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## Removal Of Arsenic In Aqueous Solution By Low Cost Adsorbent: A Short Review

**Lokendra Singh Thakur, Pradeep Semil\***

Department of Chemical Engineering, Govt. Engineering College, Ujjain, Madhya Pradesh 456010, India.

\*Corres.author : [pradeepsemil@gmail.com](mailto:pradeepsemil@gmail.com)  
Mobile Number +919926703172

**Abstract:** The presence of arsenic in waters, especially groundwater, has become a worldwide problem in the past decades. High arsenic concentrations have been reported recently from the Argentina, Bangladesh, Canada, China, Chile, Hungary, Mexico, Poland, Taiwan, USA, Japan and India. Among 21<sup>th</sup> countries in different parts of the world affected by groundwater arsenic contamination, the largest population at risk is in Bangladesh followed by West Bengal in India. There are numbers of arsenic removal methods, which include coagulation followed by precipitation, membrane separation, anion exchange, etc. Arsenic pollution has emerged as a serious public health concern in Pakistan also. 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. Some low-cost adsorbents are superior including treated slags, carbons developed from agricultural waste, biosorbents, goethite and some commercial adsorbents, which include resins, gels, silica, treated silica tested for arsenic removal come out to be superior. In 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, methods of arsenic removal, low cost adsorbents, wastewater.

### 1.0 Introduction

The name arsenic (As) is derived from the Greek word *arsenikon* means yellow orpiment. This element is notorious as king of all poisons. Arsenic appears in three allotropic forms: yellow, black and grey, the stable form is a silver-gray, brittle crystalline solid. It tarnishes rapidly in air, and at high temperatures burns forming a white cloud of arsenic trioxide. The most important inorganic species are arsenate (As V) and arsenite (As III). Arsenic exists in the -3, 0, +3 and +5 oxidation states. Environmental forms include arsenious acids ( $\text{H}_3\text{AsO}_3$ ,  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_3\text{AsO}_3^{2-}$ ), arsenic acids ( $\text{H}_3\text{AsO}_4$ ,  $\text{H}_3\text{AsO}_4^-$ ,  $\text{H}_3\text{AsO}_4^{2-}$ ), arsenites, arsenates, methyl arsenic acid, di methyl arsenic acid, arsine, etc. It is a silver-grey brittle crystalline solid with atomic weight 74.9, specific gravity 5.73, melting point 817°C (at 28 atm), boiling point 613°C and vapor pressure 1mm Hg at 372°C (Wikipedia). Arsenic is one of the most toxic metal ions and possesses a serious health risk in many countries of

the world. Countries like Bangladesh, China, India<sup>1</sup>, United States, Chile, Taiwan, Vietnam, Mexico, Argentina, Poland, Canada, Hungary, New Zealand and Japan are affected with arsenic contamination. Among these, Bangladesh and West Bengal of India are highly arsenic polluted areas where arsenic concentration in water is much higher than that of WHO limit (10 $\mu$ g/L) (WHO (Ed.), 2004). Naturally, arsenic occurs in different oxidation states. In water, it may appear in both organic and inorganic forms. Inorganic forms of arsenic such as As (III) and As (V) are the most harmful to human health. As (III) is significantly more toxic and mobile than As (V). It is also more difficult to remove by conventional treatment methods. Therefore, most purification techniques require pre-oxidation of As (III) to As (V) for effective arsenic removal, causing added complexity.

## 2.0 Sources Of Arsenic

Arsenic occurs in rock, soil, water, air and in biota found in environment in many forms but in natural waters, it is mostly found as trivalent arsenite, or pentavalent arsenate. Combustion of fossil fuels is a source of arsenic in the environment through atmospheric deposition. Due to naturally occurring organic matter in the sediments, the ground waters are anoxic and rich in iron. With an average arsenic concentration of 159 $\mu$ g/L, the contamination levels varied from 1 to 3050 $\mu$ g/L in rural groundwater samples from private small-scale tube wells. In a highly affected rural area, the groundwater used directly as drinking water had an average concentration of 430 $\mu$ g/L. 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. 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<sup>2</sup>, which is slightly above the average terrestrial abundance<sup>3</sup> of 1.5 to 3 mg/kg<sup>3</sup>.

