Importance of Polymeric ligand exchange (PLE) method in removal of Arsenic from contaminated groundwater

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Abstract

Arsenic toxicity and its widespread substantial distribution is becoming a major concern throughout the world. Recently, vast areas of North-eastern States of India have been detected with high concentration (range 50-986 µg/l) of ground water arsenic. The level is distressingly significant when compared to the permissible limits quoted by WHO (World Health Organization) and BIS (Bureau of Indian Standards) (10 µg/l and 50 µg/l respectively). Several methods of selective As removal have been developed, such as precipitation, adsorption and modified iron and ligand exchange. There are two types of mechanisms involved with As removal: Coulombic or ion exchange; and Lewis acid-base interaction. Solution pH is one of the major controlling factors limiting removal efficiency since most of the above-mentioned methods depend on complexation through electrostatic effects. The different features of two different As species make the selective removal process more difficult, especially under natural conditions. Most of the selective As removal methods involve hydrated Fe(III) oxides through Lewis acid-base interaction. Polymeric ligand exchange (PLE) for selective removal of arsenic from drinking water in the presence of strong competing anions (e.g. sulfate). Compared to Strong Base Anion Exchanges (SBA), which is currently recommended by the U.S. EPA, PLE resins exhibited much improved arsenic selectivity. Equilibrium isotherm tests also demonstrate 60 ~ 120 times orders of magnitude greater selectivity for arsenic by the PLE.

Keywords : Arsenic toxicity, Precipitation, Adsorption, Polymeric ligand exchange, Strong Base Anion Exchanges

Introduction

Arsenic mostly exists in two types of oxidation states which are arsenate (As^{5+}) and Arsenite (As^{3+}). These two oxidation states are interconvertible by oxidation of As^{3+} into As^{5+} and reduction of As^{5+} into As^{3+}. Arsenic also exists in another form, i.e., organic form and it is formed by biomethylation of Arsenic. Different living organisms like plants, aquatic animals like fish, crab and human body contain organoarsenic compounds. Microorganisms like Bacteria or Fungi which lack of chlorophyll undergo biological conversion of inorganic arsenic into organic arsenic and it is called as biomethylation process. High concentration of Arsenic occurs in sulphide ores and metal oxides like iron oxide. Earlier studies reveal that groundwater contaminated by Arsenic is restricted only in Ganga basin which is carried out from sulphide rich mineralised areas of Bihar and surrounding basin of deposition. Recently it was found that elevated concentration of Arsenic in wells was extended from Indo Gangatic alluvium to west and Brahmaputra alluvium. During deposition of Holocene segment sediments hydroxides are precipitated and Arsenic released during weathering of sulphide minerals is adsorbed. Latter on by redox processes iron oxides dissolves and Arsenic into aquifers through biogeochemical processes. During late Quaternary and Holocene age sediments deposited in river carry Arsenic in aqueous phase in Ganga Brahmaputra river basin. At present most of Arsenic contaminated water is due to mobilisation of Arsenic by different biogeochemical processes.

Selective removal of Arsenic

One of the challenges in many water and wastewater treatment plants worldwide is the selective removal of trace elements such as As with the presence of higher concentrations of background competing solutes such as main ions (Mandal et al., 2013; Ramana and Sengupta, 1992). Most of the conventional As removal methods that will be discussed generally pose higher removal efficiencies, but lack the ability to compete with background ions and are not cost-effective (Korngold et al., 2001; Pincus et al., 2019). Therefore, the conventional methods are jeopardized in practical applications due to economic, environmental or social aspects and, it creates several gaps for selective As removal. This challenge becomes even bigger as most of the As contaminated water systems are contaminated only with As, the fraction of which is very small compared to other dissolved chemical compounds that in addition are often essential in drinking water. Otherwise, water is often suitable for consumption. In this case, the As removal mechanism should eliminate only As to gain an efficient application approach and selective removal is, therefore, is a key goal. Moreover, the behavior of As in water is disturbing to the removal efficiency of As, as it generally decreases with increased initial As concentration. Therefore, the selective removal method should ensure a strong affinity with As despite its initial concentration. Moreover, it is a well-known fact that most of As removal methods require pre-oxidation and post-treatment steps to make sure the removal of As(III). Therefore, it is a key goal to finds and selects a method that does not require pre- and post-treatment to reduce the energy requirement and the complexity and cost of the process. The next key goal with any of the As removal methods is the reduction of waste production. In any of the non-selective treatments, large amounts of other solutes (in particular ions) are removed, and the resulting waste management is high in cost for both the environment and the economy and therefore, reduction of volumes of As-rich waste is a key goal of a selective As removal process as it can reduce the amount of waste by several orders of magnitude. Moreover, as two principal As species, i.e. As(V) and As(III) act differently,selective removal is more difficult in natural conditions.

