

Alginate-based biotechnology: a review on the arsenic removal technologies and future possibilities

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ABSTRACT

The alginate-based adsorption technologies have emerged as potential methods for arsenic removal from drinking water. The adsorbents (iron oxide, hydroxide, nano zero valent iron (nZVI), industrial waste, minerals, magnetite, goethite, zirconium oxide, etc.) are impregnated into alginate beads to produce the media. The biocompatibility, rough surface with large area, and amorphous and high water permeable bead structure improve arsenic adsorption efficiency while the regeneration process is simpler than the conventional adsorbents. In recent years, studies have reported laboratory-scale applications of alginate beads, encapsulated and impregnated with adsorbents, for arsenic removal from drinking water. The arsenic removal efficiencies were reported to be over 95% with a wide range of concentrations (10–1,000 parts per billion) and pH (3.0–7.5). However, commercial- and/or mass-scale applications have not been reported yet, due possibly to overall cost, complexity, reusability, and arsenic waste-laden sludge management. In this paper, research achievement on arsenic removal using alginate-based adsorbents has been reviewed. The review was performed in context to alginate bead development, adsorbent encapsulation and impregnation, application, performance, and regeneration. The advantages and limitations of the methods were analyzed and the scopes of future research were identified for mass scale domestic and industrial applications.

Key words | alginate-based technologies, alumina impregnated alginate beads, arsenic removal, drinking water, iron impregnated alginate beads

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INTRODUCTION

Arsenic contamination of drinking water is a concern in many countries due to its toxic and carcinogenic effects. Inorganic arsenic has been characterized as a human carcinogen (IARC 2016) with a slope factor of 1.5 per mg/kg-day (USEPA 2016). Approximately 140 million people in more than 70 countries are suffering from arsenic poisoning in groundwater, which has imposed various degrees of risk to humans due to long-term exposure (Kabir & Chowdhury 2017). Arsenical skin lesions were common among people in Bangladesh, parts of India, Vietnam, and Cambodia (Chakraborti *et al.* 2004; Chowdhury *et al.* 2016). The most common effects from long-term exposure to arsenic include

cancer, skin lesions, gastrointestinal disorder, peripheral neuropathy, diabetes, renal damage, and cardiovascular disease (ATSDR 2016). Smith *et al.* (2000) reported that arsenic in drinking water in Bangladesh could have led to 200,000–270,000 deaths from cancer. A few well-known arsenic-affected countries include Bangladesh (Chakraborti *et al.* 2004, 2013), India (Von Ehrenstein *et al.* 2006; Krishna *et al.* 2009), China (Wade *et al.* 2009; Xia *et al.* 2009), Iran (Wade *et al.* 2009; Xia *et al.* 2009), Austria, New Zealand, Northern Afghanistan, Northern Mali, Thailand, Taiwan (Ning 2002), and Mexico and Argentina (Chowdhury *et al.* 2016). The populations from rural areas in the

arsenic-affected developing countries are the most vulnerable group, due mainly to the absence of modern technologies, high cost of arsenic treatment, and complexity of treatment technologies (Chowdhury *et al.* 2016). To protect humans, the regulatory agencies around the globe have set maximum limits on arsenic in drinking water. The US Environmental Protection Agency (USEPA), World Health Organization (WHO), Health Canada, and European Union (EU) limit the concentration of inorganic arsenic in drinking water to 10 parts per billion (ppb) (EU 2014; Health Canada 2017; WHO 2017; USEPA 2018).

Among different forms of arsenic (e.g., As(0), As(-III), As(III) and As(V)), the pentavalent (arsenate) and trivalent (arsenite) are the dominating species in groundwater. The toxicity of arsenite is 20–60 times higher in comparison to arsenate. Moreover, As(III) is thermodynamically more stable at reducing conditions of groundwater (Cullen & Reimer 1989) and more mobile than As(V) (Jain & Singh 2012). Researchers from many countries have been working on different technologies (oxidation/precipitation, coagulation/co-precipitation, ion exchange, membrane, and sorption technologies) to remove arsenic from groundwater. Among these methods, adsorption has been widely used for arsenic removal from groundwater (Kanel *et al.* 2005; Huang *et al.* 2010, 2012; Thakur *et al.* 2010; Li *et al.* 2011; Jiang *et al.* 2013; Mueller 2016). However, poor efficiency, failure to reduce arsenic to below the WHO guideline value of 10 ppb of inorganic arsenic, high capital and operational costs, sludge generation, and operational difficulties are the major barriers against the mass-scale application of most of the available technologies (Shih 2005; Ahmed 2001; Jadhav *et al.* 2015; Kabir & Chowdhury 2017). The low-cost arsenic treatment technologies (e.g., oxidation, chemical precipitation, coagulation-precipitation-filtration, etc.) are generally less effective in reducing As(III) to below the guideline value (Ahmed 2001; Ali *et al.* 2001; Hug *et al.* 2001; Chakravarty *et al.* 2002; Joshi & Chaudhuri 2002; Khan *et al.* 2002; Ahmed 2001). However, adsorption with minerals or biomaterials have shown high removal efficiency for As(III) and As(V). The iron-based adsorbents (e.g., iron oxide, hydroxide), iron minerals, and alumina (Al₂O₃) have shown higher performances in removing As(III) and As(V). Several past studies reported higher affinity of iron oxide or hydroxide with As(III) and As(V)

(Payne & Abdel-Fattah 2005; Giles *et al.* 2011). The specific surface area of any adsorbent is increased with decreasing the particle size and higher rate of removal is anticipated with higher surface area. Past studies have reported the increase of efficiency in removing As(III) and As(V) by decreasing the size of iron particles (i.e., magnetite) (Yean *et al.* 2005; Mayo *et al.* 2007). Mayo *et al.* (2007) reported 200 times increase of efficiency in removing As(III) and As(V) by decreasing the size of magnetite particles from 300 nm to 12 nm. The maximum adsorption capacity increases 20 times and 10 times for As(III) and As(V), respectively, by decreasing the size of magnetite particles from 300 nm to 20 nm (Yean *et al.* 2005). In addition, regeneration and reuse of adsorbents can reduce the overall cost and arsenic-laden sludge, which is important to the low-income and developing countries. Through the conventional approaches, it is often difficult to regenerate and reuse the iron-based adsorbents, due mainly to high reactivity and nano-scale particle size (Dixit & Hering 2003; Chung *et al.* 2014).

The doping, packing, or coating of iron-based adsorbents with support materials (e.g., activated carbon, zeolite, sand, or polymer) have improved arsenic removal efficiency (Gupta *et al.* 2005; Maji *et al.* 2011; Deliyanni *et al.* 2013; Chen *et al.* 2014). However, the overall cost of such adsorbents (e.g., nanoparticle), sludge generation, and reusability have been the major issues (Chowdhury *et al.* 2016). Use of the amorphous alginate beads as support material is likely to address these issues. The biocompatibility, high water permeability, low price, and abundance of raw materials in the marine environment are a few of the advantages of using alginate. Previous studies have reported the application of alginate beads, encapsulated with iron-based adsorbents (mineral akageneite, goethite, hydrous iron oxide, Fe containing water treatment residuals) in arsenic treatment (Basu *et al.* 2015; Ociński *et al.* 2016; Sigdel *et al.* 2016). These adsorbents showed >95% removal of arsenic for a wide range of initial concentrations (10–1,000 ppb) and pH (3.0–7.5) (Basu *et al.* 2015; Ociński *et al.* 2016).

