Review

Application of low-cost adsorbents for arsenic removal: A review

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The presence of arsenic in waters, especially groundwater, has become a worldwide problem in the past decades. The current regulation of drinking water standard has become more stringent and requires arsenic content to be reduced to a few parts per billion. There are numbers of arsenic removal methods, which include coagulation followed by precipitation, membrane separation, anion exchange, etc. The use of low-cost adsorbent obtained from an environmentally friendly materials, has been investigated as a replacement for the current expensive methods of removing arsenic from solution. Natural materials or waste products from certain industries with a high capacity for arsenic can be obtained, employed, and disposed of with little cost. Modification of the adsorbents can also improve adsorption capacity. The aim of this article is to review briefly arsenic chemistry and previous and current available technologies that have been reported in arsenic removal. The technical feasibility of various low-cost adsorbents for arsenic removal from contaminated water has been reviewed.

Key words: Arsenic speciation, methods of arsenic removal, low-cost adsorbents, wastewater.

INTRODUCTION

Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below these limits have potential for long-term contamination, because heavy metals are known to be accumulative within biological systems (Benhima et al., 2008). Arsenic is one of the most toxic metal ions and possesses a serious health risk in many countries of the world, which could increase the risk of skin, lung and kidney cancer (Chen et al., 1992). The major source of arsenic pollution in the environment is the smelting of ores such as those of gold, silver, copper and others. Arsenic from these sources is distributed in the air, water, soil and finds its way into the human system by way of direct inhalation or through contamination of food and consumer products. The world health organisation (WHO) recommended that many authorities reduce their regulatory limits and it has

established a provisional guideline value of 10 µg/l for arsenic in drinking water. For example in Europe (Directive 98/83/CE), and in the USA (United States Environmental Protection Agency, 2001), where they were lowered from 50 to 10 µg As/L (0.13 µM) (WHO, 2004). Processes to remove excess arsenic from drinking water and wastewaters are therefore urgently required. Arsenic exists in both organic and inorganic forms in nature; inorganic arsenic is mostly found in natural water systems. Generally, inorganic arsenic has two different oxidation states, that is, trivalent and pentavalent, in natural aqueous systems (Elizalde-Gonzalez et al., 2001; Chutia et al., 2009). The mobility of arsenical forms in waters is very dependent on pH, Eh conditions and presence of different chemical species (Smedley et al., 2002). Pentavalent arsenic (As(V), arsenate) is stable in oxidative condition and exists as a monovalent ($H_2AsO_4^-$) or divalent ($HAsO_4^{2-}$) anion, while trivalent arsenic (As (III), arsenite) is stable in reductive conditions (Grossl et al., 1997) and exists as an uncharged ($H_3AsO_3^0$) or anionic species ($H_2AsO_3^-$). Generally, inorganic arsenic is more toxic than organic arsenic, and As(III) is

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approximately ten times more toxic than As(V) (Pontius et al., 1994).

Many various physicochemical techniques have been developed to remove arsenic from aqueous solution. The conventional methods for arsenic removal are membrane techniques, chemical precipitation, coagulation and flocculation, ion-exchange or chelation, adsorption by activated carbon (Nguyen et al., 2009; Choonga et al., 2007; Fierro et al., 2009; Hossain, 2006; Mohan and Pittman, 2007a; Atkinson, 2006; Mondal et al., 2006; Sun et al., 2006), etc. But these methods have several disadvantages, which include incomplete metal removal, high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries. Adsorption processes are effective techniques and they have long been used in the water and wastewater industries to remove inorganic and organic pollution for its easy handling, minimal sludge production and its regeneration capability. Granular or powdered activated carbon is the most widely used adsorbent (Fierro et al., 2009) but their use is usually limited due to their high cost. These constraints have caused the search for alternative methods that would be efficient for arsenic sequestering. Such a possibility offers a method that uses sorbents of biological origin (Bailey et al., 1999; Babel and Kurniawan, 2003; Mohan and Pittman, 2007a). But more recently, the search for new effective biosorbents involving removal of arsenic from wastewater has directed attention and natural sorbents are searched among many vegetable and waste materials from food and agricultural industry. These materials can be considered as low cost adsorbents and require little processing and abundant in nature (Mohan and Pittman, 2007a; Ranjan, 2009; Carja et al., 2008; Chen, 2008; Genc-Fuhrman et al., 2004; Mohan et al., 2007b). There are large numbers of studies in the literature in which various adsorbents are used for removal of arsenic from aqueous solution. Two recent reviews reported by Mohan and Pittman (2007a) and Hossain (2006) can be referred for the other possible adsorbents for the removal of arsenic oxyanions. Although these materials are regarded as cheap and effective adsorbents, there are several problems (their impurities, unknown stability and regeneration, low adsorption capacity and slow kinetics) associated with their uses (Ranjan, 2009; Chen, 2008; Rahaman et al., 2008; Gimenez et al., 2007). For the past few years, the focus of the research is to use cheap materials as potential adsorbents and the processes developed so far are based on exploring those natural adsorbent, which can improve economic and bring cost effectiveness (Benhima et al., 2008).

