Review on Application of Low-Cost Adsorbents for Arsenic   Removal

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Abstract
Arsenic's history in science, medicine and technology has been overshadowed by its notoriety as a poison in homicides. Arsenic is viewed as being synonymous with toxicity. Dangerous arsenic concentrations in natural waters, especially in ground water has become a worldwide problem and often referred to as a 20th–21st century calamity. The current regulation of drinking water standard has become more stringent and requires arsenic content to be reduced few parts per billion. There are numbers of arsenic removal methods, which include coagulation followed by view precipitation, membrane separation, anion exchange, adsorption etc. Some low-cost adsorbents are superior including Dry plants, red mud, fly ash, zeolites, blast furnace slag's, hydrotalcites, hydroxides and various bio-adsorbents are include bio-char , methylated yeast biomass , fungal biomass , chicken feathers , alginate 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.

Keywords: Arsenic Speciation, Arsenic Removal, Low-Cost Adsorbents.

Introduction
Back Ground of The Review
Arsenic is classified as a Group A carcinogen by the United States Environmental Protection Agency. The high arsenic concentrations in the environment result from natural sources and human activities such as waste chemicals, the smelting of arsenic bearing minerals, the burning of fossil fuels, and the application of arsenic compounds in many products [1]. Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below the limits have potential for long-term contamination, because heavy metals are known to be accumulative within biological systems [2].

 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 is widely found in the Earth's crust in oxidation states of –3, 0, +3 and +5, often as sulphides or metal arsenide's or arsenates. In water, it is mostly present as arsenate (+5) but under anaerobic conditions, it is likely to be present as arsenite (+3) [3]. 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), arsenate) is stable in reductive conditions [4] and exists as an uncharged (H_3AsO_{30}) or anionic species (H_2AsO_3-). Environmental forms include arsenious acids (H_3AsO_3, H_3AsO_3 and $H3AsO_3^{2-}$), arsenic acids (H_3AsO_4, H_3AsO_4-, and $H_3AsO_4^{2-}$), arsenites, arsenates, methyl arsenic acid, dimethyl arsenic acid, arsine, etc. 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.

The existence of arsenic in groundwater, and eventually in drinking water, is a serious environmental and health problem in several developing regions [5]. Generally, inorganic arsenic is more toxic than organic arsenic, and As(III) is approximately ten times more toxic than As (V) due to greater combining affinity with the thiol (–SH) part of the protein via soft–soft acid–base interaction [6]. However, at low arsenic concentrations found in drinking water even before treatment, As(V) is instantly converted on ingestion into As(III), and the toxicity of dissolved arsenic is therefore in practice independent of oxidation state. Bodies such as USEPA, EU and WHO specify only total arsenic for drinking water [7].

It usually occurs in natural waters at concentrations of less than 1 or 2 µg L^{-1} and finds its way into the human system by way of

direct inhalation or through contamination of food and consumer products. The Processes to remove excess arsenic from drinking water and wastewaters are therefore urgently required. The mobility of arsenical forms in waters is very dependent on pH, Eh conditions and presence of different chemical species [8]. 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 etc [9]. 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. Among them, adsorption is considered to be a relatively simple, efficient and low-cost arsenic removal technique, especially convenient for application in rural areas [10].

Among all types of conventional and non-conventional adsorbents, commercially available activated carbons have been extensively used for arsenic removal because of their extended surface area, micro/mesoporous structure and significant adsorption capacity 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.

But more recently, the search for new effective bio sorbents 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 [11]. 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 oxy anions. 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 [12]. 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 [13].

Discussion
This review discusses general description of the sources and toxicity of arsenic, their speciation and the various conventional methods for arsenic removal such as membrane techniques, coagulation or flocculation, ion-exchange or chelation, adsorption , membrane filtration by using low cost adsorbent ,which have been reported in scientific reference.

Sources of Arsenic
Sources of As that arise from human activities include mining and processing of ores and manufacturing using As-bearing sulfides.

Smelters in numerous countries, including Canada, Chile, Italy, South Africa, the USA, and the former USSR have processed metal ores (mainly Copper, but also zinc, gold, and tin) that contain As. The smelting process, both recent and ancient, has released As to the air and soils both locally and globally. Arsenic (As) is a metalloid element (atomic number 33) with one naturally occurring isotope of atomic mass 75, and four oxidation states (-3, 0, +3, and +5) [14].

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 arsenic (As)-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust [14]. 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. 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, which is slightly above the average terrestrial abundance of 1.5 to 3 mg/kg [15].