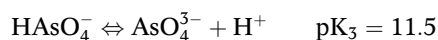
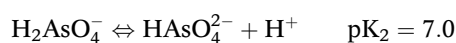
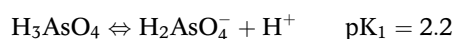
In this paper, research achievements on alginate-based adsorbents in removing arsenic from water have been reviewed. The review on the state of the research was performed in context to alginate bead development, adsorbent

encapsulation and impregnation, application, performance, and regeneration. The advantages and limitations of the methods were analyzed and the scopes of future research were identified. The knowledge to date and scopes of future research were also highlighted.

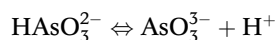
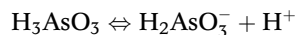
STATES OF ARSENIC IN WATER

In natural water, arsenic species are mainly found in trivalent and pentavalent forms. The colloidal or particulate states contribute 10–20% of total arsenic in water (Brandhuber & Amy 1998) and the dissolved state contributes the most. The particulate, colloidal, and dissolved states of arsenic are defined as $>0.45 \mu\text{m}$, 3,000 Da to $0.45 \mu\text{m}$ and $<3,000$ Da, respectively (Brandhuber & Amy 1998). The colloidal and dissolved states of arsenic increase with the increase of dissolved organic matter (DOM) in groundwater. The colloidal fraction of arsenic also depends on the iron to carbon ratio and molecular distribution of humic acid. The pH of water plays an important role with the maximum particulate arsenic at pH of 4.0 (Bauer & Blodau 2009). In groundwater, arsenite [As(III)] is dominant and in surface water, arsenate [As(V)] is dominant. In natural water, the following reactions are very common in the forms of arsenic.

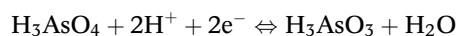
Dissociation of arsenate [As(V)]:



Dissociation of arsenite [As(III)]:



Redox reaction:



CURRENT TECHNOLOGIES FOR ARSENIC REMOVAL

Arsenic removal technologies can be divided into five major categories: precipitation, membrane separation, adsorption, ion exchange, and biotechnology, of which, biotechnology has become the latest trend. Each of the categories has several advantages and limitations. There is no single technology to remove arsenic to below the WHO guideline value at low cost (Kabir & Chowdhury 2017). Research development on the four categories of technologies is summarized below. In addition, the biotechnology is investigated thoroughly with specific focus on alginate-based technologies.

Precipitation

Precipitation includes coagulation and flocculation, or oxidation followed by precipitation and separation (Pal 2015). In this process, chemicals are added to convert the soluble arsenic into insoluble arsenic compounds that lead to precipitation (Kabir & Chowdhury 2017). The coagulation-flocculation processes include alum or iron coagulation, lime softening, electrocoagulation, and co-precipitation with manganese and iron (Singh *et al.* 2015). In general, removal of As(III) is difficult, which is typically converted into As(V) through oxidation for enhanced performance during the removal process (Kartinen & Martin 1995; Bissen & Frimmel 2003; Neppolian *et al.* 2008; Nicomel *et al.* 2016). The oxidation processes include oxidation by oxidants, including chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), hydrogen peroxide (H_2O_2), chloramine (NH_2Cl), permanganate (MnO_4^-), and ferrate (FeO_4^{2-}) (Emett & Khoe 2001; Johnston & Heijnen 2001; Bissen & Frimmel 2003; Lee *et al.* 2003; Ghurye *et al.* 2004; Dodd *et al.* 2006; Mondal *et al.* 2006; Vasudevan *et al.* 2006; Sharma *et al.* 2007). The oxidation technologies also include photochemical oxidation, photocatalytic oxidation, and biological oxidation (Singh *et al.* 2015). It is to be noted that As(III) is more toxic than As(V), followed by monomethylarsonate (MMA) and dimethylarsinate (DMA), respectively (Jain & Singh 2012).

Precipitation can be used as the first stage of treatment to produce large quantities of water while the product

water needs further treatment. These processes cannot reduce arsenic to below the WHO guideline value. These methods produce large amounts of arsenic-concentrated sludge (Singh *et al.* 2015), which needs careful handling to avoid environmental pollution. This technology is often considered to be less feasible for the treatment of water (Nicomel *et al.* 2016).

Membrane separation

Membranes have microscopic pores, which act as a barrier for selective constituents. The separation of arsenic is achieved by two methods: size exclusion based on the pore size and Donnan exclusion through charge repulsion (Shih 2005). The most common membrane processes for arsenic removal include reverse osmosis (RO), forward osmosis (FO), microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), electrodialysis (ED), and porous ceramic membranes (PCM) (Kabir & Chowdhury 2017). MF or UF alone cannot remove dissolved arsenic from water due to its large pore sizes (Velizarov *et al.* 2004). To make MF or UF effective, it is necessary to increase the particle size of arsenic-bearing species. Coagulation and precipitation followed by MF or UF can be an effective process for arsenic removal (Singh *et al.* 2015). NF and RO are effective in reducing arsenic to below 10 µg/L. In addition, they are more effective in removing arsenate than arsenite, indicating the needs of prior oxidation of water (Nicomel *et al.* 2016). However, these processes appear to be costly.

Adsorption

The adsorption processes are efficient in removing arsenic at a relatively lower cost (Zhang *et al.* 2007). The commonly used adsorbents are alumina, activated carbon, iron oxides, zeolites, clay, TiO₂, FePO₄ (amorphous), MnO₂, MnO₂-loaded resin, gibbsite, goethite, kaolinite, zirconium-loaded activated carbon, natural zeolites (e.g., clinoptilolite), clinoptilolite-iron oxide, Portland cement, iron oxide-coated cement, titanium dioxide-loaded Amberlite XAD-7 resin, and iron (III)-loaded chelating resin, etc. (Giménez *et al.* 2007, 2010; Zhang *et al.* 2007; Oliveira *et al.* 2008; Anjum *et al.* 2011; Swarnkar & Tomar 2012; Han *et al.* 2013; Sun *et al.* 2013; Pal 2015).

The alumina- and iron-based adsorption processes are efficient in reducing arsenic to below 10 µg/L, although are relatively costly (Chowdhury *et al.* 2016). The low-cost adsorbents often have limited success in reducing arsenic to below this value (Kabir & Chowdhury 2017). Adsorption processes generally do not need additional chemicals. It is easier to set up the processes without producing harmful by-products (Zhang *et al.* 2005; Jang *et al.* 2008). The efficiency of adsorption is highly dependent on the concentration of different ions and pH. For example, low pH (range: 3–5) is preferred for adsorption of arsenate [As(V)] whereas the favored pH for adsorption of arsenite [As(III)] is in the range of 4–9 (Lenoble *et al.* 2002). In the presence of other ions (e.g., phosphate and silicate), the efficiency can be decreased due to the loss of adsorption sites (Giles *et al.* 2011). Further, efficiency of the processes is dependent on the adsorbent itself. The processes are likely to produce arsenic-laden sludge, which needs careful handling and disposal.

Ion exchange

In ion exchange, the ions in the feed water are exchanged by the ions in the solid resin phase. The exchange occurs between the similarly charged ions depending on the exchange affinity of the resin. For arsenic removal, the strong-base anion exchange resins are used. The anionic charged functional group of the resins are exchanged by oxy-anionic species of pentavalent arsenic compounds (e.g., H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻) (Choong *et al.* 2007). Thus, peroxidation of As(III) to As(V) is needed to improve the efficiency of ion exchange process. However, the excess oxidant should be removed to protect the sensitive resin from damage (Singh *et al.* 2015). The efficiency of the process depends on the type of resin, alkalinity, pH, and concentration of competing ions, such as sulfate and nitrate (Singh *et al.* 2015). The concentrations of total dissolved solid can affect the efficiency significantly (Singh *et al.* 2015). These processes can reduce arsenic to below 10 µg/L. However, the cost is likely to be very high in comparison to the other methods (Chowdhury *et al.* 2016).