The aim of this paper is to provide general description of the sources and toxicity of arsenic, their speciation, and low cost adsorbents for arsenic removal. Different techniques in removing arsenic viz. precipitation, coagulation, membrane filtration, ion exchangers and adsorption will be discussed. The factors influencing adsorption of arsenic will also be discussed.

SOURCES OF ARSENIC

Arsenic (As) is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. The most common As minerals are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of these minerals occur in mineralised areas and are found in close association with the transition metals. It is generally accepted that arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust (Smedley and Kinniburgh, 2002). Though not a major component, arsenic is also often present in varying concentrations in other common rock-forming minerals. Since the chemistry of arsenic follows closely that of sulphur, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Arsenic may also present in the crystal structure of many other sulphide minerals as a substitute for sulphur. High As concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as sorbed species. Arsenic concentrations in igneous rocks are generally low. The concentration of arsenic in sedimentary rocks is typically in the range of 5 to 10 mg/kg (Webster, 1999), which is slightly above the average terrestrial abundance of 1.5 to 3 mg/kg (Mandal and Suzuki, 2002).

ARSENIC CHEMISTRY

Arsenic forms and mobility

Arsenic rarely occurs in a free state, it is largely found in combination with sulphur, oxygen, and iron (Driehaus et al., 1995; Jain and Ali, 2000). In groundwater, arsenic combines with oxygen to form inorganic pentavalent arsenate and trivalent arsenite. Unlike other heavy metalloids and oxyanion-forming elements, arsenic can be mobilized at the pH values typically found in surface and groundwaters (pH 6.5 to 8.5) and under both oxidizing and reducing conditions (Baeyens et al., 2007). While all other oxyanion-forming elements are found within the µg/L range, arsenic can be found within the mg/L range (Smedley and Kinniburg, 2002).

Arsenic can occur in the environment in several oxidation states (−3, 0, +3 and +5), often as sulfides or metal arsenides or arsenates [WHO, 2008]. In natural water its predominant forms are inorganic oxy-anions of
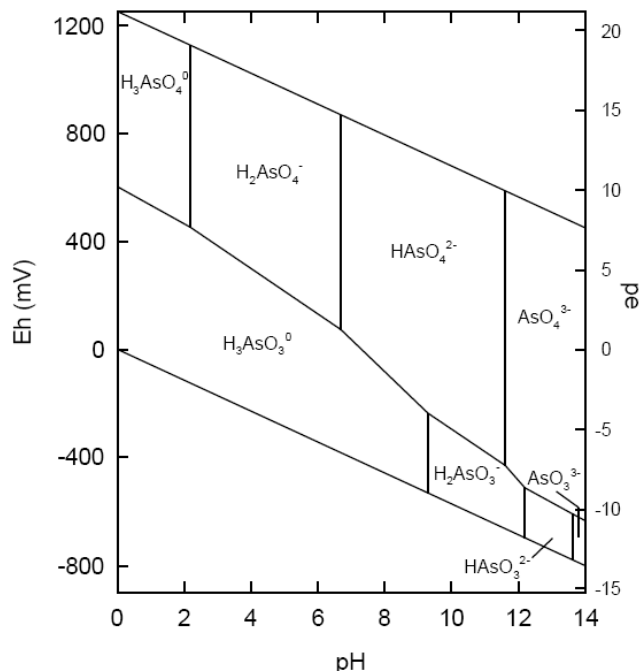
Figure 1. Eh/pe-pH diagram for arsenic speciation.

Figure 2. Distribution of arsenate (a) and arsenite (b) as a function of pH.

trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) (Smedley and Kinniburg, 2002). It usually occurs in natural waters at concentrations of less than 1 or 2 µg L^{-1}. However, in natural groundwater reservoirs where there are sulfide mineral deposits and sedimentary deposits derived from volcanic rocks, the concentrations can be significantly increased (up to 12 mg L^{-1}). The toxicity of different arsenic species varies in the order arsenite > arsenate > monomethylarsonate > dimethylarsinate. Trivalent arsenic is about 60 times more toxic than arsenic in the oxidized pentavalent state, and inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds (Jain and Ali, 2000). The organic forms of arsenic are quantitatively insignificant and are found mostly in surface waters or in areas severely affected by industrial pollution (Smedley and Kinniburg, 2002). Increased risks of arsenic related diseases have been reported to be associated with ingestion of drinking-water at concentrations of < 50 µg L^{-1} (WHO, 2008). The relative concentrations of As(III) to As(V) vary widely, depending on the redox conditions in the geological environment (Jain and Ali, 2000).

