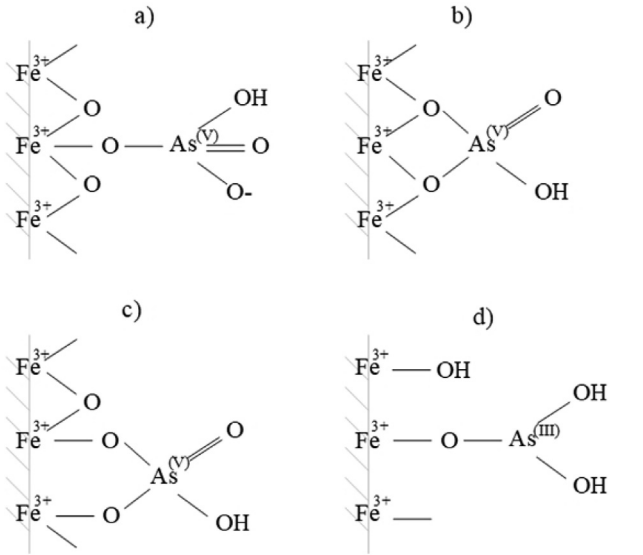

Fig. 3. Arsenic inner-sphere complexation (a) monodentate mononuclear, (b) bidentate mononuclear, (c) bidentate binuclear for As(V) (mod. from Cheng et al., 2008); and (d) monodentate complex for As(III) (mod. from Yoon et al., 2016).

2.1. Operational aspects of SAR technology

SAR technology bases on the periodically (alternating cycles) but continuously (long term) infiltration of oxygen-enriched water into the aquifer to ensure a permanent state of oxidation/adsorption zones. The continuous interchange between infiltration and abstraction phases allows the adsorption to take place while oxidation zones are formed. Once an oxidation zone is developed, more water can be safely extracted. Here, the volumetric ratio determines the efficiency of the mitigation system (van Halem et al., 2010a). The efficiency Q_E of the SAR process is expressed either as the ratio of extracted to injected water volume V_E/V_i or by the ratio $(V_E\text{-}V_i)/V_E$. For example, if the extracted volume is twice as large as the injected volume, then $V_E/V_i = 2$ and $(V_E\text{-}V_i)/V_E = 0.5$. Higher volumetric coefficients V_E/V_i may affect the stability of the oxidation zones. These may also decay as a result of disturbances during the process, what will result in higher concentration of iron-(hydr) oxides near the extraction zone of the well and narrowed adsorption zones for Mn(II). The oxidation species (e.g. manganese oxides) can then be reduced and a mobilization may occur. It is therefore important that oxidation conditions achieved in the aquifer are kept, even in the long term, and that the volumetric coefficient is not exceeded.

The remobilization of arsenic after the adsorption onto HFOs is, furthermore, a potential risk of the process. However, the process kinetics of the remobilization have not yet been quantified or studied in detail. Nevertheless, long time experience with SIR has showed that formed iron oxides are very stable with time and have a much higher density than freshly build flocks. Regarding the blocking of the well and/or the aquifer, it is proven that in situ process by aeration prolongs the life expectancy of the wells (Grischek et al., 2015). The precipitated iron and manganese accumulate in the aquifer and favor the adsorption of dissolved iron

and manganese by providing more surface areas (Zhang et al., 2017b). With time, iron and manganese are removed more effectively from the aqueous phase. However, the proper development of precipitation zones is very important to achieve higher removal efficiencies, which may take up to ten or more injection cycles (Tredoux et al., 2004).

The precipitation of iron and manganese only occurs when the equilibrium is displaced towards the oxidative side through the addition of oxygen-enriched water. The large pore volume provided by the reaction zone in the underground around the well and underneath favors the precipitation of iron (Ahmad, 2012). Also, when operated properly and continuously, the tube well used for abstraction and infiltration cycles will be permanently protected by the oxygenated water front which effectively blocks the transport of reduced iron and manganese to the borehole and prevents the clogging of pumping equipment and screens.

With time, the precipitated iron may settle to more stable forms (e.g. hematite), which have a smaller volume than the first formed hydrated oxides (e.g. ferrihydrite) (Tredoux et al., 2004). Precipitates of iron and manganese show also the smallest size in a coarse aquifer. By the proper development of the oxygenation zone and operation of the plant, the loss of pore volume in the aquifer happens only slowly and its permeability is not be reduced even after many years, so that no long term risks of clogging of the aquifer is expected (Mettler et al., 2001).

Other important hydrological requirements for the safe operation of the SAR include the type of aquifer. Porous aquifers with high specific surface values like sand or gravel layers are well suitable, whereas clay and marl aquifers are not appropriate. Furthermore, the influence of natural flow of groundwater needs to be considered. Hereby, a raw water analysis to estimate operational cycle duration and infiltration to abstraction ratios must be carried out before starting any pilot trials. A proper construction and safe sealing of boreholes and wells to prevent negative influences on the aquifer, e.g. by surface water infiltration, is highly important (Grischek et al., 2015).