Arsenic Chemistry
Arsenic forms and Mobility
Arsenic rarely occurs in a free state, it is largely found in combination with sulphur, oxygen, and iron [16]. In groundwater, arsenic combines with oxygen to form inorganic pentavalent arsenate and trivalent arsenite. Unlike other heavy metalloids and oxy anion-forming elements, arsenic can be mobilized at the pH values typically found in surface and ground waters (pH 6.5 to 8.5) and under both oxidizing and reducing conditions [17]. While all other oxyanion-forming elements are found within the μg/L range, arsenic can be found within the mg/L range [14]. Arsenic can occur in the environment in several oxidation states (−3, 0, +3 and +5), often as sulfides or metal arsenide's or arsenates.

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. The organic forms of arsenic are quantitatively insignificant and are found mostly in surface waters or in areas severely affected by industrial pollution. Increased risks of arsenic related diseases have been reported to be associated with ingestion of drinking-water at con-

centrations of < 50 µg L– 1. The relative concentrations of As (III) to As (V) vary widely, depending on the redox conditions in the geological environment [16].

Arsenic Speciation

Arsenic is perhaps unique among the heavy metalloids and oxy anion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vanadium, chromium, uranium and rhenium) in its sensitivity to mobilisation at the pH values typically found in ground waters (pH 6.5–8.5) and under both oxidising and reducing conditions However, relative to the other oxy anion-forming elements, arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. Selenium is mobile as the selenate (SeO_4^{3-}) oxyanion under oxidising conditions but is immobilized under reducing conditions either due to the stronger adsorption of its reduced form, selenite (SeO_3^{3-}), or due to its reduction to the metal. Chromium can similarly be mobilized as stable Cr(VI) ox anion species under oxidising conditions, but forms cationic Cr(III) species in reducing environments and hence behaves like other trace cations (i.e. is relatively immobile at near-neutral pH values) [14].

Figure 2: Eh/pe-pH diagram for arsenic speciation.

Redox potential (Eh) and pH are the most important factors controlling speciation of arsenic (and, to some extent, solubility) (Figure 2). 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 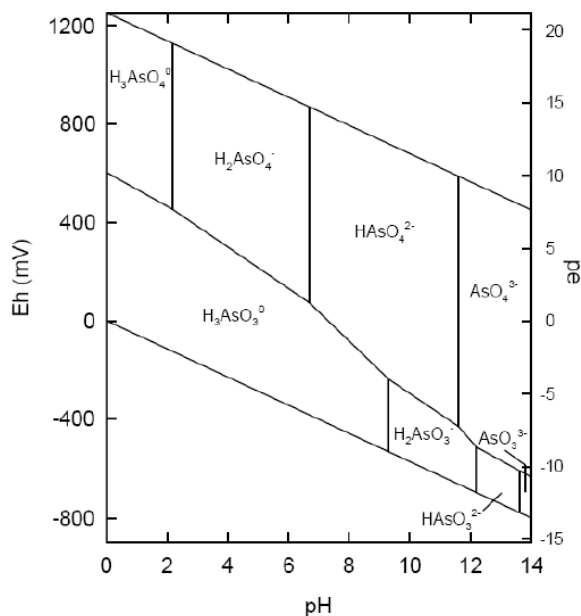species H_3AsO_3 is dominant. In contrast to the pH dependency of As (V), As (III) was found virtually independent of pH in the absence of other specifically adsorbed anions. Most often, more trivalent arsenic is found in reducing groundwater conditions than pentavalent arsenic, whereas the converse is true in oxidizing groundwater conditions.

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

The dissociation reactions and corresponding equilibrium constants of H_3AsO_4 and H_3AsO_3 are shown in Table 1 . 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.

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 co-precipitated arsenic. Therefore high arsenic waters are not expected where there is a high concentration of free sulphide.

Conventional Methods o Arsenic Removal

There are several treatment methods of arsenic removal, which include coagulation or floccuation, membrane separation, ion exchange and adsorption etc.

Coagulation or flocculation

The most heavily documented treatment methods for arsenic removal involve coagulation and filtration, either using metal salts or lime softening. This treatment can effectively remove many suspended and dissolved constituents from water besides arsenic, notably turbidity, iron, manganese, phosphate and fluoride. Significant reductions are also possible in odour, colours, and potential for trihalomethane formation [18].

Thus coagulation and filtration to remove arsenic will improve other water quality parameters, resulting in ancillary health and esthetic benefits. However, the optimal conditions vary for removal of different constituents, and coagulation to remove arsenic may not be optimal for removal of other compounds, notably phosphate and fluoride. During coagulation and filtration, arsenic is removed through three main mechanisms :

- Precipitation: the formation of the insoluble compounds $Al(AsO_4)$ or $Fe(AsO_4)$
- Co-precipitation: the incorporation of soluble arsenic species into a growing metal hydroxide phase
- Adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms can independently contribute towards contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role. However, co-precipitation and adsorption are both active arsenic removal mechanisms. 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. An anionic floccu-lant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization [10].