Arsenic speciation

Redox potential (Eh) and pH are the most important factors controlling speciation of arsenic (and, to some extent, solubility) (Figure 1). Under oxidizing conditions at pH less than 6.9, $H_2AsO_4^-$ is the dominant species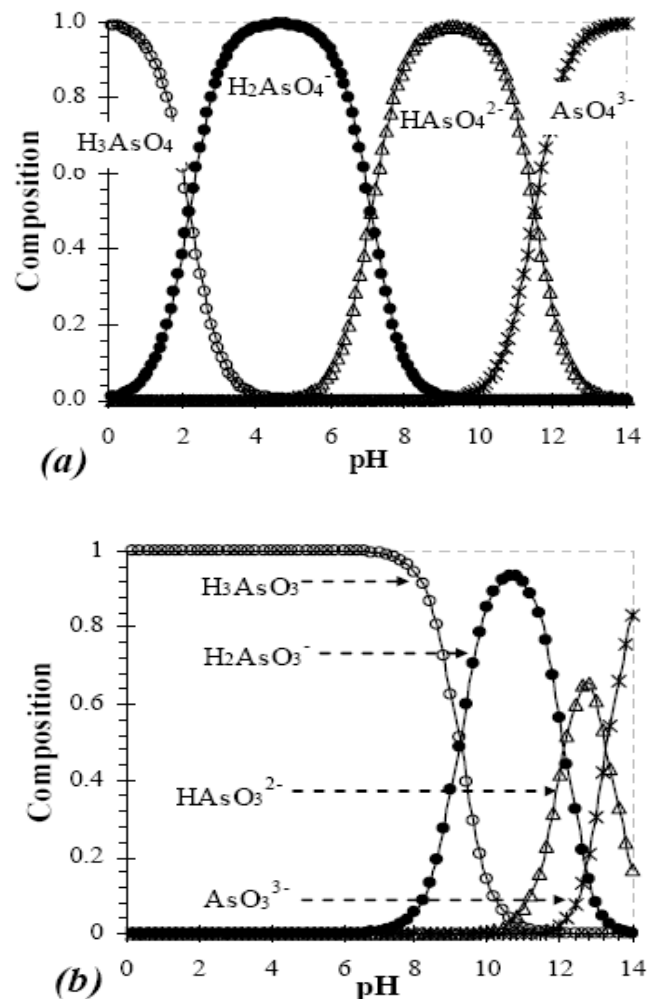, whilst at higher pH, $HAsO_4^{2-}$ becomes dominant. Under reducing conditions at pH less than 9.2, the uncharged arsenite species H_3AsO_3 is dominant. In contrast to the pH dependency of As(V), As(III) was found virtually independent of pH in the absence of other specifically adsorbed anions (Smedley and Kinniburg, 2002). Most often, more trivalent arsenic is found in reducing groundwater conditions than pentavalent arsenic, whereas the converse is true in oxidizing groundwater conditions. The dissociation reactions and corresponding equilibrium constants of H_3AsO_4 and H_3AsO_3 are shown in Table 1 (Bard et al., 1985). Figures 2a and b show the distribution of As(V) and As(III), as a function of pH, respectively (Ghimire et al., 2002). As(III) exists as non-dissociated at neutral and slightly acidic conditions and only at pH > 8 considerable amount of anionic species are found. As(V), on the other hand, is almost completely dissociated and present in the form of monovalent, divalent and trivalent anions (Ali and Aboul-Enein). In practice, most studies in the literature report speciation data without consideration of the degree of protonation.

Table 1. Dissociation constants of arsenate and arsenite.

Speciation	Dissociation reactions	pKa
Arsenate As(V)	$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	2.24
	$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$	6.69
	$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$	11.5
Arsenite As(III)	$H_3AsO_3 \rightleftharpoons H^+ + H_2AsO_3^-$	9.2
	$H_2AsO_3^- \rightleftharpoons H^+ + HAsO_3^{2-}$	12.1
	$HAsO_3^{2-} \rightleftharpoons H^+ + AsO_3^{3-}$	13.4

In the presence of extremely high concentrations of reduced sulphur, dissolved arsenic-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment (As_2S_3), realgar (AsS) or other sulphide minerals containing coprecipitated arsenic. Therefore high arsenic waters are not expected where there is a high concentration of free sulphide. Thioarsenite species will be more important at neutral and alkaline pH in the presence of very high sulphide concentrations.

CONVENTIONAL METHODS OF ARSENIC REMOVAL

There are several treatment methods of arsenic removal, which include coagulation followed by precipitation, lime softening, membrane separation, ion exchange and adsorption etc.

Coagulation or flocculation

The most heavily documented treatment methods for arsenic removal involve coagulation and flocculation, either using metal salts or lime softening. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles. Rapid mixing is required to disperse the coagulant throughout the liquid. Flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization. Apart from arsenic removal, this treatment can effectively remove many suspended and dissolved constituents from

water: turbidity, iron, manganese, phosphate and fluoride are few to mention. This technology removal is highly dependent upon initial arsenic concentration, dosage of coagulant, pH and the valence of the arsenic species.