Bio and combined technologies

The bioremediation or biotechnologies in removing arsenic are a recent trend. These technologies are divided into two

major categories: phytoremediation and bio-filtration (Mondal *et al.* 2006; Fazi *et al.* 2016). Phytoremediation is a plant-based technology where plants (e.g., Chinese brake fern) and microbes are used for arsenic removal (Lasat 2002; Cherian & Oliveira 2005; Dickinson *et al.* 2009; Behera 2013). In biofiltration, several species of bacteria (e.g., sulfate reducing bacteria, *Haemophilus*, *Paenibacillus*, *Bacillus*) are used in removing arsenic from water (Singh *et al.* 2015). However, recontamination of bacteria, their toxicity and their effects on humans are greatly unknown, which limit the application of bacteria in removing arsenic from drinking water (Singh *et al.* 2015). In recent years, biosorption has become popular in removing arsenic from drinking water (Hansen *et al.* 2006; Kumari *et al.* 2006; Boddu *et al.* 2008; Pandey *et al.* 2009; Ranjan *et al.* 2009; Baig *et al.* 2010). Biocomposites are biodegradable and eco-friendly, which has attracted many researchers in recent years (Wang *et al.* 2002; Ray 2013; Mishra 2015; Aizat & Aziz 2018). The main constituents of biocomposites are biopolymers, such as alginate, microalgae, chitin, and chitosan. These are naturally abundant, environment friendly and cost-effective (Zhang *et al.* 2013; Rahim & Mas Haris 2015). Among the biopolymers, adsorbent (e.g., iron oxide, hydroxide, minerals, or industrial by-products) impregnated, encapsulated, or coated alginate beads have shown excellent removal efficiencies (>95%) for wide ranges of initial arsenic concentrations (10–1,000 µg/L) and pH (3.0–7.5) (Bezbaruah *et al.* 2014; Singh *et al.* 2014; Ociński *et al.* 2016). Further details on the alginate-based bio and combined technologies are investigated in the following sections.

ALGINATE-BASED BIOTECHNOLOGY

Structure of alginate

Alginate is a salt of alginic acid that belongs to the exopolysaccharides. It has the non-repeating copolymers of β -D-mannuronic acid (M) and α -L-glucuronic acid (G), which are linked by 1 \rightarrow 4 glycosidic bonds (Rehm & Valla 1997; Ertesvåg & Valla 1998; Fundueanu *et al.* 1999). These comonomers can be arranged in blocks of continuous M-residues (M-blocks), G-residues (G-blocks) or alternating residues (MG-blocks). The alginate is extracted

from the cell walls of brown seaweeds (e.g., *Macrocystis pyrifera*, *Laminaria digitate*, *Laminaria hyperborea*, *Ascophyllum nodosum*, etc.), which are naturally abundant, low cost, and have low toxicity and mild gelation property, making them popular for adsorbent encapsulation (Gombotz & Wee 2012; Lee & Mooney 2012). Brown seaweeds are ground and suspended in distilled water following the addition of hydrochloric acid (HCl). The process converts the alginate in the seaweeds into insoluble alginic acid. The insoluble alginic acid is neutralized by sodium carbonate (Na₂CO₃) or sodium hydroxide (NaOH) to form soluble sodium alginate. Sodium alginate is precipitated in the presence of sodium chloride (NaCl) and washed with ethanol (Rahelivao *et al.* 2013; OMRI 2015). The molecular weight of commercially available sodium alginate varies in the range of 32,000–400,000 Da (Lee & Mooney 2012). The viscosity of alginate can be increased by decreasing pH to acidic range. The maximum viscosity is achieved at pH of 3.0–3.5 (Lee & Mooney 2012). In general, the alginate polymers formed by bacterial biosynthesis (e.g., *Pseudomonas*, *Azotobacter*) provide better physical and chemical properties for adsorbent impregnation. Alginate is widely used as a thickening or gelling agent.

Calcium alginate beads are formed by combining the aqueous solution of alginate with the cross-linking divalent cations (i.e., Ca²⁺). The G-blocks attract the divalent cations and gel structure is formed through combining the G-blocks of one polymer with the G-blocks of the adjacent polymer in chains (Lee & Mooney 2012). The most common agent for cross-linking is CaCl₂. Due to high solubility of CaCl₂, the gelation process becomes rapid (Grant *et al.* 1973), which can be controlled by the addition of phosphate buffer (e.g., sodium hexa-meta-phosphate) or cross-linking with CaSO₄ and CaCO₃ with an additional reaction time (Crow & Nelson 2006). The uniformity and strength of alginate beads are maintained by controlling the gelation rate, flow, and reaction temperature (Kuo & Ma 2001). The strength of resultant gels increases if high molecular weight alginate is used (Martinsen *et al.* 1989; Draget *et al.* 1993; Mancini *et al.* 1999; Kakita & Kamishima 2008). However, the increased viscosity of the gel often makes it undesirable in processing (LeRoux *et al.* 1999). By combining high and low molecular alginate, elastic modulus of the gel can be

increased with minimum increase in viscosity (Kong *et al.* 2002; Lee & Mooney 2012).

Preparation of cross-linked alginate beads

Calcium alginate beads (Ca-alginate)

The sodium alginate (1–3% w/v) is dissolved in deionized water to form an aqueous solution of alginate (Min & Hering 1998; Zouboulis & Katsoyiannis 2002). This solution is stirred mechanically to form a viscous solution. The viscous solution is released into CaCl₂ solution at a constant flow rate from 6 to 7 cm height, which is stirred at a rate of 60 rpm (Min & Hering 1998; Zouboulis & Katsoyiannis 2002). Ca-alginate beads are formed, which are allowed to cure and are rinsed with deionized water. Min & Hering (1998) reported very low performance of Ca-alginate on arsenic adsorption. Past studies have reported approximately 45% removal of arsenic using Ca-alginate (Singh *et al.* 2014). The Ca-alginate cross-linked with carboxymethyl cellulose showed the adsorption capacity of As(V) of 4.39 mg/g (Tiwari *et al.* 2008).

Iron alginate beads (Fe-alginate)

The aqueous alginate solution is prepared by adding sodium alginate into deionized water. The sodium alginate solution is added to ferric chloride (FeCl₃) solution at a constant rate to form Fe-alginate beads. The beads are allowed to cure and are rinsed several times with distilled water. Dong *et al.* (2011) prepared Fe-alginate beads by dropping 5 mL sodium alginate solution into 250 mL FeCl₃ solution at a constant rate of 1 mL per minute. The FeCl₃ solution was stirred at a rate of 60 rpm. The beads were allowed to cure for 6 hours (Dong *et al.* 2011). To form Fe-alginate gel beads, Fe³⁺ ions coordinate with oxygen atoms in carboxyl groups from glucose chains of alginate (Dong *et al.* 2011). The performance of Fe-alginate can be low as the physical integrity of Fe-alginate beads is poor due to excess peeling and cracking of the surface (Min & Hering 1998).

Ca-Fe alginate beads (Ca-Fe alginate)

Ca-Fe alginate beads are formed through entrapment of iron oxide/hydrous iron oxide on Ca-alginate beads. In the

beads, Ca ions act as a gel forming agent and provide a firm structure for polymeric network formation. The Fe ions replace Ca ions and develop favorable sorption sites for arsenic (Min & Hering 1998). The porous structure of beads allows the diffusion and movement of trace contaminants towards the entrapped adsorbent. Table 1 summarizes the different operating parameters for Ca-Fe bead formation. There are several approaches to produce the Ca-Fe alginate beads, which have differences in efficiencies for removal of arsenic from water (Bezbaruah *et al.* 2009, 2014).