The As remediation can be categorized into major 4 groups: ion-exchange processes, membrane separation processes, precipitative processes, and adsorptive processes which generally include pre-oxidation in case of As(III) removal needs (Abejón et al., 2015; Baskan and Pala, 2010;

Bundschuh et al., 2011; Jadhav et al., 2018; Yüksel et al., 2018). Coagulation using ferric chloride followed by microfiltration removes As(III) (after pre-oxidation) and As(V) equally but the method is not suitable for water that has trace amounts of As and it will produce a high amount of As-containing sludge (Kobya et al., 2020; Sarkar et al., 2012). In ion- exchange processes, the conventional ion-exchange methods always reduce the As removal capacity with the competition of other anions in water. Adsorptive measures have received positive attention due to their easy use and low cost (not common for all adsorbents), compared to most of the other remediation methods. Considering the environmental cost of most of the conventional methods there is significant research interest in natural-based adsorbents in order to remove As in water. With well-designed chemical modifications, the As removal was successful with these natural-based adsorbents (Asere et al., 2019; Kumar et al., 2019). Soil minerals such as iron coated pottery granules (Baig et al., 2015; Dong et al., 2009), impregnated-tablet ceramic adsorbents (Baig et al., 2015; Chen et al., 2012), agricultural waste materials such as rice polish (Baig et al., 2015; Ranjan et al., 2009) and impregnated-activated rice husk carbon (Baig et al., 2015; Mondal et al., 2007), industrial waste materials such as granulated slug (Ahn et al., 2003; Baig et al., 2015; Zhang and Itoh, 2005) and fly ash (Baig et al., 2015; Diamadopoulos et al., 1993), plant biomass such as biochars from plant materials (Allen and Brown, 1995; Allen et al., 1997; Baig et al., 2015; Mohan and Chander, 2006), aquatic biomass such as chitosan (Baig et al., 2015; Gupta et al., 2009), activated carbon materials such as Fe^{3+} impregnated granular activated carbon (Baig et al., 2015; Mondal et al., 2007), calcium impregnated granular activated carbon (Baig et al., 2015), metal-loaded coral limestone (Maeda et al., 1992; Xu et al., 2002), hematite feldspar (Singh et al., 1996; Xu et al., 2002), sandy soils (Kuhlmeier, 1997; Xu et al., 2002), lanthanum loaded silica gel (Xu et al., 2002), activated alumina (DeMarco et al., 2003; Kim et al., 2004), and activated mud (Genç- Fuhrman et al., 2004) are some of the adsorptive materials that have been used for As removal in water.

Generally, the electronic structure of As (especially of arsenate (As(V)) is very similar to phosphorus/phosphate and so the chemistry of As is comparable with that of phosphorus (Bui et al., 2019). Therefore, the removal of As interferes with the presence of phosphate or phosphorus compounds (Basu et al., 2014). Other than phosphorus, the presence of silicate, sulfate, chloride and bicarbonate are some of the ions that can interfere with As removal andwill also be removed, together with As increasing waste product and cost while reducing the lifetime of the removal unit (Basu et al., 2014; Gu et al., 2005).

Most of the conventional or modified conventional As treatment methods require further removal techniques such as micro-filtration, to meet the guidelines, creating less cost-effectiveness in the whole process (An et al., 2005). The commercially available resins as ion-exchangers are economically less competitive for As removal as they have a lack of selectivity toward As.

Conception of Polymeric ligand exchange

The concept of ligand-exchange-based separation was first introduced by Helfferich (1962). Generally, a PLE is composed of

a) a cross-linked hosting resin that can firmly bind with a transition metal such as copper and iron, and

b) metal ions that are immobilized to the functional groups of the hosting resin. While sharing many common features with standard ion exchanges, a ligand exchange employs transition metal ions as its terminal functional groups. As a result, ligand exchange involves concurrent Lewis acid-base (LAB) interactions (metal-ligand complexation) and electrostatic interactions between the fixed metal ions and target anionic ligands. While conventional anion exchanges' selectivity for various anions is only governed by electrostatic interactions, the affinity of a PLE is determined by both the ligand strength and ionic charge of the ligands. In his pioneering work, Helfferich (1962) prepared some of the very first PLEs by loading a transition metal (Ni or Cu) onto commercial cation exchange resins. Because the charges of the loaded metal ions are neutralized by the negative charges of the resins' functional groups, the PLEs could only sorb some neutral ligands such as ammonia and diamine (Helfferich, 1962). Later, Chanda et al. (1988) prepared a new PLE for selective removal of arsenic by loading ferric ions onto a weak base chelating resin (known as DOW 3N) with di(2-picolyl)amine groups. They observed that this PLE was able to remove ~140 bed volumes (BVs) of arsenate-laden water and that the saturated PLE can be regenerated using 1 M of NaOH. However, because of the weak Lewis acid characteristics of ferric ions, the amount of Fe^{3+} loaded was low. As a result, the PLE's capacity for arsenate was very limited. Moreover, the loaded iron was nearly completely stripped off the hosting resin during regeneration, and reloading of Fe^{3+} was necessary after each cycle of operation. Realizing the critical drawbacks of Fe^{3+} ions, Ramana and SenGupta (1992) prepared a PLE by loading Cu^{2+} onto a weak base chelating resin (known as DOW 2N) with 2-picolylamine groups. Since Cu^{2+} is a much stronger Lewis acid than $Fe^{3+,}$ which is in accord with the Irving and Williams order, a much greater metal-loading capacity was observed. The copper loaded DOW 2N showed orders of magnitude of greater selectivity for arsenate and selenate in the presence of competing sulfate ions than commercial SBA resins.