Ferric salts are common in the uses of coagulant. Of all the coagulants studied, ferric chloride and ferric sulphate have been most successful. Yuan et al. (2003) studied a combination system of ferric sulphate coagulation and filtration in arsenic removal. The method is economic and effective. Zouboulis and Katsoyiannis (2002) studied arsenic removal by applying a modification of a conventional coagulation and flocculation process.

The coagulants were found to be efficient regarding arsenic removal and had achieved up to 99% of arsenic removal. Karcher et al. (1999) and Guo et al. (2000) also reported the uses of ferric chloride and lime-polyferric sulphate as the coagulants. Han et al. (2002) used ferric chloride and ferric sulphate as flocculants in arsenic removal. The results have shown a significant arsenic removal through adsorption mechanism onto the ferric complexes present. Wickramasinghe et al. (2005) also studied the application of ferric based coagulants in treating the city groundwater that has been contaminated by arsenic. The results of the bench-scale experiments conducted indicate that coagulation with ferric ions followed by filtration is effective in reducing arsenic concentration in the water tested. However, the actual efficiency of removal is highly dependent on the raw water quality.

However, problems with this technique are the safe separation, filtration, and the handling and disposal of the contaminated coagulant sludge. Moreover, in many instances it seems to be difficult to lower the arsenic concentration to the acceptable level by this technique.

Membrane filtration

Some synthetic membranes are permeable to certain dissolved compounds but exclude others. Because of their selective permeability for different compounds, such membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate compounds. High pressures are required to cause water to pass across the membrane from a concentrated to dilute solution. For this reason membrane separation is addressed as a pressure driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). Microfiltration can be used to remove bacteria and suspended solids with pore sizes of 0.1 to micron. Ultrafiltration will remove colloids, viruses and certain proteins with pore size of 0.0003 to 0.1 microns. Nanofiltration relies on physical rejection based on molecular size and charge. Pore sizes are in the range of 0.001 to 0.003 microns. Reverse osmosis has a pore size

of about 0.0005 microns and can be used for desalination. High pressures are required to cause water to pass across the membrane from a concentrated to dilute solution. In general, driving pressure increases as selectivity increases. It is clearly desirable to achieve the required degree of separation (rejection) at the maximum specific flux (membrane flux/driving pressure). Separation is accomplished by microfiltration membranes and ultrafiltration membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in nanofiltration membranes and reverse osmosis membranes (Choong et al., 2007). Lately advancement of membrane technology has taken place in the name of electro-ultrafiltration (Weng et al., 2005), which is found to possess good potential in treating arsenic from water. Shih (2005) had showed an overview of arsenic removal on pressure driven membrane process and explored the parameters that may influence the arsenic removal efficiency by membrane technologies such as source water parameters, membrane material, membrane types and membrane process.

Ion exchange

Ion exchange is a physical or chemical process in which ions held electrostatically on the surface of a solid phase are exchanged for ions of similar charge in a solution. It is a reversible interchange where there is no permanent change in the structure of the solid. The solid is typically a synthetic anion exchange resin, which is used to remove particular contaminants of concern. Ion exchange is commonly used in drinking water treatment for softening (that is removal of calcium, magnesium etc. in exchange of sodium) as well as removing nitrate, arsenate, selenate etc. from municipal water (Clifford, 1999). For arsenic removal, an ion exchange resin, usually loaded with chloride ions at the "exchange sites", is placed in vessels. The arsenic containing water is passed through the vessels and the arsenic "exchanges" for the chloride ions. The water exiting in the vessel is lower in arsenic but higher in chloride than the water entering the vessel. Eventually, the resin becomes "exhausted"; that is, all or most of the "exchange sites" that were loaded with chloride ions become loaded with arsenic or other anions. The chloride ions that used to be on the resin were exchanged for the arsenic and other anions that were in the treated water. The effect of the presence of sulphate, competition with other anions, is an important factor to ion exchanger treatment of arsenic. Sulphate levers can limit the applicability of ion-exchanger as arsenic treatment. Jackson and Miller (2000) reported that sulphate was reported not to influence As(V) sorption by ferrihydrite but resulted in a considerable decrease in As(III) sorption below pH 7, with the largest decrease at the lowest pH. Due to its higher treatment cost compared to conventional treatment technologies, ion exchange application is limited primarily to small-to-medium-scale. However, sulphate, selenium, fluoride, and nitrate compete with arsenic and can affect the removal process. So the low selectivity in the presence of other competing anions (Tsuji, 2002) has made this process less attractive. Other factors affecting the use of the ion exchange process include contact time and spent regenerant disposal.

Adsorption

Adsorption is a process that uses solids for removing substances from either gaseous or liquid solutions.