In Ca-Fe alginate beads, Fe can be added before or during the gel formation. In the first approach, sodium alginate (Na-alginate) is dissolved in 1–3% (w/v) of deoxygenated deionized water, which is mixed vigorously by a magnetic stirrer for about 3–5 hours at room temperature to achieve an homogeneous mixture. The solution is kept resting for at least 30 minutes and the air bubbles are expelled out. The iron-based adsorbent (e.g., nZVI, minerals of Fe, Fe containing waste) is added to the solution and stirred with a glass rod to obtain a well-mixed sample, which is kept resting for at least 30 minutes to expel the air bubbles from the solution. The solution is passed dropwise into Ca²⁺ solution at a specific flow rate and height. The solution is stirred continuously during pumping to convert the whole amount into beads. The beads are hardened in CaCl₂ solution for 6–9 hours to achieve adequate hardness and porosity (Bezbaruah *et al.* 2014). In the second approach, FeCl₃ is added to the Ca²⁺ solution instead of Na-alginate. A solution containing CaCl₂ (0.1–0.3 M) and FeCl₃ (0.1–0.5 M) is mixed at a slow (60 rpm) speed (Min & Hering 1998; Banerjee *et al.* 2007; Singh *et al.* 2014) and the Na-alginate solution is added drop-wise to the Ca-Fe solution at a constant flow rate (300–400 mL/hr). Typically, one drop/sec of solution is added from a height of 6–12 cm. Earlier studies have reported the use of a peristaltic pump to ensure appropriate flow rate (Escudero *et al.* 2009). The mixture is allowed to perform cross-linking reaction for an extended period (9–24 hr) to complete the immobilization of Fe ions in the beads, which are then dried at room temperature for 3 days (Sánchez-Rivera *et al.* 2013).

Min & Hering (1998) reported approximately 94% removal of arsenic using the Ca-Fe beads. Banerjee *et al.* (2007) reported complete removal of inorganic arsenic using Ca-Fe alginate beads where the rate of removal was

Table 1 | Operational parameters for different alginate beads

Method	Na-alginate solution (W/V)	Bead formation	Gelation	Bead size	Curing time	Reference
Alginate beads were treated with Fe(III)	2%	Peristaltic pump, 0.30 mm ID tubing, 7 cm height	0.1 M FeCl ₃ solution	2 mm	3 days	Min & Hering (1998)
Iron oxide loaded alginate beads for arsenic removal	2%	One drop of polymer solution dispensed per second, pipet tip positioned 6 cm above	0.3 M CaCl ₂ solution	3 mm	24 hr	Zouboulis & Katsoyiannis (2002)
Composite alginate–goethite beads	1%/4%	Plastic pipe at tip of pipette, 6 cm height, 400 rpm	0.3 M/0.5 M CaCl ₂ solution	2.23 mm	24 hr	Lazaridis & Charalambous (2005); Basu <i>et al.</i> (2015)
Iron was doped in calcium alginate beads	3%	Drop wise addition, continuous stirring	0.1 M FeCl ₃ and 0.1 M CaCl ₂ ·2H ₂ O, ratios: 1:99, 10:90, 20:80, 30:70 and 40:60 (v/v)	1.5–1.7 mm	24 hr	Banerjee <i>et al.</i> (2007)
Waste metal hydroxide entrapped into calcium alginate	1%	Peristaltic pump, 350 mL/h flow rate	0.1 M CaCl ₂ solution	3 mm	24 hr	Escudero <i>et al.</i> (2009)
Nanoscale zero-valent iron immobilized in alginate bead	2%	Peristaltic pump	0.05 M Fe ³⁺	1 mm	48 hr	Kim <i>et al.</i> (2010)
Entrapment of iron nanoparticles in calcium alginate	2%	Peristaltic pump, 0.5 mm ID tubing, 2.5 mL/min flow rate	3.5% (v/v) of CaCl ₂	0.5 mm	9 hr	Bezbaruah <i>et al.</i> (2009)
Magnetite (Fe ₃ O ₄) particles encapsulated in calcium alginate	N/A	Synthesized magnetite dripped through a needle connected to a high voltage power generator	N/A	Diameter of 309.6 μm (particles)	N/A	Lim <i>et al.</i> (2009)
Magnetite nanoparticles in calcium alginate	2%	40% w/w beads with magnetite nanoparticles were produced by dispersing magnetite nanoparticles into Na-alginate	0.2 M CaCl ₂	2 mm	24 hr	Luna-Pineda <i>et al.</i> (2009)
Cross-linking of ferric hydroxide colloids into Ca-alginate	2% alginic acid	0.70 mL/min dropwise addition of alginic acid, 60 rpm magnetic stirring	0.1 M CaCl ₂ and 0.02 M FeCl ₃	2.2 ± 0.3 mm	24 hr	Sánchez-Rivera <i>et al.</i> (2013)

(continued)

Table 1 | continued

Method	Na-alginate solution (W/V)	Bead formation	Gelation	Bead size	Curing time	Reference
Immobilization of magnetite nanoparticles into composite gel beads	2%	Addition of the solution of Fe ₂ O ₃ (2% w/v) and Na-alginate (2% w/v) into CaCl ₂ solution	10% w/v CaCl ₂	2–3 mm	12 hr	Harikumar & Joseph (2012)
Akaganeite nanorods entrapped in alginate beads	2%	Akaganeite nanorods added to Ca-alginate via electrostatic droplet method	1% CaCl ₂	400–2,000 μm		Cho <i>et al.</i> (2014)
Calcium cross-linked alginate nanoparticles for the removal of pentavalent arsenic ions	N/A	1,000 rpm shaking, 30 min, 30 °C	0.5 M CaCl ₂	31–43 nm (nanoparticles)	2 hr	Singh <i>et al.</i> (2014)
Fe(III) cross-linked alginate nanoparticles for the removal of pentavalent arsenic ions	N/A	1,000 rpm shaking, 30 min, 30 °C	0.5 M FeCl ₃	31–43 nm (nanoparticles)	2 hr	Singh <i>et al.</i> (2014)
Nano zero valent iron (nZVI) loaded alginate beads	2%	Peristaltic pump, 0.5 mm ID tubing, 2.5 mL/min flow rate	4.6% CaCl ₂	3.4 ± 0.13 mm	6–9 hr	Bezbaruah <i>et al.</i> (2014)
Hydrous iron oxide was loaded into alginate beads	3%	Addition of hydrous iron oxide, 4 hr magnetic mixing	3% (v/v) of CaCl ₂	1.1 mm	6 hr	Sigdel <i>et al.</i> (2016)
Water treatment residuals (WTR) alginate bead	1–4% (w/w)	Mixture of WTR suspension and Na-alginate solution added to CaCl ₂ solution	0.1 M CaCl ₂	2.5 mm	48 hr	Ociński <i>et al.</i> (2016)
Hydrous ferric oxide immobilized into alginate beads	3%	Addition by 5 mL syringe having 1.7 mm diameter needle	0.05 M CaCl ₂	3 mm	Overnight	Jung <i>et al.</i> (2017)