This technology removal is highly dependent upon initial arsenic concentration, dosage of coagulant, pH and the valence of the ar-senic species. Ferric salts are common in the uses of coagulant. Of all the coagulants studied, ferric chloride and ferric sulphate have been most successful studied a combination system of ferric sulphate coagulation and filtration in arsenic removal [19]. The method is economic and effective 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.

The results have shown a significant arsenic removal through adsorption mechanism onto the ferric complexes present. 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 compounds. Membrane by filtration is effective in reducing arsenic concentration in the water tested and 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 it seems to be difficult to lower the arsenic concentration to the acceptable level by this technique [10].

Membrane filtration

Synthetic membranes are available which are selectively permeable: the structure of the membrane is such that some molecules can pass through, while others are excluded, or rejected. Such membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate filtration has the advantage of removing many contaminants from water, including bacteria, salts, and various heavy metals [18]. 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.

Two classes of membrane filtration can be considered: low-pressure membranes, such as microfiltration and ultra filtration; and high-pressure membranes such as nanofiltration and reverse osmosis. Low-pressure membranes have larger nominal pore sizes, and are operated at pressures of 10-30 psi. The tighter high-pressure membranes are typically operated at pressures from 75 to 250 psi, or even higher.
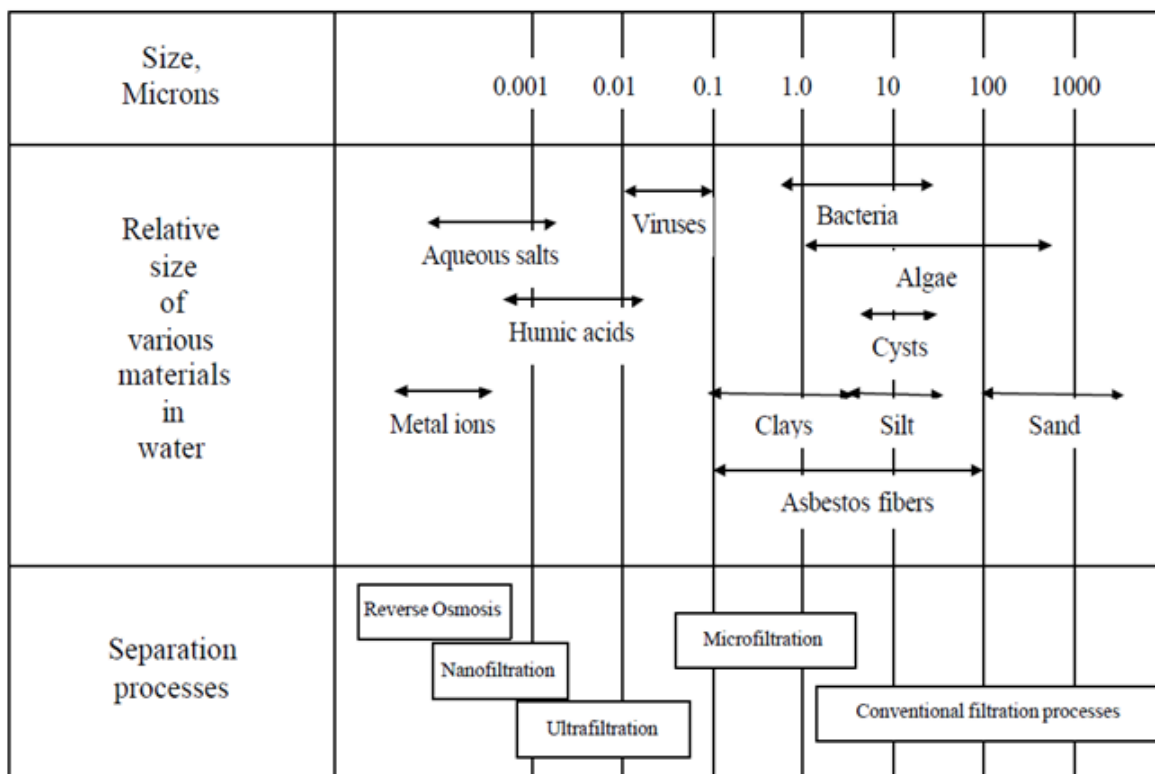
Figure 3: Pore size of various membranes, and size of materials subject to filtration

Microfiltration can be used to remove bacteria and suspended solids with pore sizes of 0.1 to micron. Ultra filtration 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 [10].