Adsorption phenomena are operative in most natural physical, biological, and chemical systems. Adsorption operations employing solids such as activated carbon, metal hydrides and synthetic resins are used widely in industrial applications for purification of waters and wastewaters. Activated carbon is also commonly used as the material in arsenic treatment (Wennrich and Weiss, 2004; Huang and Fu, 1984; Gimbel and Hobby, 2000). The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH etc. Many activated carbons are available but few are selective. These are expensive as well. Therefore the research thirst over the years is leading to find improved and tailor-made materials, which will meet several requirements such as regeneration capability, easy availability, cost effectiveness etc. Consequently, low-cost adsorbents have drawn attention to many researchers and characteristics as well as application of many such adsorbents are reported. However, low-cost adsorbents are discussed herein after.

Low-cost adsorbents

In the adsorption process activated carbon is most popular and widely used adsorbent in wastewater treatment throughout the world, but the high prices and regeneration cost of activated carbon limits their large-scale use for the removal of inorganic and organic pollutants, and has encouraged researchers to look for low cost adsorbing materials (Bailey et al., 1999). Recently, adsorption of arsenic using natural materials or the wastes products from industrial or agricultural operations has emerged as an option for developing economic and eco-friendly wastewater treatment processes. Numerous low-cost adsorbents have so far been studied for the removal of arsenic from water and wastewater. Dry plants, red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides and various

bioadsorbents are few to mention. Removal of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compound contents, which have metal-binding functional groups such as carboxyl, hydroxyl, sulfate, arsenate and amino groups. Mohan and Pittman (2007a) observed that the loss of metal ions from their solutions in the presence of natural materials may be due to the adsorption on surface and pores, and to complexation by these materials. Below shows several of natural materials that have been used as adsorbents for arsenic removal.

Dried plants are natural materials widely available and studied as an alternative adsorbent for different heavy metals. Examples of proposed plant leaves as efficient in removing metal ions from water are reed (Salim and Robinson, 1985) for cadmium, poplar for lead and copper (Salim and Robinson, 1985; Salim et al., 1992), cinchona for copper and lead (Salim et al., 1992; Al-Subu, 2002), pine for cadmium and nickel (Al-Asheh and Duznjak, 1997; Salim et al., 1994) and cypress for aluminium (Sayrafi et al., 1996), Nile rose plant powder for lead ions (Abdel-Halim et al., 2003). Salim et al., (2003) reported the removal of zinc from aqueous solutions by 15 species of plant leaves. They found that the removal efficiency of zinc dependent on the plant species used. Dry plant leaves of thyme, sage, banana, mint, anise and oleander plants have also been suggested as natural, simple and cheap adsorbent for efficient removal of several metal ions from polluted water (Abu-El-Halawa et al., 2003). In our laboratory, we also showed that crushed dried plants such as *Asphodelus microcarpus*, *Asparagus albus*, *Carpobrotus edulis Euphorbia echinus, Launea arborescens, Senecio anthophorbium* and *Withania frutescens* which grow in the Agadir area can play the role of adsorbent of pollutants such as arsenate with high efficiency (Chiban et al., 2005, 2009, 2011a, 2011b, 2011c). We also used Romanian *C. rhizome* plant for arsenate removal from aqueous solution. The results showed that the maximum adsorption capacity of arsenate on *Cyperus rhizome* plant was 22.04 mg/g at initial arsenate concentration of 1 g/l (Chiban et al., 2011d). It has also been shown that the order in the efficiency of fixation depend on the plant used. Moreover, the efficiency of arsenate adsorption depends on different parameters (size of crushed plants which must be less than 50 µm, report m/V between crushed vegetal mass and volume of solution to be treated, solution concentration and pH). It is noteworthy that vegetable materials represent a potential source of abundant low-cost adsorbents and there is no environmental or technical reason which impedes the preparation of adsorbents by using those materials.

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Owing to their low cost, abundance, high adsorption properties and potential for ion-exchange, clay materials are a strong candidate as adsorbents. There are several types of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). The adsorption capabilities of clays generally result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positive charged species. In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite, and Fuller's earth as such and in modified form to adsorb not only inorganic but also organic molecules (Nayak and Singh, 2007).

Chitosan, one of the common bioadsorbents, is produced from chitin, which is the structural element in the exoskeleton of crustaceans (shrimp, crabs, shellfish etc.) (Amit and Mika, 2009). Chitin, a long-chain polysaccharide, is the most widely occurring natural carbohydrate polymer next to cellulose. Various researches on chitosan have been done in recent years and it can be concluded that chitosan is a good adsorbent for all heavy metals. Dambies et al. (2000) tested the adsorption of As(V) onto molybdate-impregnated chitosan gel bead and reported that the sorption capacity increased with the impregnation and optimum pH was 3. Powdered chitosan, obtained from shrimp shell, was converted into bead form (Chen and Chung, 2006) and used to remove arsenic from water in both batch and continuous process.