## 3.0 Human Toxicology And Environment Effects

Arsenic is one of the most toxic elements that can be found. Despite their toxic effect, inorganic arsenic bonds occur on earth naturally in small amounts. Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic. Levels of arsenic in food are fairly low, as it is not added due to its toxicity. But levels of arsenic in fish and seafood may be high, because fish absorb arsenic from the water they live in. Luckily this is mainly the fairly harmless organic form of arsenic, but fish that contain significant amounts of inorganic arsenic may be a danger to human health. Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer. A very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage with both men and women. *Finally, inorganic arsenic can damage DNA.* So the arsenic occurs aversive effects on human are classified as *Chronic Arsenic Poisoning, Dermatological Effects, Cardiovascular Effects, Neurological Effects, and Cancer Effects.*

The arsenic cycle has broadened as a consequence of human interference and due to this, large amounts of arsenic end up in the environment and in living organisms. Arsenic is mainly emitted by the copper producing industries, but also during lead and zinc production and in agriculture. It cannot be destroyed once it has entered the environment, so that the amounts that we add can spread and cause health effects to humans and animals on

many locations on earth. Plants absorb arsenic fairly easily, so that high-ranking concentrations may be present in food. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that already contain eminent amounts of arsenic and will die as a result of arsenic poisoning as the fish is decomposed in their bodies.

#### **4.0 Limitation Of Arsenic In Drinking Water**

Arsenic in drinking water can affect human health and is considered as one of the most significant environment causes of cancer in the world<sup>4</sup>. Therefore, it is necessary to mention the levels of an As in drinking water and its chemical speciation<sup>5</sup>. The FAO health limit for As in groundwater was until recently 50 µg/L, but in view of recent incidences of As poisoning in the Indian subcontinent, a decrease to 5-10 µg/L is being considered by a number of regulatory bodies throughout the world. The WHO guideline for As in drinking water is 10 µg/L. However, many countries have retained the earlier WHO guideline of 50 ppb (0.05 mg/L) as their standard or as an interim target including Bangladesh and China. In 2001, US-EPA published a new 10 ppb (0.01 mg/L) standard for arsenic in drinking water, require public water supplies to reduce arsenic from 50 ppb (0.05 mg/L) permissible limits for drinking water in different countries are reviewed.

#### **5.0 Conventional Method Of Arsenic Removal**

Remediation of arsenic contaminated water has thus become a major environmental issue. Several approaches for metal-treatment wastewater have been described including chemical and surface chemistry processes. Sensitive operating conditions, low efficiency, and production of secondary sludge demanding additional expensive disposal are inherent limitations in the application of these methods<sup>6-8</sup>. There are many non conventional method and conventional methods for arsenic removal. The conventional methods for arsenic removal are oxidation- precipitation, coagulation-flocculation filtration<sup>9</sup>, adsorption, ion exchange and membrane filtration like reverse osmosis<sup>10</sup> and nanofiltration. Each of the above processes has its own advantages and disadvantages which make the difficulty to select a suitable process. The disadvantages of traditional methods are high cost (coagulation–flocculation–filtration, oxidation and nanofiltration), high sludge production (coagulation–flocculation, electrochemical treatment), membrane fouling (nanofiltration), and constant monitoring of the ions concentration (ion exchange). Comparing all the disadvantages of above mentioned processes, adsorption is considered as one of the most popular method for arsenic removal from aqueous solutions, and is currently considered as an efficient and economic method for water treatment. Similar to ion exchange, constant monitoring would be required for adsorption water treatment. 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.

The cost of the process only depends on the cost of the adsorbent. Adsorbents derived from agriculture wastes, industrial by products/wastes, biological origin are also contributing good performance towards arsenic removal.

#### **5.1 Coagulation Or Flocculation Method**

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. Many types of coagulants are able for arsenic removing processing. The coagulants were found to be efficient regarding arsenic removal and had achieved up to 99% of arsenic removal<sup>11</sup> also reported the uses of ferric chloride and lime-polyferric sulphate as the coagulants.

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.

## 5.2 Ion Exchange Method

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<sup>12</sup>. 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 levels can limit the applicability of ion-exchanger as arsenic treatment. Tsuji<sup>13</sup> 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 has made this process less attractive<sup>14</sup>. Other factors affecting the use of the ion exchange process include contact time and spent regenerate disposal.