34 mg/kg at pH of 3.0. Overall, arsenic removal of 85–100% was obtained using the Ca-Fe alginate beads. Earlier studies have reported that the iron-based adsorbents (i.e., nano zero valent iron (nZVI), minerals of Fe) entrapped in Ca-alginate beads do not lose their adsorption capacity (Bezbaruah *et al.* 2009), which is an advantage over the conventional adsorbents. Zouboulis & Katsoyiannis (2002) examined the performance of three different types of Ca-alginate beads in

removing arsenic: Ca-alginate beads doped with hydrous iron oxide (HIO), coated with HIO, doped and subsequently coated with HIO. The most efficient was Ca-alginate beads doped and subsequently coated with HIO (Zouboulis & Katsoyiannis 2002). To complete the coating, the Ca-alginate beads and Ca-Fe alginate beads are treated with an Fe(NO₃)₃ solution at pH 5, where ferric oxides are insoluble. The optimum duration for Fe coating was reported to be

24 hr, and for longer duration (i.e., 96 hr), arsenic removal rate was reported to be the same as 24 hr. By increasing the concentration of $\text{Fe}(\text{NO}_3)_3$ solution, iron content on the beads can be increased. Alginate beads filled in a glass column (height: 40 cm, inner diameter: 2.86 cm and porosity: 0.33) were used as a fixed bed. The maximum amount of arsenic sorbed onto Ca-alginate beads doped with HIO, coated with HIO, doped and subsequently coated with HIO were 4.75 μg of As/g, 2.6 μg of As/g, and 7.2 μg of As/g of wet alginate beads, respectively (Zouboulis & Katsoyiannis 2002). The effluent concentrations of As(V) were lower than the WHO guideline value of 10 $\mu\text{g}/\text{L}$ for 80, 45, and 230 bed volumes in the Ca-alginate beads doped with HIO, coated with HIO, and doped and subsequently coated with HIO, respectively. The initial As(V) concentration in this study was 50 $\mu\text{g}/\text{L}$ (Zouboulis & Katsoyiannis 2002).

Cross-linked alginate nanoparticles

The aqueous and oil phases of alginate solutions are prepared by liquefying Na-alginate with deionized water and paraffin oil, respectively. For Fe cross-linking, FeCl_3 is added during the vigorous mixing of these solutions (1,000 rpm for 30 min). Following 2 hr of cross-linking reaction at controlled temperature (30 °C), brownish white iron cross-linked alginate particles are formed, and the size of particles was found to be in the range of 31–43 nm (Singh *et al.* 2014). Approximately 70% of As(V) was removed by using these iron cross-linked alginate nanoparticles (Singh *et al.* 2014). However, for Ca cross-linking, CaCl_2 is added instead of FeCl_3 during the mixing of the solutions (1,000 rpm for 30 min). Following 2 hr of cross-linking reaction at controlled temperature (30 °C), white calcium cross-linked alginate particles are formed (Singh *et al.* 2014). Using these nanoparticles, 45% of As(V) was removed (Singh *et al.* 2014). As a whole, Table 1 summarizes different operating parameters for cross-linked alginate nanoparticles.

Alginate-based technologies for arsenic removal

Hydrous iron oxide

The metal oxide adsorbents (e.g., ferric oxides, aluminum oxides) have shown high adsorption efficiency for arsenic

removal (Manning *et al.* 2002; Giles *et al.* 2011; Hua *et al.* 2012; Reddy *et al.* 2013). The hydrous iron oxide (HIO) or iron (III) oxide-hydroxide impregnated alginate beads have a large surface area (e.g., 348 m^2/g) with high porosity, which is effective in arsenic removal (Wilkie & Hering 1996; Sigdel *et al.* 2016). Previous studies have reported 4.4–13.8 mg/g of arsenic (As(V)) adsorption using HIO impregnated alginate beads (Zouboulis & Katsoyiannis 2002; Jung *et al.* 2017) (Table 2). In the presence of Cu(II) ions, an increase in adsorption was reported (Jung *et al.* 2017). For Na-alginate to iron ratio of 9.0:1.0, adsorption of As(III) and As(V) were reported to be 47.8 mg/g and 55.1 mg/g, respectively (Sigdel *et al.* 2016). Sarkar *et al.* (2010) reported >99% removal of As(III) and As(V) using ferric hydroxide microcapsule-loaded alginate beads (Table 2). With excess HIO in alginate beads, adsorption of As(V) showed a decreasing trend, due possibly to the reduction of adsorption area while an increase in residence time increased adsorption capacities for As(III) and As(V). The optimum range of pH was 6–9 although slightly acidic solution was favorable for As(V) adsorption (Sigdel *et al.* 2016). At higher pH, negatively charged adsorption sites were increased, leading to increased repulsive forces, which reduced arsenic adsorption capacity (Jung *et al.* 2017).

Magnetite

Magnetite (Fe_3O_4) nanoparticles (MNP) are porous materials and have high adsorption capacity for arsenic (Liu *et al.* 2015). The ultra-sonicated MNP functionalized with 2,3-dimercaptosuccinic acid (DMSA) were mixed with Na-alginate and added to CaCl_2 solution to produce MNP-encapsulated alginate beads (Luna-Pineda *et al.* 2009). The adsorption capacities of MNP alginate beads were 1.10 mg/g and 1.04 mg/g for As(V) and As(III), respectively (Luna-Pineda *et al.* 2009), which was much lower than the MNP only. The adsorption capacities of MNP were 4.78 mg/g and 3.34 mg/g for As(V) and As(III), respectively (Luna-Pineda *et al.* 2009). The lower adsorption rates for MNP alginate beads were attributed to the carboxylic groups or sulfur atoms in the alginate structure as the MNP was functionalized with DMSA. For an aqueous solution of 2 mg/L of

Table 2 | Performance of different adsorbents coated/impregnated in alginate beads

Adsorbent	Advantage	Disadvantage	Comment	Reference
Fe(III) treated alginate beads	Up to 94% removal of As(V) from solution was achieved for an initial As(V) concentration of 400 µg/L by equilibration with 20 Ca-Fe beads at pH 4 for 120 hr	Slow sorption kinetics	Desorption of alginate beads was not performed	Min & Hering (1998)
Fe-coated Ca-Fe alginate beads	The maximum amount of arsenic adsorbed onto the alginate beads was found to be 7.2 µg of As/g of wet alginate bead, or 1.8 µg of As/mg of Fe	Preoxidation step is essential to achieve maximum arsenic removal	Most efficient when coating period is 24 hr	Zouboulis & Katsoyiannis (2002)
Iron-doped calcium beads	96.6% adsorption of As(V) at pH 3 and 40% adsorption of As(III) at pH 8. Maximum adsorption was found at 20 minutes for pH 3	Up to 70% As(V) can be removed from Ca-Fe beads	Highly effective in removing As(V) within the concentration ranges 20–50 mg/kg	Banerjee <i>et al.</i> (2007)
Magnetite (Fe ₃ O ₄) particles encapsulated by calcium alginate	Maximum adsorption capacity of As(V) ions is 6.75 mg/g	Preoxidation of As(III) is necessary	Adsorption is higher at low pH	Lim & Chen (2007)
Adsorption onto alginate and carboxymethyl cellulose beads	Adsorption capacity 4.39 mg/g for As(V)	Adsorption rate decreases if temperature is greater than 26 °C	Adsorption capacity remains same after desorption of the beads	Tiwari <i>et al.</i> (2008)
Alginate-based magnetic nanocomposites	The uptake capacity of magnetite was 1.10 mg/g sorbent and 1.04 mg/g sorbent for As(V) and As(III) species, respectively. The corresponding removal efficiencies were 45.9% and 32.3%	The uptake capacity of the beads is lower than the bare magnetic nanocomposites	Desorption of alginate beads was not performed	Luna-Pineda <i>et al.</i> (2009)
Microencapsulated particles of ferric hydroxide (size 1–10 microns) encapsulated in Ca-alginate	Loading capacity 3.8 mg As/g of adsorbent, removal efficiency >99% for both As(V) and As(III) for initial concentration 300 µg/L	Safe disposal of the bed is necessary	A bed of 6 cm height packed with alginate beads in 40 mm diameter polymethyl methacrylate pipe	Sarkar <i>et al.</i> (2010)
Ca-Fe(III) alginate beads	Maximum uptake 0.364 (mg/g) for As(V) and 0.117 (mg/g) for As(III). Initial As concentration of 100 µg/L removed up to 54% for As(III) (at pH 4.0–8.0) and 80% for As(V) (maximum at pH 2.0)	The sorption of As(V) decreases with increasing pH	As(V) could be desorbed up to 100% and As(III) can be desorbed up to 84.60% using 10% (v/v) sulfuric acid	Sánchez-Rivera <i>et al.</i> (2013)
Calcium alginate/activated carbon composite beads (GC)	Maximum As(V) adsorption (66.7 mg/g at 30 °C) at 60 min	Lower adsorption at acidic pH	Desorption of alginate beads was not performed	Hassan <i>et al.</i> (2014)