Zeolites are basically hydrated alumino-silicates having micro-porous structure that can accommodate a wide variety of cations without any change in structure. It has been received increasing attention for pollution control in wastewater treatment. However, most of zeolites have been made synthetically; some of them are made for commercial use while others created by scientists to study their chemistry. At present, there are 191 unique zeolite frameworks identified, and over 40 naturally occurring zeolite frameworks are known (Baerlocher et al., 2007). Zeolites have been received increasing attention for pollution control as standard components in wastewater treatment (Kesraoui-Ouki and Kavannagh, 1997). Wang and Peng (2010) reviewed natural zeolites utilization in water and wastewater treatment. Xu et al. (2002) studied adsorption and removal of As(V) from drinking water by aluminum-loaded shirasu-zeolite and found its effectiveness over a wide range of pH (3 to 10). Common competing anions such as chloride, nitrate, sulfate etc. had little effect on As(V) adsorption but arsenate greatly interfered with the adsorption.

Red mud is a ferric hydroxide material, the by-product of smelting and refining of ores containing gold, cobalt, silver, copper and iron. It has been used to develop effective adsorbents to remove arsenic from aqueous solutions. Arsenic adsorption on red mud is pH dependent and an acidic solution having pH range 1.1 to 3.2 favored As(V) removal while alkaline aqueous medium (pH ≈ 9.5) was effective for As(III) removal (Altundogan et al., 2000). Heat and acid treated red mud

has also been reported to have better adsorption capacity for arsenic removal (Altundogan et al., 2002).

Fly ash is one of the residues generated in the combustion of coal. It is generally captured from the chimneys of power generation facilities. The availability of fly ash is so high that at many places its disposal is a problem. As such, a number of workers have attempted to use it as an adsorbent in pollution control. Removal of arsenate at pH 4 was reported higher than that at pH 7 or 10 by using fly ash collected from coal power stations (Diamaddopoulos et al., 1993).

Numerous biological materials have been tested for removal of toxic ions from aqueous solutions over the last two decades. However, only a limited number of studies have investigated the use of bioadsorbents e.g., bio-char (Mohan et al., 2007b), methylated yeast biomass (Seki et al., 2005), fungal biomass (Say et al., 2003), chicken feathers (Teixeira and Ciminelli, 2005), alginate (Zouboulis and Katsoyiannis, 2002) to remove arsenic from aqueous solution. It is noteworthy that biological materials represent a potential source of abundant low-cost adsorbents and there is no environmental or technical reason which impedes the preparation of adsorbents by using those materials.

Besides these, various other materials such as wood, peat, clay, kaolin, goethite, humic acid, human hair, hematite or feldspar, pine needles, cactus leaves, polymer materials, tea leaves, tree fern, leater waste, orange juice residue, coconut coir pith, ferruginous manganese ore, etc have also been explored as low cost adsorbents. The values of maximum adsorption capacity of the adsorbents for the removal of arsenic reported in the literature are given in Table 2. As the adsorption capacity of the adsorbent varies with the initial arsenic concentration, solution pH and other experimental conditions, it may be difficult to compare the values directly. The adsorption capacity differences of arsenate ions uptake are ascribed to the properties of each adsorbent such as adsorbent structure, functional groups and surface areas (Ozsoy and Kumbur, 2006).

Factors affecting adsorption

The pH of the medium is one of the most critical parameter in the adsorption process of arsenic from aqueous solutions. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbents (Chiban et al., 2011d). The standard range of pH in drinking water varies from 6.5 to 8.5, and therefore the investigation of the effect of wide range of pH on arsenic removal is needed. The pH effect on the arsenic adsorption by low-cost adsorbents is dependent on the types of adsorbent.

The contact time of adsorbate and adsorbent has a great importance in batch adsorption experiments,

because it depends on the nature of the system used. Consequently, it is important to establish the time dependence of such systems under various process conditions. The effect of contact time on arsenate adsorption has also been investigated (Chiban et al., 2009, 2011d). It was observed that the adsorption capacity of arsenate on dried plants increased with increasing contact time until equilibrium time was reached.

Among the process parameters frequently investigated in the literature, temperature is shown to affect adsorption capacity. When adsorption capacity increased with temperature, the process was claimed to be endothermic, and vice versa. The thermodynamic parameters present the essential parameters for subsequent engineering evaluation on the ultimate uptake of the adsorbents, and, hopefully, also provide insights to the adsorption mechanisms thus applied for further use in process modification and optimization. Usually, the adsorbate uptake decreases with increasing temperature due to the exothermic nature of the simple adsorption reaction. The As(V) adsorption on both calcined and uncalcined Layered double hydroxides (LDHs) was reported as an exothermic process (Yang et al., 2005). Whereas, Chiban et al. (2011d) observed that the percentage of As(V) adsorption by dried plants increased with increasing temperature from 25 to 40°C. The negative values of free energy change ($\Delta G°$) indicated the spontaneous nature of the adsorption and positive values of enthalpy change ($\Delta H°$) suggested the endothermic nature of the adsorption process. This result is also supported by the increase in value of uptake capacity of adsorbents with the rise in temperature. Han et al. (2006) stated that the increasing sorption capacity of the sorbent with temperature is attributable to the enlargement of pores and or the activation of the sorbent surface. In addition to that, the positive value of entropy ($\Delta S°$) revealed that the degrees of free active sites increased at the solid–liquid interface during the adsorption of As(V) onto dried plants.