The subsurface iron and arsenic removal has been investigated in different studies. A distinction is drawn between two types of SAR approaches: one without using any addition of chemicals injecting only aerated natural groundwater, and one which, besides aeration, also doses dissolved Fe(III). Since the removal of arsenic requires a higher concentration of Fe than of As, the latter approach has been applied in grounds where iron is naturally too low. Nevertheless, the most common type of SAR makes use of high natural Fe levels. Both approaches are considered in the following sections.

2.2. Subsurface arsenic removal (SAR) technology by dosing Fe and aerated water

Welch et al. (2008) studied subsurface arsenic removal with a combination of aerated water and the injection of ferric chloride in two wells with depths of >30 m in Carson Valley, NV, USA. Arsenic concentrations in groundwater beneath Carson Valley in western USA typically exceeded the 10 $\mu g\,L^{-1}$ drinking water standard with concentrations of around 30–36 $\mu g\,L^{-1}$. The groundwater was typically alkaline (pH > 8) and had dissolved Fe concentrations lower than a few tens of $\mu g\ L^{-1}$. Both wells had similar total As concentrations; however, one aquifer had high concentrations of As(III) and the other contained mostly As(V).

During the pilot trials the following chemical and physical processes were applied: 1) Injection of Cl_2 which oxidized As(III) to As(V) during a reaction time of about 7 min 2) Cl_2 subtraction to prevent formation of undesirable disinfection by-products in the aquifers 3) Injection of dissolved O_2 and Fe(II) to form Fe-oxide in the aquifer and HCl to lower the pH 4) Outgassing of CO_2.

The Fe(II) concentration in the injection water ranged between 0.15 and 6.35 $mg\,L^{-1}$ and the pH was 5.3–6.4. By setting the flow rate about 120 $L\,h^{-1}$, the injected water volume was 790–2880 L and the extracted volume was 1340–3900 L, which amounted to a SAR efficiency Q_E of up to 0.6. The time between the end of injection and the beginning of withdrawal was generally about 1 h. After conducting several trials, the extracted water achieved As levels as low as 1 and 6 $\mu g\,L^{-1}$; however, during some withdrawal periods Fe and Mn concentrations exceeded U.S. secondary drinking water standards (0.3 and 0.05 $mg\,L^{-1}$, respectively) (U.S. EPA, 2012). The authors concluded that the evaluation of optimum design parameters needs further investigation.

Miller (2008) combined the pulsed injection of aerated water and ferrous iron to remove As(V). The pilot trials were conducted at the San Antonio Field Laboratory (SAFL) located in a valley-fill aquifer in central New Mexico. The testing was successful in reducing ambient arsenic concentrations (38–42 $\mu g\,L^{-1}$) and iron concentration (0.189 $mg\,L^{-1}$) to below the drinking water standard by multiple, daily injections of air and iron in short-duration pulses. The investigation was able to show a clear trend towards lower arsenic concentrations only after the addition of iron. An incremental increase in arsenic removal capability was achieved at the site. Some difficulties were caused by iron pre-oxidation in the apparatus, which should be reduced to better control the amount of iron injected for the same effect.

Chen and Leung (2016) proposed an *in-situ* technique using injection of ferric iron and a NaOH solution to force the precipitation iron and the arsenic co-precipitation. First, the ferric iron solution and NaOH were injected into a well with arsenic contamination. The ferric iron hydrolyzed and precipitated as amorphous ferric hydroxide (HFO) in the local aquifer surrounding the well. Arsenite and arsenate could be then intercepted and sorbed onto HFO in the adsorption zone. Although the technology was proven to be feasible, the major drawback of this approach was the injection of chemicals into the aquifer that may cause unexpected biochemical and geochemical effects in the subsurface system with unknown long-term consequences.