(continued)

Table 2 | continued

Adsorbent	Advantage	Disadvantage	Comment	Reference
Iron(III) oxide-hydroxide/ chloride, mineral akaganeite [Fe ³⁺ O(OH,Cl)]	Reduced As to 0.9 ppb from 100 ppb in 10 min	The adsorption capacity was higher in bare akaganeite nanorods	With increasing akaganeite loading removal efficiency also increased	Cho <i>et al.</i> (2014)
NZVI entrapped calcium (Ca)-alginate beads (3.4 ± 0.13 mm) used for As adsorption	Initial 50–10,000 µg/L aqueous arsenic reduced up to 85– 100% within 2 hr, groundwater with 53 µg/L As(V) reduced to below 10 µg/L within 1 hr	Preoxidation of As(III) is necessary	NZVI entrapped in Ca- alginate bead particles do not lose reactivity entrapped in Ca-alginate beads	Bezbaruah <i>et al.</i> (2014)
Fe(III) cross-linked alginate nanoparticles (31–43 nm)	Equilibrium loading capacity 0.0553 ± 0.0016 mg/g. Removal efficiency 69.12% for initial As(V) concentration of 1,000 µg/L	Separating nanoparticles from treated water is difficult	Adsorption decreases with increase in arsenic concentration	Singh <i>et al.</i> (2014)
Iron bearing hydroxide mineral goethite (α-FeO(OH)) (size 60–900 nm) impregnated calcium alginate (Cal-Alg- Goe) beads	Removal is over 95% for concentration range of 10– 10,000 ppb. Maximum adsorption 30.44 mg/g. Reduced to 8–25 ppb from 10 to 500 ppb initial concentration	Adsorption decreases in acidic and alkaline condition	Optimum goethite loading is 18%	Basu <i>et al.</i> (2015)
Water treatment residuals (WTR) alginate beads	Maximum sorption capacity 3.4 mg/g for As(III) and 2.9 mg/g for As(V) in pH range of 3.0–7.5	Pretreatment of WTR is necessary	Entrapment of WTRs into alginate beads slowed down the adsorption rate	Ociński <i>et al.</i> (2016)
Hydrous zirconium oxide (HZO) immobilized alginate beads	Maximum sorption capacities of 32.3 and 28.5 mg/g for As(III) and As(V)	Bare HZO has higher adsorption capacity	Simultaneously removal of cation and anion is possible	Kwon <i>et al.</i> (2016)
Hydrous iron oxide (HIO) loaded alginate beads	Adsorption efficiency for both As(III) and As(V) increased with increasing HIO loading, 47.8 mg/g adsorption for As(III) and 55.1 mg/g adsorption for As(V) at pH range 6–9	Less efficient at low and high pH	Effective in removing both As(V) and As(III)	Sigdel <i>et al.</i> (2016)
	The maximum sorption capacity of As(V) was 13.8 mg/g after 168 hr. The adsorption level of As(V) was high in strongly acidic pH solution	Adsorption rate decreases sharply if pH > 7	Simultaneous removal of As and Cu is possible	Jung <i>et al.</i> (2017)

arsenic, Harikumar & Joseph (2012) reported 75% and 97.5% removal of As(III) using 10 g and 25 g of MNP alginate beads, respectively. In the MNP alginate beads, 98.7% and 39% of arsenic was arsenite in nitrogen and air purged conditions, respectively (Lim *et al.* 2009).

Industrial waste

Metal oxides containing industrial waste (e.g., water treatment plant residuals (WTR)) entrapped within the matrix of Ca-alginate beads were efficient in removing arsenic (Ociński *et al.* 2016). A mixture of ultra-sonicated WTR

and Na-alginate was dripped into CaCl_2 solution to produce the WTR alginate beads. *Ociński et al. (2016)* reported the sorption capacities of WTR alginate beads of 3.4 mg/g and 2.9 mg/g for As(III) and As(V), respectively, for a wide range of pH (3.0–7.5). Based on the WTR amount in alginate beads and utilization, the adsorption capacities were reported to be 38.2 mg/g and 32.6 mg/g for As(III) and As(V), respectively. However, these were much lower than the WTR only (132 mg/g and 77 mg/g for As(III) and As(V), respectively). The WTR had a surface area of 120 m^2/g and was composed of iron oxides and oxo-hydroxides (25% Fe) and manganese oxides (5% Mn). The negatively charged carboxylic groups in alginate beads were responsible for the reduced capacities of WTR alginate beads. The ratio of Na-alginate and metal oxides is a critical parameter for arsenic adsorption. The best performance was noted for the beads prepared with 5% WTR and 1% alginate solution (*Ociński et al. 2016*). The higher concentrations of alginate solution increased carboxyl groups, which reduces arsenic adsorption capacity.

Iron minerals

Iron containing mineral (e.g., goethite [$\alpha\text{-FeO(OH)}$]; akaganeite [$\text{Fe}^{3+}\text{O(OH,Cl)}$]) impregnated alginate beads have been investigated for arsenic removal (*Cho et al. 2014*; *Basu et al. 2015*). Increase of goethite in alginate beads increased arsenic adsorption capacity while the optimum sorption rate was reported for 18% goethite (*Basu et al. 2015*). However, higher amounts of goethite (>24%) led to the failure of bead structure and imparted brittleness to beads. For a wide range of initial arsenic concentrations (10–10,000 ppb), goethite-encapsulated Ca-alginate beads removed 90% of arsenic at pH of 3.0–7.5 and temperature of 2,535 °C (*Basu et al. 2015*).

Nano zero valent iron

Impregnation of nZVI in alginate beads has been demonstrated in removing arsenic from groundwater (*Kanel et al. 2005*; *Bezbaruah et al. 2014*). A batch study on nZVI-entrapped Ca-alginate showed 85–100% removal of As(V) from an initial concentration of 1–10 mg/L (*Bezbaruah et al. 2014*). The nZVI had a surface area in the range of

22–54 m^2/g (*Moraci & Calabrò 2010*). The As(V) was removed by surface precipitation and/or adsorption (*Su & Puls 2001*). The spontaneous adsorption and co-precipitation of iron oxides/hydroxides following oxidation of nZVI removed As(III) from water (*Kanel et al. 2005*). *Kanel et al. (2005)* reported an easy retrieval of arsenic-laden nZVI without losing performance. The low solubility of alginate beads in water and poor leaching of nZVI from the beads are the advantages of using nZVI for drinking water applications (*Bezbaruah et al. 2014*).