Desorption or *regeneration*

Desorption studies will help to elucidate the nature of adsorption process and to recover the phosphate from low cost adsorbents individually. Moreover, it also will help to regenerate the adsorbents so that it can be used again to adsorb phosphate ions, and to develop the successful adsorption process. Various alkaline solutions and salt solutions or the mixture of these solutions have been successfully used to desorb arsenate-loaded adsorbent. In our previous studies, we have shown that more than 90% of arsenate can be desorbed from *W. frutesence* plant using 0.07 M NaOH. The arsenate desorption was dependent on the anion species and their concentrations in the desorbing solutions. The abilities of various anions to desorb arsenate from dried plants were

Table 2. Comparison of adsorption capacity (Q_{max}, mg/g) of various adsorbents to remove arsenic.

Adsorbent	Initial pH	$C_{Initial}$ (mg/l)	Ions	Q_{max} (mg/g)	References
Muscovite	4.2 - 5.5	-	As(III)	2.91	Chakraborty et al. (2007)
Biotite	4.1 - 6.2	-	As(III)	0.30	Chakraborty et al. (2007)
Tea fungal biomass	7.2	0.9 - 1.3	As(III)	0.45	Murugesan et al. (2006)
Fish scale	4	0.2 - 1	As(III)	0.247	Rahaman et al. (2008)
Orange juice residue	10.0	-	As(III)	97	Ghimire et al. (2002)
Natural Muscovite	5.6	100	As(III)	0.33	Jung-Seok et al. (2010)
Biomass	6	100	As(III)	0.047	Pokhrel and Viraraghavan (2008)
Uncalcined chloride-LDHs	-	0.432	As(III)	0.086	Gillman (2006)
Hematite,	-	-	As(III)	31.3	Gimenez et al. (2007)
Magnetite	-	-	As(III)	25.6	Gimenez et al. (2007)
Goethite	5.5	-	As(III)	12.5	Ladeira and Ciminelli. (2004)
Goethite	9	-	As(III)	4	Lenoble et al. (2002)
Raw mixed (hydr)oxide	8	5 - 500	As(III)	26.8	Escudero et al. (2009)
Biotite	4.6 - 5.6	-	As(V)	0.45	Chakraborty et al. (2007)
Tea fungal biomass	7.2	0.9 - 1.3	As(V)	0.31	Murugesan et al. (2006)
Raw mixed (hydr)oxide	8	5 - 500	As(V)	26.8	Escudero et al. (2009)
I. hispidus biomass	2	10 - 500	As(V)	59.6	Sari and Tuzen (2009)
Rice polish	4	0.1-1	As(V)	0.14	Ranjan (2009)
Modified zeolite Y	6	10 - 50	As(V)	1.34	Yusof and Malek. (2009)
Maghemite nanoparticles	3	1 - 11	As(V)	50.0	Tuutijärvi et al. (2009)
Fish scale	4	0.2 - 1	As(V)	0.026	Rahaman et al. (2008)
L. nigrescens	2.5	50 - 600	As(V)	45.2	Hossain (2006)
Tea fungal biomass	7.2	0.9	As(V)	4.95	Hossain (2006)
Bone char	10	0.5 - 1.5	As(V)	1.43	Chen (2008)
Leather waste	1	10 - 100	As(V)	26	Oliveira et al. (2008)
Calcium alginate	5 - 6	6	As(V)	6.75	Lim and Chen (2007)
Red mud	3.5	10	As(V)	0.52	Altundogan et al. (2002)
Red mud	2.3	2.5 - 30	As(V)	0.51	Altundogan et al. (2000)
Coconut coir pith	7	5 - 100	As(V)	13.57	Anirudhan and Unnithan (2007)
Chotosan	4	400	As(V)	58	Mcafee et al. (2001)
Chotosan	3.5	0 - 10	As(V)	14.16	Kwok et al. (2009)
C. rhizoma	8	1000	As(V)	22.04	Chiban et al. (2011d)
W. frutescens	8	1000	As(V)	16.88	Chiban et al. (2009)
Orange juice residue	3.1	-	As(V)	132	Ghimire et al. (2002)
Alumina	6 - 8	140	As(V)	25	Wasay et al. (1996)
Natural Muscovite	6	100	As(V)	0.791	Jung-Seok et al. (2010)