## 5.3 Membrane Filtration Method

Membrane technology is a promising one to remove arsenic from water. Membranes are typically synthetic materials with billions of pores or microscopic holes that act as a selective barrier, the structure of membrane allows some constituents to pass through, while others are excluded or rejected. The movement of molecules across the membrane needs a driving force, such as pressure difference between the two sides of the membrane. Different type of membrane technologies, such as reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) are employed in the removal of arsenic from water. Microfiltration can be used to remove bacteria and suspended solids with pore sizes of 0.1 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<sup>15</sup>. Lately advancement of membrane technology has taken place in the name of electro-ultra filtration which is found to possess good potential in treating arsenic from water<sup>16</sup>.

However, problems with this technique are the selective the membrane materials, pH consideration, high process cost to small scale treatment.

## 5.4 Other Potential Approaches Method

Other potential approaches would include the use of phytoremediation or rhizo filtration. Python remediation use green plants to remove pollutants from the environment and render them now available. Rhizofiltration is defined as the use of plant roots to adsorb, absorb, concentrate and precipitate metal from solution. Several plants species are known to accumulate metals from environment including water hyacinth which grows in waterways in many parts of the world and has been used as a model system for studying the uptake of metal ions by aquatic plants. Biomaterial produced from dried water hyacinth roots can provide a simple, effective and yet cheap method for removing arsenic from contaminated water. It has been found that more than 93% of arsenite and 95% of arsenate were removed within 60 minutes of exposure to a powder produced from dried roots. Some researchers have shown that certain types of bacteria can play an important role in catalysing biological arsenic removal processes. Biosorption is a passive immobilization of metals by biomass. Mechanisms of cell surface sorption are independent of cell metabolism. These are based upon physicochemical interactions between metal and functional groups of the cell wall. The microorganism's cell wall mainly consists of polysaccharides, lipids and proteins, which have many binding sites for metals. This process is independent

of the metabolism and metal binding is fast. Bioaccumulation, in contrast, is an intracellular metal accumulation process which involves metal binding on intracellular compounds, intracellular precipitation, methylation and other mechanisms.

Most remediation methods discussed more effectively remove arsenic from water containing high initial arsenic concentrations (usually >100 mg/L) but residual arsenic concentrations exceed the 0.05 mg/L water quality standard used in most countries. Conventional and non-conventional treatment technologies for aqueous arsenic remediation were compared. In villages in India and Bangladesh, a highly successful technology may not succeed in rural areas unless it fits into the rural circumstances and is well accepted by the masses. Technology development is only possible when a partnership exist involving proper village level participation. Arsenic removal technologies all suffer from one or more drawbacks, limitations and scope of application.

## 6.0 Adsorption Method For Arsenic Removal

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of solid, and becomes bound by physical and chemical interactions. Adsorption phenomena are operative in most natural physical, biological and chemical systems. Physical adsorption is caused mainly by Vander Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Chemical adsorption is caused by bounding between the adsorbate molecules. Bio adsorption is based on biosorption. These are cell metabolism means physicochemical interaction between metal and functional groups of cell wall<sup>17</sup>. 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<sup>18-20</sup>.

### 6.1 Arsenic Remediation By Activated Carbon

Consequently, attempts have been made in order to find new simple and efficient techniques. For dilute concentration, adsorption is one of the suitable methods of arsenic removal. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH etc. Many activated carbons are available but few are selective. Selective adsorption utilizing biological materials, mineral oxides, activated carbon, or polymer resins, has generated increasing excitement<sup>21</sup>. The use of carbon extends for back into history. Charcoal was used for drinking water filtration by ancient Hindus in India and carbonized wood was a medical adsorbent and purifying agent in Egypt by 1500 b.c.<sup>22</sup>. Modern activated carbon industrial production was established. In 1901 replace bone-char in sugar refining<sup>23</sup>. Powdered activated carbon was first produced commercially from wood in Europe in the early 19<sup>th</sup> century and was widely used in the sugar industry. Activated carbon was first reported for water treatment in the United States in 1930. Activated carbon is *a crude form of graphite with a random or amorphous highly porous structure with a broad range of pore sizes, from visible cracks and crevices, to crevices of molecular dimensions*<sup>24</sup>. Active carbons have been prepared from coconut shells, bones, bagasse, bark, blood, coal, coffee beans, cereals, carbon cobs, fertilizer waste slurry, fish, etc. Wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) are most commonly used<sup>25</sup>. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. Many activated carbons are available commercially but few are selective for heavy metals. They are also expensive. Despite carbon's prolific use to treat wastewater, it remains expensive, requiring vast quantities of activated carbon. Improved and tailor-made materials are sought. Substitutes should be easily available, cheap and, above all, be readily regenerated, providing quantitative recovery.