Krüger et al. (2014) conducted pilot trials on *in-situ* immobilization of arsenical chemical warfare agents (CWA) at a contaminated military site in Northern Germany. The site showed concentrations of CWA containing arsenic ranging from 30 $\mu g\,L^{-1}$ up to 9.0 $mg\,L^{-1}$ (arithmetic mean: 2.4 mg As L^{-1}). CWA showcased arsenic mainly in organic form as phenylized As compounds. The proportion of inorganic As(III) and As(V) in total As ranged from 6 to 87%. Two remediation wells (depth: 15 and 19 m) were installed for pumping and infiltration. Total arsenic was measured to 1.3 and 2.5 $mg\,L^{-1}$, respectively. Krüger et al. (2014) showed that organic arsenic compounds from CWA could be precipitated by adding different Fe(II) compounds. $FeCl_2$ and $FeSO_4$ showed the best removal efficiency of total As of about 80%. The treatment unit consisted of three 500 L tanks: aeration tank, degassing tank, and buffer tank. The water was infiltrated in cycles, each one consisting of four steps: 1) Infiltration of Fe(II)Cl_2 dissolved in water (up to 118 $g\,L^{-1}$) stripped with N_2 in order to decrease dissolved oxygen (DO) concentration; 2) Infiltration of dissolved Fe into the aquifer; 3) Infiltration of aerated water to induce oxidation of Fe and precipitation of HFO; and 4) Infiltration of untreated water for dilution in order to reduce the risk of clogging the well. It was demonstrated that total As could be reduced to less than 0.4 $mg\,L^{-1}$, with the main advantage that no contaminated sludge or adsorption material had to be disposed of. However, the main challenge here was the clogging problem due to the precipitation of HFO in the screen of the well. Furthermore, the authors mentioned that this remediation technique could also be used to treat groundwater with

naturally occurring As in order to produce drinking water.

2.3. Subsurface arsenic removal (SAR) technology by only dosing aerated water

The first pilot trials using SAR were conducted in the 1990s by Rott et al. (1996) in Germany with groundwater characterized by anoxic conditions and high values of Fe(II), Mn and As, which occurred mainly in its trivalent form. The trials (26 cycles) were carried out with two wells of 30 and 50 m depth with total As of 38 and 25 $\mu g\,L^{-1}$, respectively (As(III) = 24 and 25 $\mu g\,L^{-1}$, Fe = 1.97 and 0.29 $mg\,L^{-1}$; Mn = 0.35 and 0.29 $mg\,L^{-1}$). After running six cycles, water in both wells reached values in compliance with the German drinking water standard regarding iron (0.2 $mg\,L^{-1}$ (TrinkwV, 1990)). However, only the first well provided good drinking water quality with regard to Mn (0.05 $mg\,L^{-1}$) and As (10 $\mu g\,L^{-1}$). This well could be operated up to a water volume efficiency of $Q_E = 0.75$ whereas the Q_E of the second well was limited to 0.5. Throughout the four-month trials, more than 30,000 m^3 treated water were extracted. The limited removal efficiency of the second well was explained by strong inhomogeneities in the aquifer that resulted in an insufficient formation of an oxidation zone in the aquifer.

van Halem et al. (2010a) studied iron and arsenic removal as a low-cost technology for community-based water supply in Bangladesh. Two wells in Manikganj district west of Dhaka were selected as test grounds for the study. Both sites showed the same total dissolved arsenic concentration (145 $\mu g\,L^{-1}$) with an As(III) fraction of around 82–85% and higher concentrations of iron (1.0; 15 $mg\,L^{-1}$) and manganese (2.5; 0.3 $mg\,L^{-1}$). The pilot set-up was connected to the existing hand-pump of an existing tube well with 31 m depth and perforated well length of 3 m. The extracted groundwater was aerated, sand-filtered and passed through an adsorptive arsenic filter. The maximum injection volume was limited to 1 m^3. Treated water reached As levels of <10 $\mu g\,L^{-1}$ and iron BDL. The study was conducted by varying the ratio between abstracted and injected water volume as it is the volumetric ratio that determines the efficiency of the system. Typically abstraction started 12–16 h after injection. Results showed a much faster rising of arsenic concentrations than of iron concentrations in the second well. However, several cycles were needed to achieve effective removal of iron and arsenic. The comparison indicated that the occurrence of a high iron level in the groundwater did not promote the effective co-removal of arsenic during subsurface treatment since both wells showed similar breakthrough curves for arsenic at the same volumetric ratio of abstracted and injected volumes.

Furthermore, the authors concluded that injection of oxygen at higher concentrations (<1–5.3 mg $O_2\,L^{-1}$) promoted the subsurface removal of iron. However, the better retention of iron did not enhance the co-removal of arsenic. Subsurface iron removal increased with every successive cycle, so that the ratio of abstracted to injected volume would rise. On the other hand, arsenic removal efficiency was not sufficient and a breakthrough of 10 $\mu g\,L^{-1}$ was observed before a volume ratio (abstracted to injected) of 1 was reached. This was attributed to the short contact times (20 min) within the oxidation zone and the presence of competing anions such as phosphates as it has previously been discussed in section 2.