Table 2. Cont'd

Mixed rare earth oxides	6.5	50	As(V)	2.945	Raichur, and Panvekar (2002)
Polymeric alginate beads	6	80	As(V)	8.33	Dewangan et al. (2009)
Iron Oxide-Coated	6	100	As(V)	0.059	Pokhrel and Viraraghavan (2008)
Uncalcined Mg–Al LDHs	Natural	10 - 70	As(V)	32.6	Lazaridis et al. (2002)
Calcined Mg–Al LDHs	Natural	50 - 700	As(V)	615	Lazaridis et al. (2002)
Calcined Mg–Fe LDHs	6.5	206	As(V)	202	Carja et al. (2005)
Coconut-shell carbon	5	50 - 200	As(V)	2.4	Lorenzen et al. (1995)
Maghemite	3	0.001 - 1	As(V)	50.0	Tuutijärvi et al. (2009)
Magnetite	8	-	As(V)	46.7	Yean et al. (2005)

reported to follow the order $HPO_4^{2-} > SO_4^{2-} > NO_3^-$, which was consistent with their competitiveness in the adsorption by adsorbents (Chiban et al., 2009, 2011d). The effective desorption of As(V) from adsorbent couldbe achieved using a mixed solution of NaCl and NaOH (Elizalde-Gonzalez et al., 2001; Lenoble et al., 2002).

A number of studies have shown that arsenic-loaded adsorbents could be regenerated with NaOH or NaCl solution. Thus far only limited research works have reported on the recovery of arsenate from different adsorbents (Gillman, 2006, Chiban et al., 2009). In our laboratory, we have also reported that after saturation with As(V) the used plant was regenerated with 0.07 M sodium hydroxide and the maximum desorption percentage of As(V) was found to be 92% (Chiban et al., 2009, 2011d). The adsorption efficiency of the regenerated *W. frutescens* plant particles is found to be more than 52% compared to the fresh plant.

Competitive anions

The efficiency of the adsorbent in the removal of arsenic in the treatment of industrial or urban wastewaters is affected by the selectivity between various common chemical species. The adsorption in multi-component systems is complicated because ion–ion competition and ion–surface interactions are involved. Multi-component interactions take place at the active adsorption sites where the solid–liquid phase equilibrium will emerge, showing a different capacity for single ions with a new set of isotherms. The interpretation of multi-component systems has proven to be complex and it may be a function of one or all of the following parameters: ionic radius, electronegativity, pH system, and the availability of the active sites on the adsorbent. The effect of the ionic interactions (Chiban et al., 2011a) on the adsorption may be represented by the ratio of the maximum adsorption capacity for arsenic ion in the presence of the other ions, q^{mix}, to the adsorption capacity for the arsenic ion when it is present alone in the solution, q^0. When $q^{mix}/q^0 > 1$ adsorption is promoted by the presence of other ions; when $q^{mix}/q^0 = 1$ there is no visible net interaction; when $q^{mix}/q^0 < 1$ adsorption is suppressed by other ions. There are many published literature reporting the effect of competitive anions on arsenic adsorption by low cost adsorbents, and the anion affinity or anion intercalation capability of adsorbents. In our previous work (Chiban et al., 2011d) we have studied the adsorption of arsenate ions from single, binary and multi-component systems by *W. frutescens* and *C. rhizome* plants. The results showed that the presence of Cl^-, NO_3^-, Mg^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions in solution with As(V) ions have no significant effect on arsenate adsorption capacity, whereas HPO_4^{2-} strongly interfered negatively. The effect of competing anions on As(V) adsorption by dried *W. frutescens* plant was found to reduce in the order $HPO_4^{2-} > SO_4^{2-} > Cl^- > NO_3^-$ (Chiban et al., 2009). In general, it could be concluded that the anions of higher valence have a more significant interfering effect than the monovalent anions in the arsenate adsorption by dried plants. Among the divalent anions, HPO_4^{2-} appears to be the most competitive anion that retards the adsorption of arsenate anions by dried plants.

CONCLUSION

Arsenic pollution of water is a major problem faced worldwide. The adsorption of arsenic from Aqueous solution plays an important role in water pollution control and in recent years. There has

been considerable interest in the use of low-cost adsorbents. However, from the literature reviewed, many researchers have tried to exploit naturally occurring materials as low-cost adsorbents, for arsenic removal. The arsenic adsorption capacities of low cost adsorbents presented vary, depending on the characteristics of the individual adsorbent, concentration of arsenic, pH, temperature, and contact time. Adsorption technology, utilizing natural materials and agricultural wastage either in natural form or modified form is highly efficient for the removal of arsenic from aqueous solutions and offers a cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques.

Most of this work has shown that natural materials can be good adsorbents for arsenic. Several workers have reported the potential use of dry plants as good substrates for the removal of heavy metals such as arsenic from wastewaters. Therefore, low-cost adsorbents and at the same time natural adsorbents can be viable alternatives for the treatment of metals-contaminated wastewater. This aspect needs to be investigated further in order to promote large-scale use of non-conventional adsorbents. In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness.

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