Zirconium oxide

The zirconium-based oxides are stable, nontoxic, and water insoluble with an approximate surface area of 327.1 m^2/g (*Cui et al. 2012*). The zirconium oxide-encapsulated alginate beads (ZOAB) have been demonstrated for arsenic removal (*Kwon et al. 2016*). The maximum adsorption capacities of ZOAB were reported to be 32.3 mg/g and 28.5 mg/g for As(III) and As(V), respectively (*Kwon et al. 2016*). Adsorption of As(III) was increased for pH up to 7.0 whereas adsorption of As(V) was high in acidic conditions (*Kwon et al. 2016*). The ZOAB had a surface area of approximately 13.2 m^2/g , which was higher than the alginate beads (2.4 m^2/g) (*Kwon et al. 2016*). Formation of cracks due to hydrous zirconium oxide might have increased the surface area. Adsorption of arsenic was increased in the presence of Cu(II) ions, due possibly to co-removal of Cu(II) and arsenic (*Kwon et al. 2016*).

Coconut shell charcoal

Coconut shell charcoal is a highly porous material with ash of approximately 3% and a surface area of 1,150–1,250 m^2/g (*Mohan & Pittman 2007*). Coconut shell charcoal Ca-alginate beads (CCAB) have a foamy micro and mesoporous surface (*Hlaing et al. 2011*). *Hlaing et al.* reported up to 76.8% removal of As(V) with an initial concentration of 500 ppm. The increase of CCAB dose increased the adsorption capacity. The CCAB can also be used for the co-removal of arsenic, lead, and cadmium (*Hlaing et al. 2011*).

Polymer beads

In addition to alginate beads, several polymer beads (e.g., hybrid ion exchanger (HIX), hybrid anion exchanger (HAIX), cationic hydrogels, chitosan) were also demonstrated for arsenic removal (De Marco *et al.* 2003; Cumbal & Sengupta 2005; Barakat & Sahiner 2008) (Table 3). The HIX is an inexpensive, durable and widely available adsorbent (Cumbal & Sengupta 2005), which can be regenerated on site by using caustic soda and subsequent short carbon dioxide-sparged water rinses (De Marco *et al.* 2003). HAIX can also be regenerated by rinsing with a mixture of brine and sodium hydroxide (Cumbal & Sengupta 2005). Barakat & Sahiner (2008) reported up to 98% removal of arsenate using the cationic hydrogel. The chitosan-coated biosorbents have a surface area of 125.2 m²/g and the sorption capacities were 56.5 and 96.5 mg/g for As(III) and As(V), respectively (Boddu *et al.* 2008).

COMPARISON OF ALGINATE-BASED ADSORBENTS

The Ca-Fe alginate beads were reported to remove 94.0% of As(V) for the initial concentration of 400 µg/L (Min & Hering 1998). Banerjee *et al.* (2007) reported 100% removal of As(V) for the initial concentration of 20.0 mg/L. However, Min & Hering (1998) reported slow sorption kinetics at pH 4.0, leading to slow increase in adsorbed As(V) mass from

48 hr to 120 hr. On the other hand, Banerjee *et al.* (2007) achieved equilibrium in 20 min at pH of 3.0. For similar beads, Sánchez-Rivera *et al.* (2013) achieved up to 80% and 54% removal of As(V) and As(III), respectively, and the corresponding adsorption capacities were 0.364 mg/g and 0.117 mg/g, respectively. Zouboulis & Katsoyiannis (2002) used a glass column filled with Ca-Fe alginate beads. The height and inner diameter of the glass column was 40 cm and 2.86 cm, respectively. Zouboulis & Katsoyiannis (2002) achieved As(V) adsorption up to 4.75 µg/g of Ca-Fe alginate beads. Using the Fe-coated Ca-Fe alginate beads, Zouboulis & Katsoyiannis (2002) were able to reduce As(V) and As(III) to below 10 µg/L using an initial concentration of 50 µg/L, although the removal efficiency for As(III) was poor. The adsorption capacity for As(V) was reported to be 7.2 µg/g (Zouboulis & Katsoyiannis 2002). The volume of treated water was 11.5 L and 2.25 L for As(V) and As(III), respectively (Zouboulis & Katsoyiannis 2002).

Ca-alginate beads doped with Fe₃O₄ adsorbed up to 6.75 mg/g of As(V) of adsorbent (Lim & Chen 2007). The goethite and amorphous oxide-based alginate beads had the As(V) adsorption capacities of 4 and 7 mg/g, respectively (Basu *et al.* 2015). The goethite impregnated Ca-alginate removed 95% of As(V) for the initial concentrations in the range of 10–10,000 µg/L (Basu *et al.* 2015). The maximum adsorption capacity was reported to be 30.44 mg/g. Ferric hydroxide microcapsule-loaded Ca-alginate beads removed 99% of As(III) and As(V) from the initial

Table 3 | Performance of different polymer beads

Adsorbent	Advantage	Disadvantage	Reference
Spherical macroporous cation-exchange polymer beads (HIX)	For nearly 5,000 bed volumes, final arsenic concentration less than 50 µg/L	Intraparticle diffusion was identified as the primary rate-limiting step for both As(III) and As(V) sorption	De Marco <i>et al.</i> (2003)
Polymer-supported hydrated iron(III) oxide nanoparticles	Sharp decrease in concentration	The Donnan membrane effect did not allow permeation of arsenate into the polymer phase	Cumbal & Sengupta (2005)
Cationic hydrogels	The maximum removal efficiency values obtained were 97.6%, 93.1%, 80.4%, and 73.1% for 25, 50, 75, and 100 ppm As(V) concentration, respectively	Not effective against As(III)	Barakat & Sahiner (2008)
Chitosan-coated alumina	The sorption capacity was 56.5 mg/g and 96.5 mg/g for As(III) and As(V), respectively. Effective over wide range of pH	Adsorption experiments at lower concentrations should be carried out	Boddu <i>et al.</i> (2008)

concentration of 300 µg/L while the uptake capacity was 3.8 mg/g (Sarkar *et al.* 2010). Cellulose acetate butyrate (CAB) polymer was used to encapsulate ferric hydroxide microparticles, which was effective in removing As(III).

The Ca-alginate nanoparticles removed 45% of As(V) with the adsorption capacity up to 0.034 mg/g. However, the iron cross-linked Ca-alginate nanoparticles removed 69.1% of As(V) and the adsorption capacity was up to 0.057 mg/g (Singh *et al.* 2014). Ca-alginate doped with magnetite nanoparticles removed 96% and 32% of As(V) and As(III), respectively, and the uptake capacities were 4.78 and 3.34 mg/g of adsorbent, respectively (Luna-Pineda *et al.* 2009).

Akaganeite nanorods (18.3 mg) encapsulated in Ca-alginate micro beads (2 mL) reduced As(V) from 100 µg/L to 0.9 µg/L (Cho *et al.* 2014). The size of the nanorods was in the range of 21–43 nm. Increase in the size of micro beads from 400 µm to 2,000 µm increased the residual arsenic concentration two times (Cho *et al.* 2014). The nZVI entrapped Ca-alginate beads removed 85–100% arsenic from the initial concentrations in the range of 50–10,000 µg/L (Bezbaruah *et al.* 2014). Hydrous zirconium oxide-loaded Ca-alginate beads showed the sorption capacities for As(V) and As(III) of 32.3 mg/g and 28.5 mg/g, respectively (Kwon *et al.* 2016).