van Halem et al. (2010b) also conducted anoxic column experiments with natural groundwater to simulate the shifting redox conditions in the oxidation zone during subsurface iron and arsenic removal. The column experiments provided controlled conditions for the investigation of the adsorptive-catalytic oxidation mechanism by spiking the water with As(III). The operational mode of injection–abstraction at the test facility was simulated in the 2D plug flow environment of the columns with down flow 1.0 $L\,h^{-1}$ for both injection and abstraction. The water samples showed average pH of 7.1, almost constant temperature of 12 °C, iron concentrations of 5.3 $mg\,L^{-1}$, manganese concentrations of 0.61 $mg\,L^{-1}$ and phosphate concentrations of 1.13 $mg\,L^{-1}$. In the column experiments, As(III) was dosed at different concentrations (232, 112, and 67 $\mu g\,L^{-1}$) in order to study the effect of changing the Fe:As ratio in groundwater on the adsorptive removal efficiency of arsenic. Iron concentrations in the groundwater remained constant, thus the respective Fe:As ratios were 28, 63, and 103. For the testing, oxygen-rich (8.9 $mg\,L^{-1}$) drinking water was dosed to the columns for 1.5 pore volume (transparent PVC, length: 80 cm, inner diameter: 36 mm); after a waiting period of 16 h the columns were restarted with natural groundwater and monitored for the retardation of arsenic and iron. It was assumed that, as in the subsurface process, homogeneous oxidation and precipitation were extremely limited as were heterogeneous oxidation and adsorption processes, hence the mechanism of adsorptive-catalytic oxidation dominated.

The efficiency of subsurface iron removal (van Halem et al., 2010b) was much higher than could be explained by the adsorptive-catalytic oxidation in the column experiments. Hence other processes (e.g. biotic or transport mechanisms) must contribute to the iron removal efficiency of the system.

It was shown that arsenic adsorption during subsurface treatment was controlled by the amount of adsorbed oxidized iron and not by the amount of removed iron. This was significant for the operation of the process since it became apparent that the oxygen concentration of the injection water did not control the arsenic removal, but rather the injection volume. van Halem et al. (2010b) also found no relation between the amount of removed arsenic and the Fe:As ratio of the groundwater. Rather, the authors suggested that the removal of arsenic was limited by competing ions such as phosphate.

van Halem et al. (2009b) compared subsurface adsorption mechanisms with adsorption treatment technologies using iron(-hydr)oxide media, which is a popular low cost-technique. Iron precipitates from SIR plants have been characterized in previous research to contain mainly goethite FeO(OH) (50–100%), as well as traces of ferrihydrites. The latter is also called “amorphous iron oxide” or hydrous ferric oxide (HFO). With time, HFO transforms into stable iron oxides like goethite, which is one of the most stable ferric oxides. This process is considered the main reason why iron precipitates do not clog the subsurface pores since the volume of amorphous HFO is reduced by the crystallization processes. The oxidation process of As(III) to As(V) in the presence of oxygen was slow and took several days. Research also showed that remobilization of adsorbed arsenic occurred stepwise and slowly, and that the efficiency of arsenic adsorption on iron oxides depended on the pH and presence of interfering anions, such as phosphate. With increasing pH, the adsorption of As(V) decreased whereas the adsorption of As(III) showed a maximum around neutral pH (Hsia et al., 1994; Pierce and Moore, 1982). Furthermore, the adsorption of As(V) was reduced by half when phosphate was present at pH 7 and a ratio of PO_4^{3-}/As of 10. The observed effect of phosphate concurs with their previous studies (van Halem et al., 2010a, 2010b).

Gude et al. (2016) investigated the natural arsenic removal capacity at three groundwater treatment plants in the Netherlands with arsenic levels of 10–26 $\mu g\,L^{-1}$ in order to identify operational parameters to obtain As concentrations < 1 $\mu g\,L^{-1}$. Groundwater treatment in the Netherlands usually comprises aeration and subsequent sand filtration without using any chemicals. Gude et al. investigated the interaction between As, Fe, PO_4^{3-}, Mn and NH_4^+ after aeration and during rapid filtration in the natural groundwater matrix. They showed that As(III) was not efficiently removed in the supernatant water after aeration, even after extending residence time (12.4–13.9 min). Despite the fact that all Fe(II) was

precipitated into filterable HFO flocs, most naturally occurring As(III) remained mobile achieving only 20–48% removal with 1.4–4.2 mg L^{-1} precipitated Fe(II). However, added As(V) was readily adsorbed. Moreover it was shown that the improved As(III) removal from the aerated supernatant water occurred in the rapid sand filter also after 60 min residence time. This was credited to the accumulation of manganese on the sand filter grains, which lead to the catalytic oxidation of As(III) by manganese oxides and the readily adsorption of oxidized As(V) onto HFO flocs (Nitzsche et al., 2015b). This improved removal efficiency by the filter bed was not observed for PO_4^{3-}. However, NH_4^+ and Mn, which showed no removal in the supernatant water, were completely removed by the sand filter bed. NH_4^+ removal was attributed to biological activity in the filter bed (nitrification reaction) while the Mn oxidation could have been both biotic and abiotic.