#### 6.1.1 Carbon Surface Chemistry

Carbon surface chemistry has been reviewed<sup>26</sup>. This surface chemistry depends upon the activation conditions and temperatures employed. Activation refines the pore structure. Mesopores and micropores are formed yielding surface areas up to 2000 m<sup>2</sup>/g. The acidic groups on activated carbons adsorb metal ions<sup>27</sup>. Surface area may not be a primary factor for adsorption on activated carbon. High surface area does not necessarily mean high adsorption capacity<sup>28</sup>.

### 6.2 Low Cost Adsorbents

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<sup>29</sup>.

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. Recently, the nano practicals of adsorbents are analysis for increasing effluents treated efficiency. As (III) and As (V) adsorption on to five different sorbents activated carbon (AC), absorptions mittel3 (AM3), granulated iron hydroxide (GIH), zero valent iron ( $\text{Fe}^0$ ), zirconium-loaded activated carbon (Zr-AC). Batch and column method were used. The sorption of arsenate followed the sequence  $\text{Zr-AC} \gg \text{GIH} = \text{AM3} > \text{Fe}^0 > \text{AC}$  (Daus et al., 2004). As-GAC for arsenic removal from drinking water maximum iron loading were 7.89% for draco 20×50 and 7.65 wt % for draco 20×40. The BET specific surface area and porosity all decreased after iron impregnation. The maximum adsorption capacity of untreated GAC GAC-Fe (0.05m), GAC-Fe- $\text{O}_2$  (0.05m), GAC-Fe- $\text{H}_2\text{O}$  (0.05m) GAC-Fe-Nalco (0.05m), were  $3.78 \times 10^1$ ,  $2.96 \times 10^3$ ,  $1.93 \times 10^3$ ,  $3.94 \times 10^3$ ,  $6.57 \times 10^3$   $\mu\text{g As/g}$  respectively<sup>30</sup>. As (III) and As (V) removal from water was studied using a char carbon (CC) derived from fly ash. The maximum adsorption at optimum condition (159ppm, pH 7.2) is 30.5 mg/g. and (490ppm, pH 2.2) is 34.5 mg/g for CC and AC respectively [30]. The efficiency of As (V) adsorption by activated carbon produced from oat hull is decreased from 3.09 to 1.57  $\text{Asg}^{-1}$  when the value of pH increased 5 to 8<sup>31</sup>.

The As (V) removal by an iron-impregnated activated carbon using the surface complexation model (SCM) was strongly dependent<sup>32</sup>. Activated carbon treated with iron salt solution to improve arsenic adsorption with concentration of salt, pH, and contact time<sup>33</sup>. The activated carbon was prepared from coconut husk carbon with 1.8 parts of weight of sulfuric acid (18M) at 150°C for 24 h. The carbonized material (CHC) was water washed to remove acid and dried at 105°C. The CHC (10 g) was mixed with 100mL of 100 m mol/L copper solution (initial pH 8.5). The mixture was shaken for 24 h at 30°C and filtered<sup>34</sup>. The resulting copper-impregnated coconut husk carbon (CuCHC) was water washed until the filtrate was copper free. Optimum As(III) adsorption conditions on this copper-impregnated activated carbon were established. Maximum adsorption capacity occurred at pH 12.0. Capacity increased going from 30°C to 60°C. Spent adsorbent was regenerated using 30%  $\text{H}_2\text{O}_2$  in 0.5M  $\text{HNO}_3$ . Zirconium-loaded activated carbon for arsenic removal from aqueous solution. Iron containing mesoporous carbon (IMC) on silica tempted for the arsenic removed. The IMC had a BET surface area of  $401 \text{ m}^2/\text{g}$ . slightly lower than that of mesoporous carbon ( $503 \text{ m}^2/\text{g}$ ). Maximum adsorption capacities of 5.96 mg As/g for arsenite and 5.15 mg As/g for arsenate were obtained.