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 ultra filtration membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in nanofiltration membranes and reverse osmosis membranes [20]. Membrane filtration requires relatively high-quality influent water. Lately advancement of membrane technology has taken place in the name of electro-ultra filtration [21], which is found to possess good potential in treating arsenic from water 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 electro-statically 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. These resins are based on a cross-linked polymer skeleton, called the 'matrix'. Most commonly, this matrix is composed of polystyrene cross-linked with divinylbenzene. Charged functional groups are attached to the matrix through covalent bonding, and fall into four groups (Clifford, 1999):

• Strongly acidic [e.g. sulfonate, $-SO_3-$]
• Weakly acidic [e.g. carboxyl ate, $-COO-$]
• Strongly basic [e.g. quaternary amine, $-N+(CH_3)_3$]
• Weakly basic [e.g. tertiary amine, $-N(CH_3)_2$]

The acidic resins are negatively charged, and can be loaded with cat ions (e.g.Na+), which are easily displaced by other cations during water treatment. This type of cation exchange is most commonly applied to soften hard waters. Conversely, strongly basic resins can be pre-treated with anions, such as Cl-, and used to remove a wide range of negatively charged species. Clifford gives the following relative affinities of some common anions for a type 1 strong-base anion resins :

$OH- > H_2AsO_4- > Si(OH)_3O- > HSeO_3- > F- > SO_4^{2-} > CrO_4^{2-} >> HCO_3- > Cl- > NO_3- > Br- > I-$.

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. The 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 [22]. 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 has made this process less attractive. Other factors affecting the use of the ion exchange process include contact time and spent regenerated disposal [23].

Adsorption

Adsorption technique usually involves with the purposive removal of arsenic from water using granular media. High surface area, spherical shape, improved porosity, elevated adsorption capacity and least waste generation characteristics of granular adsorbents make the adsorptive technique more appropriate [24]. The appropriateness of adsorption technologies for low skilled communities arises mostly from its sludge-free operation nature and 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 waste waters. Activated carbon is also commonly used as the material in arsenic treatment [25].

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 [10].

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. 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 bio-adsorbents 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, sulphate, arsenate and amino group. Reaserchers 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 [26].

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 for cadmium, poplar for lead and copper (Salim and Robinson, 1985; Salim et al., 1992), cinchona for copper and lead, pine for cadmium and nickel and cypress for aluminium, Nile rose plant powder for lead ions [27]. 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 [28]. It 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. 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. 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 mineral such as bentonite, kaolinite, diatomite, and Fuller's earth as such and in modified form to adsorb not only inorganic but also organic molecules [29].

Chitosan, one of the common bio adsorbents, is produced from chitin, which is the structural element in the exoskeleton of crustaceans (shrimp, crabs, shellfish etc.). 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 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 and used to remove arsenic from water in both batch and continuous process [30].

Zeolites are basically hydrated alumino-silicates having micro-porous structure that can accommodate a wide variety of cat ions 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. Zeolites have been received increasing attention for pollution control as standard components in wastewater treatment reviewed natural zeolites utilization in water and wastewater treatment studied adsorption and removal of As (V) from drinking water by aluminium-loaded shirasu-zeolite and found its effectiveness over a wide range of pH (3 to 10) [31].

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 [32].

Heat and acid treated red mud has also been reported to have better adsorption capacity for arsenic removal. As such, a number of workers have attempted to use fly ash 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. 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 bio-adsorbents e.g., bio-char [33], methylated yeast biomass [34], fungal biomass [35], chicken feathers [36], alginate [37] to remove arsenic from aqueous solution.

It is a 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. 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 [10]. 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 [38].

Factor 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 [39]. 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 [40].

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. 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 [41]. 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 indicated the spontaneous nature of the adsorption and positive values of enthalpy change 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 [42]. He 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.

sDesorption 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. 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 reported to follow the order $HPO_4^{2-} > SO_4^{2-} > NO_3^-$, which was consistent with their competitiveness in the adsorption by adsorbents [39]. The effective desorption of As (V) from adsorbent couldbe achieved using a mixed solution of NaCl and NaOH. A number of studies have shown that arsenic-loaded adsorbents could be regenerated with NaOH or NaCl solution [10].

Conclusion

The adsorption of arsenic from aqueous solution plays an important role in water pollution control, Specially in the use of low-cost adsorbents such as Dry plants, red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides. The arsenic adsorption capacities of low cost adsorbents are vary, depending on the characteristics of the individual adsorbent, concentration of arsenic, pH, temperature, and contact time. Adsorption technology, utilizing natural materials either in natural form or modified form is highly efficient for the removal of arsenic from aqueous solutions. It offers a cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques and also can be good adsorbents for arsenic specially 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. 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 effective.

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