Sen Gupta et al. (2009) conducted a study in Kasimpore, 25 km from Kolkata (India). The main sources of water for the village were shallow and tube wells. Preliminary studies revealed that 70% of the tube wells had arsenic concentrations above 50 μg L^{-1}. Plastic shower heads were used to oxygenate the water to DO levels up to 6 mg L^{-1} by spraying it in a plastic tank in certain operating sequences (delivery, rest, infiltration). The typical aerated water infiltration and extraction volumes were 2000 L and 4000 L respectively with flow rate at around 2.7 m^3 h^{-1}. An As level of below 10 μg L^{-1} in the extracted water could be achieved finally. The operation cost was estimated at USD 1.0 per day for producing 2000 L of extracted water.

The results have been documented in a report (Sen Gupta, 2008) for the different pilot trials of six plants in rural locations in West Bengal, India in a project financed by the World Bank. All plants were managed by local water users and supplied water to the local population. The results showed that the SAR process was able to reduce the total arsenic content from 150 to 300 μg L^{-1} to below 50 μg L^{-1} with a capacity of 3–4 m^3 per cycle at efficiency Q_E of 0.33–0.5. Although no concentrations below the WHO standard of 10 μg L^{-1} were achieved, the results show that the SAR process is a feasible arsenic removal technique suitable as a low cost treatment. However, the authors didn't provide further information regarding iron concentrations or other raw water parameters which can explain the high efficiency results regardless both – high recovery rates and still relative lower oxygen concentrations.

Rott and Kauffmann (2008) carried out a field test using SAR in Kashimpur, a rural community in West-Bengal, India. The *in-situ* treatment plant was operated manually at a well with 37 m depth, alternately draining and infiltrating into the same well. The low-cost aeration occurred by passing the groundwater through three shower heads and storing in a tank before infiltration. During the first period, 4 m^3 were delivered and 2 m^3 were infiltrated. The cycles during the first phase consisted of 80 min delivery, 30 min intermission and 40 min infiltration, adding up to a total time of 2.5 h. In a subsequent second phase the volume of infiltration was increased to 6 m^3, extending the cycle time to 7 h in total. After having run the SAR system for about 16 months, a significant drop of the initial arsenic concentrations of 150–300 μg L^{-1} in the delivery water was observed and stable concentrations below 10 μg L^{-1} were achieved after 19 months operation. This decrease could be explained by the fact that, during the field trial, traces of iron accumulated in the oxidation zone; at a particular time there was enough iron present to make higher arsenic removal possible.

Rahman et al. (2014) analyzed the subsurface arsenic removal in two wells (approx. 22 m depth) at Muradnagar Upazila, Comilla district, Bangladesh with As concentration of around 200 μg L^{-1} and Fe level of 12.6 and 8.7 mg L^{-1}, respectively. Larger injection volume, lower pumping rate and intermittent pumping had positive effects on arsenic removal indicating that arsenic adsorption was kinetically limited. After injecting 1 m^3 of aerated water, a maximum of 3 m^3 of water with As < 50 μg L^{-1} was extracted, of which 2 m^3 were used for drinking (in compliance with Bangladesh MCL of 50 μg L^{-1}) and the remainder was used for re-injection. Besides pumping rate and injection volume, the pH of the water played a major role. The pH of injection water was always above 8, whereas the pH of extraction water always started below 8, which was attributed to formation of H^+ ions due to Fe(II) oxidation (see Eq. (1–2)). The results also showed that higher pH was essential for better As adsorption on HFO, which increased up to a pH value of 8.5, but decreased above this value (Kartinen and Martin, 1995). The cost for 1 m^3 treated water was estimated at USD 2.0.

Sarkar and Rahman (2001) carried out SAR trials with groundwater at Maijdee area, Bangladesh with three shallow tube wells (screen depth 10–12 m). The iron and arsenic levels were measured as 1.0, 2.4, 1.0 mg L^{-1} and 0.11, 0.52 and 1.3 mg L^{-1}, correspondingly. 500 L aerated water were re-injected; after 12 h 3 m^3 were extracted. They were able to reduce the arsenic level by 50% up to an extraction of 2.5 m^3. However, only the treated water from the tube well with an As level of 0.11 mg L^{-1} could comply with the Bangladeshi MCL of 50 μg L^{-1}. The rather low As reduction was mainly attributed to the relatively low level of dissolved oxygen in the aerated water (5 mg L^{-1}). Monitoring of the injected and pumped water was therefore suggested. Furthermore, Sarkar and Rahman (2001) also recommended having an iron content 10 times higher than the arsenic level for increasing SAR potential.

The influence of dissolved oxygen in the infiltrated water is in agreement with van Halem et al. (2010a) and was also shown in a study of Visoottiviseth and Ahmed (2008). The study revealed that the *in-situ* oxidation method was able to meet the Bangladesh standard of 50 μg L^{-1} when the arsenic level in the groundwater was less than 100 μg L^{-1}. Treatment efficiency improved if the dissolved oxygen level of recharge water or the quantity of recharge water in the aquifer increased.