Mondal et al., 2006 studied the removed arsenic from a simulated contaminated ground water by adsorption onto  $\text{Fe}^{3+}$ -impregnated granular activated carbon (GAC-Fe) in the presence of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mn}^{2+}$ . The effects of shaking time, pH, and temperature on the percentage removal of As (III), As (V),  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and Mn have been reported. The shaking time for optimum arsenic removal was 8h for GAC-Fe and 12h for GAC, respectively. Maximum As (V) and As (III) removal was in the pH range of 5–7 and 9–11, respectively, for both the adsorbent.

The adsorption of arsenic from drinking water by an aluminum-loaded shirasu-zeolite ( $\text{AL-SZP}_1$ ) was slightly dependent the initial pH over a wide range. The adsorbed As (V) ions were desorbed by 40Mm aqueous  $\text{NaOH}^{35}$ . Compare the two oxides to arsenic removal by phosphate and manganese oxides and investigated the adsorption at different pH value, surface area, and contact time. Phosphate present at concentration of  $600 \mu\text{g/L}$  had an adverse effect on As (III) removal and reduced the overall efficiency from 80% to 30%<sup>36</sup>. However, phosphates did not affect the oxidation of As (III). Remove arsenates from water with activated alumina (AA) and iron oxide-impregnated AA.

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 3.0<sup>37</sup>. Powdered chitosan, obtained from shrimp shell, was converted into bead form and used to remove arsenic from water in both batch and continuous process<sup>38</sup>. Red mud is a ferric hydroxide material, the by-product of smelting and refining of ores containing gold, cobalt, silver, copper and iron. 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<sup>39</sup>. Heat and acid treated red mud has also been reported to have better adsorption capacity for arsenic removal<sup>40</sup>. Fly ash is one of the residues generated in the combustion of coal. It is generally captured from the chimneys of power generation facilities. 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<sup>41</sup>.

### 6.3 Bio-Sorbents

Biosorption is a passive immobilization of metals by biomass. Mechanisms of cell surface sorption are induced by cell metabolism. These are the physicochemical interactions between metal and functional groups of cell wall. The microorganism's cell wall mainly consists of polysaccharides, lipids, and proteins. The properties of biomass are studied<sup>42</sup>. Chitosan, one of the common bioadsorbents, is produced from chitin, which is the structural element in the exoskeleton of crustaceans (shrimp, crabs, shellfish etc)<sup>43</sup>. 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 3.0. Powdered chitosan, obtained from shrimp shell, was converted into bead form and used to remove arsenic from water in both batch and continuous process. Bio-char<sup>44</sup>, methylated yeast, biomass<sup>45</sup>, fungal biomass<sup>46</sup>, chicken feathers<sup>47</sup>, alginate<sup>48</sup>, an algae<sup>49</sup>, waste black tea by fermentation used as adsorbents to remove arsenic from aqueous solution<sup>50</sup>. Human hairs as adsorbents are used.

### 6.4 Natural Wastes And Agriculture Wastes

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. Clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite<sup>51</sup>. 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. Dried plants are natural materials widely available and studied as an alternative adsorbent for arsenic removal. The water lettuce, an aquatic plant, used as an adsorbent for arsenic removal. The range of 0.25 to 5.0 mg/L from 22.8% to 82.0% of the As was removed for a biomass loading of 20 g/l at pH 7.0 for 144 h<sup>52</sup>. The sorption capacity was 1.43 mg/g biomass. The *garccinia combogia* an indigenous plant to remove trivalent arsenic. 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 for pollutants such as arsenate with high efficiency<sup>53-58</sup>. They used the Romanian *C. rhizome* plant for arsenate removal from aqueous solution and found that the maximum adsorption capacity of arsenate on *Cyperus rhizome* plant was 22.04 mg/g at an initial arsenate concentration of 1 g/l<sup>59</sup>. The order of efficiency of fixation depends on the plant used. Moreover, the efficiency of arsenate adsorption depends on different parameters (size of crushed plants which must be less than 50  $\mu\text{m}$ , ratio of m/V between crushed vegetal mass and volume of solution to be treated, solution concentration and pH). *Wheat and rice husk*, *banana*, *pea* and *peanut peels*, and *sohanjana leaves* etc were chosen as adsorbent material. After washing with tap water, these were dried in an oven at 100°C for 24 hours and homogenized in a blender to utilize as adsorbents. Lignin and cellulose in agricultural material contained aldehydes, ketones, carboxylic, alcohols, ether and phenolic groups, which assist in binding with heavy metal ions<sup>60</sup>. In this connection, most commonly used adsorbents for arsenic were *Maringa oleifera*<sup>61</sup>, rice husk<sup>62</sup>, orange peels<sup>63</sup>, banana peels<sup>64</sup>, jute stick<sup>65</sup> and rice polish<sup>66</sup> etc. are reviewed.