To achieve selective removal of phosphate, Zhao and SenGupta (1997) developed and characterized a model PLE, referred to as DOW 3N-Cu, by loading Cu^{2+} ions onto the chelating resin DOW 3N resin. Compared to DOW 2N, DOW 3N contains one more (2-picolyl)amine group per functional group. As a result, the copper capacity for DOW 3N nearly doubles that for DOW 2N (Henry et al., 2004). DOW 3N-Cu showed unusually high selectivity for phosphate in the presence of high concentrations of sulfate, chloride, nitrate, and bicarbonate (Zhao and SenGupta, 1998). Figure 1.3 depicts the functional group of such a PLE (designated as DOW 3N-Cu), where a chelating resin containing nitrogen as electron donor atoms is employed as the metal hosting polymer. Metal ions (Cu^{2+}) are firmly immobilized on the polymer surface by covalently bonding with the N donor atoms. Since the nitrogen atoms are predominately in their free base form at pH >3 (Zhao, 1997), the positive charges of loaded Cu^{2+} ions remain available to interact with anions in the aqueous phase. Moreover, since only a fraction of the copper's 6 coordination bonding sites are consumed for binding copper onto the polymer surface, the immobilized Cu^{2+} ions remain capable of complexing with target ligands from the aqueous phase. Consequently, the $Cu2^{+}$-tailored PLE can interact with anionic ligands, such as arsenate, in the aqueous phase through concurrent Lewis acid-base interaction (metal-ligand complexation) and electrostatic interactions. Compared to conventional strong base anion exchanges where electrostatic interaction governs the resins' selectivity, PLE's selectivity sequence is strongly controlled by the ligand characteristics of anions due to the additional Lewis-acid-base interaction. The PLE's unusually high selectivity toward strong ligands is due to strong interactions between the resins' metal functional groups (Lewis acid) and the target ligand's electron donor atoms (Lewis base) (Zhao and SenGupta, 2000; 1998a; 1998b; Zhao, 1997). Strong ligands, such as phosphate and arsenate, will be preferred by a PLE over sulfate, which virtually reverses the selectivity sequence of commercial SBA resins.

The arsenate/sulfate exchange reaction can be depicted by eqn (1)

$$R\text{-}Cu^{2+}SO_4^{2-} + HAsO_4^{2-} \rightarrow R\text{-}Cu^{2+}HAsO_4^{2-} + SO_4^{2-}$$

where R is the resin matrix carrying the immobilized Cu^{2+} ion as its functional group. Due to the extremely strong metal-ligand interactions between Cu^{2+} and nitrogen donor atoms in the host polymer, DOW 3N-Cu exhibited very low copper bleeding when used for phosphate removal from both drinking water and municipal wastewater.

Conclusions

Selective removal of As in aqueous solutions is a challenge due to several reasons. In most cases, the common anions present in natural waters or wastewater, which are generally present in much higher concentrations are competing with As adsorption. Moreover, with changing solution pH and the redox potential in the media, the As changes into different oxidization forms, including As(V) oxyanions and neutral As(III) species, in most of the natural waters, which physically and chemically act in different ways and therefore, there exists no single removal method which can remove all of the As species satisfactorily at the same time. However, it has been identified that hydrated granular or amorphous Fe(III) has significant capability to remove As(III) and As(V) in aqueous solutions in a selective manner. To improve mechanical strength and adsorption capacities, there are attempts with the incorporation of mechanically strong materials with hydrated granular or amorphous Fe(III). Chitosan and ion- exchange resins are examples of this. The firm deposition of hydrated granular or amorphous Fe(III) in the used matrix is an important step in the preparation procedure to improve the selective As removal. Instead of Fe(III), there are some metal ions such as Cu^{2+}, $La^{3+,}$ and Al^{3+} that have been used for selective As removal and they also show significant As removal capabilities. Strong base anion exchanges are currently used to remove arsenic in the drinking water treatment process The capacity of SBA resins is severely retarded by the presence of competing anion such as sulfate. The newly-developed anion exchange polymeric ligand exchange (PLE) offers a greater selectivity and capacity for the removal of arsenic from drinking water in the presence of strong competing anions, such as chloride, sulfate, bicarbonate, and phosphate.

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