Brunsting and McBean (2014) used a solution with constant iron and arsenic concentration (5.3 mg L^{-1} and 200 μg L^{-1}) under anoxic conditions to study key factors of the SAR process ahead of possible field tests. Fe and As salts were dissolved in water with DO less than 0.05 mg L^{-1} (oxygen removal by nitrogen gas sparging) in order to mimic the anoxic groundwater of Bangladesh. The model water was then aerated and passed through a simple sand filter (L = 2 m; d = 0.5 m). With the exception of initial trials, all experiments were conducted with As(V). At a HRT of 13 h the maximum removal of arsenic was 79% at a local point in the apparatus, while a total removal of 59% between inlet and outlet was observed. In addition, Brunsting and McBean (2014) examined characteristics of iron and arsenic co-precipitation in a simplified environment by conducting a lab-scale jar test with short-time vigorous aeration and subsequent settling and sampling of supernatant solution. After the 5-day experimental period, Fe concentration dropped by only 5% whereas the As level dropped by 77%. The low Fe reduction was attributed to the lower pH at the end of the experimental period. On the other hand, this shows that a relatively small drop in iron has a large effect on the arsenic removal. Hence a large removal rate was achieved at an Fe:As mass ratio of 1.5 (molar removal ratio of 2.0). They confirmed co-precipitation as the main removal mechanism since 37% of the removed As could be re-mobilized into the solution after five days by vigorous stirring.

In order to get an overview of the different trial tests on subsurface removal of arsenic by aeration, a comparison of the several different case studies and investigations is shown in Table 2. Here, the most important parameters that play a role in the subsurface arsenic removal are shown. Besides the concentration of arsenic and iron, these are the concentration of important co-ions, and efficiency ratio of extracted to injected volume ($Q_E = V_E/Vi$).

Table 2
Overview of SAR technologies by only dosing aerated water.

Location	Fe (mg L^{-1})	Total -As (μg L^{-1})	As (III) (μg L^{-1})	As (V) (μg L^{-1})	Fe:As (mass)	Mn (mg L^{-1})	NH_4^+ (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Si (mg L^{-1})	$Q_E = (V_E\text{-}V_i)/V_E$	$Q_E = V_E/V_i$	Achieved As (μg L^{-1})	Reference
Germany	1.97; 0.29	38; 25	N/A	N/A	51.8; 11.6	0.35; 0.29	0.1; 0.09	N/A	N/A	up to 0.75 up to 0.5	up to 4 up to 4	<10 <20	(Rott et al., 1996)
Groundwater, Manikganj district, Bangladesh	15.1	145	N/A	N/A	104	0.3	N/A	5.0	N/A	0.33	1.5	<50	(van Halem et al., 2010a)
Lekkerkerk, the Netherlands, column experiments with As(III) spiked groundwater	5.3	232; 112; 67	N/A	N/A	22.8; 47.3; 79.1	0.61	N/A	3.16	N/A	~0 ~0 0.75	~0 ~0 4	<50	(van Halem et al., 2010b)
Groundwater, Muradnagar Upazila, Comilla district, Bangladesh	12.6; 8.7	203; 201	165; 162	N/A	62 43	0.27; 0.16	N/A	0.08 0.14	29.6 31.2	up to 0.67	3	<50	(Rahman et al., 2014)
Groundwater, Muradnagar Upazila, Comilla district, Bangladesh	8.6	201	162	39	43	0.16	N/A	0.14	31.2	up to 0.5	2	<50	(Rahman et al., 2015)
Groundwater, Maijdee area, Bangladesh	1.0; 2.4; 1.0	110; 520; 1270	N/A	N/A	9,3; 4.5; 0.8	N/A	N/A	N/A	N/A	0.8	5	<50 (only for well with 110 μg L^{-1} As)	(Sarkar and Rahman, 2001)
Groundwater Kashimpur, West-Bengal, India	N/A	150	N/A	N/A	N/A	2.16	BDL	N/A	N/A	up to 0.5	2	<10	(Rott and Kauffmann, 2008; Sen Gupta et al., 2009)
Groundwater, West-Bengal, India: Merudandi, Basirat Naihati, Purbapara Tepul, Gobardanga Ghetugachi, Chakdah Naserkul, Ranaghat	1.5–3.3	160–280	N/A	N/A	9–18	N/A	N/A	N/A	N/A	0.33–0.5	1.5–2	10–50	(Sen Gupta, 2008)
Schuwacht of Hydron-ZH, Gouda, the Netherlands	6	10–14	N/A	N/A	N/A	1.1	3.8	3.16	N/A	0.5	2	<9	(Appelo and De Vet, 2003)

The overall removal efficiency achieved throughout the trials to reduce arsenic concentrations to below 10 $\mu g\,L^{-1}$ was realised only by some of the studies, as mostly only the limit standard value of 50 $\mu g\,L^{-1}$ was achieved. The complexity of the different parameters and surrounding conditions makes a direct comparison between studies difficult. Although there is no clear tendency of influencing factors for the efficiency of SAR (e.g. iron:arsenic ratio, concentrations of competing ions), the better results tend to be achieved only in trials where the extraction efficiency $Q_E = V_E/V_i$ was kept low. Furthermore, experiments carried out with lower oxygenation rates showed poorer results (Sarkar and Rahman, 2001).