### 7.0 Desorption Or Regeneration

Desorption means to regenerate the adsorbents so that it can be used again to adsorb phosphate ions, and to develop the successful adsorption process. The arsenate desorption was dependent on the anion species and their concentrations in the desorbing solutions. Sorption capacities were evaluated at different pH, temperatures, As concentration ranges, adsorbent doses and As (III)/As (V) ratios. The adsorbents were used for treating ground water, drinking water, synthetic industrial wastewater, and actual wastewater, and also in batch experiments and others in column modes. Sodium hydroxide (NaOH) and strong acid are mostly used to elute both As (III) and As (V). Selection of eluent depends on the arsenic adsorption mechanism and nature of the adsorbents. At pH 1.5 the value of desorption of strong acid is more than strong base [66]. Aluminum loaded shirasu-zeolite was regenerated with 40 mM NaOH solution, iron oxyhydroxide was regenerated with 2 M NaOH solution<sup>67</sup>. Zr-loaded phosphoric acid chelating resin was eluted with 0.4 mol/L NaOH solution<sup>68</sup>. As(III) from iron oxide coated cement (IOCC) desorption used 10% NaOH solution<sup>69</sup>.

### 8.0 Conclusion

Heavy metal included 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. 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. 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.

## References

1. Chatterjee, D. Das, B.K. Mandal, T.R. Chowdhury, G. Samanta, D. Chakraborty, Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 1 *Analyst.*, 1995, 120, 643–656 .
2. Webster JG, C.P. Marshall, R.W. Fairbridge (Eds.), *Encyclopedia of Geochemistry*, Chapman Hall, London., 1999, 21–22.
3. Mandal B.K., K.T. Suzuki, Arsenic round the world: a review, *Talanta.*, 2002, 58, 201–235 .
4. Smith A.H. C. Hopenhajan-Rich, M.N. Bates, H.M. Goeden, I. Hertz-Picciotto, H.M. Duggan, R. Wood, M.Y. Kosnett, M.T. Simth, *Environment Health Perspectives.*, 1992, 97, 259 .
5. Welch A.H., D.B. Westjohn, D.R. Hel Sel, R.B. Wanty *Groundwater.*, 2000, 38, 589 .
6. Ahluwalia, S. S. and D. Goyal Removal of heavy metals from waste tea leaves from aqueous solution, *Eng. Life Sci.*, 2005, 5(2), 158-162 .
7. Kundu, S. and Gupta A. K., Arsenic adsorption onto iron oxide-coated cement (IOCC): Regression analysis of equilibrium data with several isotherm models and their optimization, *J. Chem. Engin.*, 2006, 122(1-2), 93-106 .
8. Thomas, S. Y., Choonga T. G., Chuaha Y., Robiaha F. L., Koaya G., and I. Azni Arsenic toxicity, health hazards and removal techniques from water: an overview. *Desal.*, 2007, 217(1-3) 139-166 .
9. Ning R.Y., Arsenic removal by reverse osmosis, *Desalination.*, 2002, 143(3), 237–241
10. Guo C, Zhang F, Yang X, Treatment of Ascontaining wastewater by lime-polyferric sulphate coagulating process. *Gongye Shuichuli.*, 2000, 20, 27–29 .
11. Clifford D, Ion exchange and inorganic adsorption. In *American Water Works Association, Water Quality and Treatment, A handbook of community water supplies*. 5th ed. McGraw Hill. New York., 1999.
12. Jackson BP, Miller WP, Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides, *Soil Sci. Soc. Am. J.*, 2000, 64, 1616–1622 .
13. Tsuji M, SeO<sub>3</sub><sup>2-</sup>- selective properties of inorganic materials synthesized by the soft chemical process. *Solid State Ionics.*, 2002, 151, 385-392.
14. Choong TSY, Chuah TG, Robiah Y, Gregory Koay FL, Azni I, Arsenic toxicity, health hazards and removal techniques from water: An overview *Desalination.*, 2007, 217, 139–166.
15. Weng Y-H, Hsieh LHC, Lee HH, Li KC, Huang CP, Removal of arsenic and humic substances (HSs) by electro-ultrafiltration (EUF). *J. Hazard. Mater.*, 2005, 122, 171–176
16. Veglio F., Beolchini F. Removal of heavy metals by biosorption., 1997, 44, 301-316.
17. Wennrich R Daus, Weiss H, Sorption materials for arsenic removal from water: A comparative study *Water Res.*, 2004, 38, 2948–2954.
18. Huang CP, Fu PLK, Treatment of As (V) containing water by Low Cost Adsorption. *J. Water Pollut. Control Fed.*, 1984, 56, 233–242 .
19. Gimbel R, Hobby R, Discharge of arsenic and heavy metals from activated carbon filters during drinking water treatment. *BBR, Wasser Rohrbau.*, 2000, 51, 15–16.
20. Dambies L., T. Vincent, E. Guibal, Treatment of arsenic-containing solutions using chitosan derivatives: uptake mechanism and sorption performance, *Water Res.*, 2002, 36, 3699–3710 .
21. Cheremisinoff P.N. and Arbor, carbon adsorption application, in; *carbon adsorption Handbook*, Ann Arbor Science Publication, Inc, Ann Arbor, MI., 1980, 1-54 .
22. Hamerlinck Y., Mertens D.H., Vansant E.F. (Ed.), *Activated Carbon Principles in Separation Technology*, Elsevier, New York., 1994.
23. Mantell C.L., *Carbon and graphite Handbook*, John wiley & sons, Inc, New York., 1968