REGENERATION FOR REUSE AND WASTE DISPOSAL

The reusability of alginate beads was investigated in earlier studies (Banerjee *et al.* 2007; Sánchez-Rivera *et al.* 2013; Sigdel *et al.* 2016). Sigdel *et al.* (2016) used a highly alkaline solution as the desorbing agent because the adsorption of As(III) and As(V) showed a steep decrease at very high pH. In alkaline solution, the negatively charged sites and iron adsorbent enhanced the desorption kinetics of arsenic. Following saturation, arsenic-laden alginate beads were washed with deionized water and kept in NaOH solution (0.01–0.2 M) for 10–48 hr (Sigdel *et al.* 2016), which were then neutralized using diluted mineral acid (0.01 M H₂SO₄). These were washed again using deionized water and dried prior to further application.

The pilot study on the regeneration of HIO impregnated alginate beads reported 26.7–29.1% and 51.3–56.6% removal of As(V) and As(III), respectively for up to eight

cycles, which were similar to the performances of the fresh HIO-alginate beads (30.5% and 55.7% removal of As(V) and As(III), respectively) (Sigdel *et al.* 2016). After the eighth cycle, the beads lost 15% and 20% of the initial weights for As(III) and As(V), respectively, indicating the effective regeneration and reuse of encapsulated alginate beads through the alkaline treatment. In another study, Sánchez-Rivera *et al.* (2013) reported up to 100% and >65% desorption of arsenic by sulfuric acid and hydrochloric acid, respectively. Banerjee *et al.* (2007) reported that washing of Ca-Fe alginate beads with 0.1 M HCl could desorb up to 70% As(V) while 50% of Fe was leached from the beads. Washing of Ca-Fe alginate beads with 0.1 M NaOH could desorb up to 66% of As(V). During this process, 42% of Fe was leached from the beads (Banerjee *et al.* 2007). Reduction of Fe from the regenerated beads was likely to reduce the As(V) adsorption capacities. However, these studies did not include the amounts of washing solutions used in the regeneration studies. Inclusion of the volumes of washing solutions would assist in better understanding of the regeneration process and the feasibility of regenerating the adsorbent-laden alginate beads. Further, improvement in the performances of regenerated beads is likely to reduce the overall cost for arsenic removal.

Disposal of arsenic-laden alginate beads is an issue, which needs to be minimized. Regeneration of alginate beads is likely to reduce the overall waste generation. Sánchez-Rivera *et al.* (2013) reported up to 100% and more than 65% desorption of arsenic by sulfuric acid and hydrochloric acid, respectively. The solutions with the desorbed arsenic can be safely disposed of following standard protocols. In addition, the desorbed beads can be reused for multiple cycles and the waste from the last cycle can be disposed of following the standard approach. As an example, the desorbed arsenic and the alginate beads from the last cycle after reuse can be converted into stable products to avoid environmental pollution.

FUTURE RESEARCH

Several studies have investigated the alginate-based adsorbents in removing arsenic from drinking water. However, success towards reducing arsenic to below the WHO

guideline value of 10 µg/L at low cost is limited. Future study is needed to fill the existing gaps for achieving comprehensive success. The following research directions are a few necessary steps for achieving comprehensive success in removing arsenic from drinking water at low cost:

- Alumina (Al₂O₃) is a well-known and efficient adsorbent for arsenic removal (Chowdhury *et al.* 2016; Kabir & Chowdhury 2017). However, no application of alumina-impregnated or coated alginate beads in removing arsenic was reported to date, due possibly to the high cost of alumina production and/or complexity in impregnation of alumina. In the sol-gel process of alumina production, the cost is much higher (Pal 2015). Sen & Pal (2009) used the partial thermal dehydration method to produce nano alumina with a surface area of 335–340 m²/g and the Al₂O₃ comprised approximately 92% of the powder (Pal 2015). The cost for producing the alumina in the partial thermal dehydration method was reported to be US\$1,152 per ton, which was approximately 39% lower than the gel precipitation method. Overall, 30–50% reduction of cost was achieved per m³ of water in this method (Sen & Pal 2009; Pal 2015). Further, regeneration capability of alginate beads is likely to reduce the overall life cycle cost for water treatment. Future study is needed on the application of alumina-based alginate beads for arsenic removal.
- Removal of As(V) was relatively easier than removing As(III). Despite As(V) being successfully removed using Ca-Fe alginate beads or Fe-coated Ca-Fe alginate beads, removal of As(III) was poor. Oxidation of As(III) can convert As(III) into As(V) and thus arsenic removal efficiency is likely to improve. Future study is needed to investigate the effects of oxidation on the adsorption of As(III) and As(V) by these alginate beads.
- Sarkar *et al.* (2010) reported up to 99% removal of As(III) and As(V) from an initial concentration of 300 µg/L using ferric hydroxide microcapsule-loaded Ca-alginate beads while cellulose acetate butyrate (CAB) polymer was used to encapsulate the ferric hydroxide microparticles. Future study is needed to investigate the effects of the CAB polymer to humans prior to application for drinking water. In addition, research is needed to produce low-cost polymer using naturally available materials.
- The Ca-alginate doped with magnetite nanoparticles showed promising results for removing As(V) (Luna-Pineda *et al.* 2009). However, the removal of As(III) was poor (Luna-Pineda *et al.* 2009). Future study may investigate the effects of oxidation prior to application of these beads.
- Cho *et al.* (2014) reported an increase in arsenic removal efficiency with decrease in alginate bead diameter, due possibly to the decrease of diffusional distance and increase in surface area. In their study, the akaganeite nanorods (21–43 nm) encapsulated in Ca-alginate micro beads reduced arsenic from 100 µg/L to 0.9 µg/L (Cho *et al.* 2014). Future study is needed to determine the optimum size and shape of alginate beads for maximum removal efficiency.
- The nZVI-entrapped Ca-alginate beads removed 85–100% arsenic from the initial concentrations of 50–10,000 µg/L (Bezbaruah *et al.* 2014). The low solubility of alginate beads in water and poor leaching of nZVI from the beads were the advantages of using nZVI for drinking water applications (Bezbaruah *et al.* 2014). However, production and preservation of nZVI is a challenge due to its oxidation property and deserves further study in this direction.
- In addition, several natural products (sand, red muds, fly ash, etc.) and activate carbon treated with Fe or alumina are often applied for arsenic removal from water (Chowdhury *et al.* 2016; Kabir & Chowdhury 2017). It is necessary to understand their effects to humans prior to drinking water applications. Further, application of biodegradation is a popular method for arsenic removal. However, such approach deserves critical attention for drinking water applications due to human health issues.

CONCLUSIONS

This study investigated the arsenic removal technologies for drinking water with particular focus on alginate-based biotechnologies. Adsorption is a useful technique for removing arsenic from aqueous solution. Iron and iron compounds (iron oxides, oxyhydroxides and hydroxides, goethite, akaganeite) are widely used in the alginate-based

adsorbents. Higher removal efficiency and lower cost have made it convenient for drinking water applications. Further, the iron compounds' encapsulated alginate beads can be reused following regeneration. In addition, biocompatibility, high water permeability, low price, availability, and reuse potential of alginate beads are a few of the advantages of using alginate-based adsorbents. However, several types of iron-based alginate beads often have difficulties in reducing arsenic to below the WHO guideline value and they produce large amounts of arsenic-laden waste, which is an issue for safe disposal. These issues can be addressed through the use of nano alumina impregnated alginate beads and regeneration of alginate beads for multiple applications. Future study is warranted in these directions to achieve comprehensive success in controlling arsenic in drinking water.

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