2.4. Modeling of SAR technology

Computer models are necessary to assess potential SAR processes based on specific local conditions. Some studies have aimed to develop a general tool to determine which hydrogeochemical processes are responsible for the (im)mobilization of arsenic in the subsurface during SAR, with the aim of predicting SAR performances at different locations.

Appelo and De Vet (2003) simulated an *in-situ* iron and arsenic removal project in the Netherlands by using a reactive transport model (RTM) in order to study concentration changes of CH_4, NH_4^+, Mn^{2+}, Fe^{2+}, PO_4^{3-} and As. They interpreted data from the groundwater pumping station Schuwacht of Hydron-ZH (Gouda, the Netherlands) where the water quality was monitored for the first seven cycles of *in-situ* iron removal. In this study, the injection volumes started at 30 $m^3\,h^{-1}$ for 2 days and reduced to 23 $m^3\,h^{-1}$ for 40 days. The maximum groundwater total As concentration at their site was only 14 $\mu g\,L^{-1}$, which was significantly lower than typical As levels in India, Bangladesh and South-East Asia.

They explained the principles of *in-situ* iron removal from groundwater in simple terms, based on the reaction of sorbed ferrous iron in the aquifer. The modeling was based on cation exchange in groundwater, a multicomponent process in which all the solute cations participated. The sorption reactions were calculated with the geochemical model PHREEQC-2 which included databases with representative values of the cation exchange constants (Parkhurst and Appelo, 1999). The efficiency of the process was calculated by neglecting dispersion and by limiting the sorption reactions to the zone where oxygen had penetrated.

The concentration pattern of the elements CH_4, NH_4^+, Mn^{2+}, Fe^{2+}, and PO_4^{3-} could be modeled well with known equations. Their retardation increased in successive cycles due to sorption to the iron-oxyhydroxide which was precipitated in the previous cycles. The modeled pattern generally showed the observed concentration trends, but it did not match the spike details, particularly at the beginning of the pilot trials. The modeling demonstrated that arsenite was much less sorbed than arsenate in groundwater without phosphate. However, in the presence of PO_4^{3-} the sorption of arsenate decreased to a small amount (2 (mol adsorbed L^{-1}/)/(mol solute L^{-1})) due to negative charging of the HFO surface after phosphate adsorption. The effect was greater for arsenate than for arsenite because arsenate was sorbed as a negative species, while arsenite forms a neutral surface complex (Appelo and De Vet, 2003).

Rahman et al. (2015) developed a one-dimensional radially symmetric reactive transport model in PHREEQC to model key hydrogeochemical reactions during the SAR operation. Oxidation of Fe(II) and As(III) was modeled using kinetic-rate expressions that were not considered in the work of Appelo and De Vet (2003). Cation exchange, precipitation of HFO, and surface complexation were modeled as equilibrium processes. The reactive transport model was developed for an SAR well that was located in a Holocene reduced aquifer system in Muradnagar upazila, a sub-district in Comilla, Bangladesh. The reactive transport model was subsequently applied to two other SAR wells in Bangladesh without further calibration. During the pilot phase, 5 m^3 of aerated water was injected and around 20 m^3 of groundwater was extracted in the first half of the trial. The groundwater marked a total As level of 201 $\mu g\,L^{-1}$ (162 $\mu g\,L^{-1}$ As(III) and 69 $\mu g\,L^{-1}$ As(V)) and a Fe level of 8.6 $mg\,L^{-1}$ (same well as in Rahman et al. (2014)).

Generally they included the following processes in the models for the injection, storage, and extraction phases:

Processes during injection and storage phases (Rahman et al., 2015):

- Oxidation processes: During injection, oxidation of dissolved Fe(II) creates a HFO filter or 'curtain' in the subsurface (van Halem et al., 2010a). Simultaneously, oxidation of As(III) to As(V), and of soil organic matter forming alkalinity (not included in the model) may occur.
- Iron desorption: During injection, Fe(II) desorbs from clay and soil-surfaces via cation-exchange reactions and via surface complexation reactions on HFO (Wallis et al., 2010).
- Sorption reactions: During the storage phase As(III), As(V), Fe, HCO_3^-, PO_4^{3-}, Si, and to a lesser degree other ions, sorb via surface complexation reactions to initially present and newly formed HFO (Wallis et al., 2010, 2011).