24. Pollard S.J.T., Pollard G.D., Fowler G.D., Sollars C.J. and Perry R., Science of the total Environment., 1992, 116, 31 .
25. Radovic L.R.(Ed.) Chemistry and Physics of Carbon, Vol 27, Marcel Dekker,Inc, New York., 2000.
26. Huang CP, Fu PLK, Treatment of As (V) containing water by activated carbon. J. Water Pollut. Control Fed., 1987, 56, 233–242.
27. Perrich J.R., Activated Carbon Adsorption for waste water treatment, CRC Press, Inc, Boca Raton, FL., 1981.
28. Bailey SE, Olin TJ, Bricka RM, Adrian DD review of potentially low cost sorbents for heavy metals, Water Res., 1999, 33, 2469–2479.
29. Daus Wennrich R, Weiss H, Sorption materials for arsenic removal from water: A comparative study. Water Res., 2004, 38, 2948–2954.
30. Gu Z., Fang J., Deng B., Preparation and evaluation of GAC-based ironcontaining adsorbents for arsenic removal, Environ. Sci. Technol., 2005, 39(10), 3833–3843.
31. Chuang C.L., Fan M., Xu M., Brown R.C, Sung S., Saha B., Huang C.P., Adsorption of arsenic(V) by activated carbon prepared from oat hulls, Chemosphere., 2005, 61(4), 478–483.
32. Vaughan R.L. Jr., Reed B.E., Modeling As(V) removal by a iron oxide impregnated activated carbon using the surface complexation approach, Water Res., 2005, 39(6), 1005–1014.
33. Huang C.P., Vane L.M., Enhancing As<sup>5+</sup> removal by a Fe<sup>2+</sup>-treated activated carbon, J. Water Pollut. Contr. Fed., 1989, 61, 1596–1603.
34. Zhimang G., Baolin D., Use of iron-containing mesoporous carbon (IMC) for arsenic removal from drinking water, Environ. Eng. Sci., 2007, 24(1), 113–12.
35. Xu YH, Nakajima T, Ohki A Adsorption and removal of arsenic (V) from drinking water by aluminum-loaded shirasu-zeolite. J. Hazard. Mater, B92., 2002, 275-287.
36. Ouvar d S., Simonot M.O., Water Science and Technology; Water Supply., 2002, 1, 168
37. Dambies L., T. Vincent and E. Guibal Water Research., 2002, 36, 3699.
38. Chen CC, Chung YC Arsenic removal using a biopolymer chitosan sorbent. J. Environ. Sci. Health Part A: Toxic/Hazard. Subst. Environ. Eng., 2005, 41, 645-658.
39. Altundogan HS, Altundogan S, Tumen F, Bildik Arsenic removal from aqueous solutions by adsorption on red mud. Waste Manage., 2000, 20, 761-767 .
40. Altundogan HS, Altundogan S, Tumen F, Bildik Arsenic adsorption for aqueous solution by activated red mud. Waste Manage., 2002, 22, 357-363 .
41. Diamaddopoulos E, Loannidis S, Sakellaropoulos GP As(V) removal from aqueous solutions by fly ash. Water Res., 1993, 27, 1773-1777.
42. Mohan D., Pittman C.U. Jr., Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water, J. Hazard. Mater., 2006, 137(2), 762–811.
43. B Amit, Mika S Applications of chitin- and chitosan-derivatives for detoxification of water and wastewater - A short review Adv.Colloid Interf. Sci., 2009, 152, 26–38.
44. Mohan D, Pittman Jr CU, Bricka M, Smith F, Yancey B, Mohammad J Steele PH, Alexandre-Franco MF, Gómez-Serrano V, Gong H, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. J. Colloid Interf. Sci., 2007b, 310, 57–73.
45. Seki H, Suzuki A, Maruyama H, Biosorption of Chromium(IV) and Arsenic(V) onto methylated yeast biomass. J. Colloid Interf. Sci., 2005, 281, 261-266 .
46. Say R, Yilmaz N, Denizli A, Biosorption of cadmium, lead, mercury, and arsenic ions by the fungus *Penicillium purpurogenum*, Sep. Sci. Technol., 2003, 38, 2039-2053 .
47. Teixeira MC, Ciminelli VST, Development of a biosorbent for arsenite: structural modeling based on X-ray spectroscopy. Environ. Sci. Technol., 2005, 39, 895–900 .
48. Zouboulis AI, Katsoyiannis IA, Arsenic removal using iron oxide loaded alginate beads. Ind. Eng. Chem. Res., 41, 6149–6155.
49. Hansen H.K., P. N´uñez, R. Grandon, Electrocoagulation as a remediation tool for wastewaters containing arsenic, Miner. Eng., 2006, 19(5), 521–524 .
50. Murugesan GS, Sathishkumar M, Swaminathan K, Arsenic removal from groundwater by pretreated waste tea fungal biomass. Bioresour. Technol., 2006, 97, 483–487 .
51. Shichi T, Takagi K, Clay minerals as *photochemical* reaction fields. J. Photochem. Photobiol. C: Photochem. Rev., 2000, 1, 113-130 .
52. Basu, S. Kumar, S. Mukherjee, Arsenic reduction from aqueous environment by water lettuce (*Pistia stratiotes* L.), Indian J. Environ. Health., 2004, 45, 143–150.