Processes during extraction phase (Rahman et al., 2015):

- Sorption reactions: The HFO curtain filters out As and other ions until the maximum capacity is reached and arsenic breakthrough occurs (Appelo and De Vet, 2003).
- Competitive sorption processes: When native groundwater flows towards the SAR well during the extraction phases, other ions such as Fe(II), HCO_3^-, PO_4^{3-} and silicate sorb at the same time with As(III) and As(V). This simultaneous sorption limits the removal of As. During extraction, Fe(II) also sorbs to the cation exchanger (clay minerals and organic matter) via cation exchange reactions.

The authors summarized that their model gave reasonable results for measured concentrations of As, Fe(II), Mn(II), Si, Mg, Na, and K in the extracted water of the studied SAR well. Therefore, they concluded that the key processes taking place were modeled correctly using their theoretical approach. The As removal during SAR operation was improved by high pH and Fe levels in the injection water as well as multiple injection extraction cycles of an equal water volume. Particularly, CO_2 degassing during aeration resulted in higher pH of injection water and therefore increased the As sorption. Oxidation of As(III) during SAR operation further contributed to better removal since As(V) is preferentially removed from the water. The surface complexation modeling recorded that simultaneous sorption of H_4SiO_4 particularly is an important factor for limiting As removal during SAR.

The model was also successfully applied to simulate subsurface As removal at two other subsurface wells in Bangladesh and it was pointed out that the general trend of the model is to underestimate SAR performance regarding As removal, which gives a conservative estimate from a practical point of view. However, so far the model is limited to locations with similar aquifer characteristics to the two wells studied in Bangladesh (i.e. similar hydrogeochemical conditions). The model still needs to be generalized in order to also simulate SAR performance of other wells with different aquifer characteristics worldwide.

This overview shows some of the advances made for the modeling of such complex systems. However the multi-component effects occurring in natural environments still need to be verified.

Future multiphase, multi-species and reactive kinetic transport modeling is needed which also considers modeling of coupled redox systems and conversions between different species of the same element (in particular of As, Fe, Mn, N, P, O, organic matter – also soluble complexes) and the modeling of biological activity and bacteria-triggered geochemical reactions. Such has not been considered so far in the model by Rahman et al. (2015) which modeled cation exchange, precipitation of HFO, and surface complexation as equilibrium processes. Nonetheless, this modeling included oxidation of Fe(II) and As(III) using kinetic-rate expressions that were not considered in the work of (Appelo and De Vet, 2003).

3. Conclusion

A variety of pilot scale trials on subsurface arsenic removal (SAR) by aeration have been conducted, mostly in Bangladesh and India. Unlike subsurface iron removal (SIR), which has been proven for many years as technically feasible, they have shown that SAR is not yet an established solution since it shows vulnerability to diverse geochemical conditions (e.g. pH and Fe:As ratio). High concentrations of co-ions (e.g. phosphates, carbonates, silicates) can also significantly reduce the arsenic removal rate due to similar adsorption mechanisms.

However, the WHO limit ($10\ \mu g\ L^{-1}$) can be reached with proper injection water volumes and sufficient cycle times. The addition of Fe(II) is an alternative for the *in-situ* treatment of arsenic that showed improvement on the arsenic removal efficiency. Nonetheless, SAR technologies offer the major advantage of negligible waste production and hence the potential of being the only sustainable long-term treatment option currently available.

4. Future prospects and recommendations

For better understanding of SAR processes, further studies through pilot trials to obtain long-term experiences are necessary. The most important aspects for the proper technical operation of a SAR process must include 1) an efficient aeration system to ensure complete air saturation in infiltration water, 2) controlled infiltration and abstraction volumes to avoid breakthrough of arsenic 3) a guarantee of the continuous long-term infiltration of oxygen into the aquifer so that oxidation conditions remain and leaching or breakthrough is prevented.

Before starting any pilot trials, the injected to extraction ratio must be determined from a thorough groundwater analysis. This should consider not only iron, arsenic and manganese, but also oxygen consuming agents (ammonia, methane) and competitive ions (phosphates, silicates, etc). For better understanding, long term experimental trials are mandatory, and special focus must be given to the arsenic to iron ratio, pH and redox conditions. Redox measurements in the aquifer are strongly recommended.

To produce safe drinking water in compliance with the WHO guideline value, SAR technology could be combined easily with processes offering a safe barrier such as e.g. nanofiltration or reverse osmosis where liquid concentrate streams can be also re-injected into the subsurface to avoid additional waste production.

Besides SAR for drinking water purpose, mitigation of groundwater for irrigation of crops is becoming increasingly important in future in order to avoid arsenic accumulation in the food chain. However, experience with high water demands, as needed for agriculture, are still needed to assess the economic feasibility of SAR process.

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