53. Chiban M, Benhima H, Saadi B, Nounah A, Sinan f Isotherms and kinetic study of dihydrogen and hydrogen phosphate ions ( $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ) onto crushed plant matter of the semi-arid zones of Morocco: *Asphodelus microcarpus*, *Asparagus albus* and *Senecio anthophorbium*, J. Physique IV., 2005, 123, 393-399 .
54. Chiban M, Carja G, Lehtu G, Sinan F Equilibrium and thermodynamic studies for the removal of As(V) ions from aqueous solution using dried plants as adsorbents, Arabian J. Chem., doi:10.1016/j.arabjc., 2011c, 2011.10.002 .
55. Chiban M, Lehtu G, Sinan F, Carja Arsenate removal by *Withania frutescens* plant from the south-western Morocco. Environ. Eng. Manage., 2009, 8, 1377-1383 .
56. Chiban M, Sinan F Removal of Cu (II) ions from aqueous solution by micro-particles of dried *Carpobrotus edulis* plant in a column system, Water Qual. Res. J. Canada., 2011d, 46, 259-267.
57. Chiban M, Soudani A, Sinan F, Persin M Single, Binary and multi-component adsorption of some anions and heavy metals on environmentally friendly *Carpobrotus edulis* plant, Colloids Surf. B: Biointerfaces., 2011a, 82, 267-276 .
58. Chiban M, Soudani A, Sinan F, Persin M, Characterization and application of dried plants to remove heavy metals, nitrate and phosphate ions from industrial wastewaters in a batch system. Clean -soil air water., 2011b, 39, 376-283.
59. Ofomajaa, A. E. and Ho, Y. S., Effect of pH on cadmium biosorption by coconut copra meal. J. Hazard Mater., 2007, 139(2), 356-362 .
60. Kumari P, Sharma P, S. Srivastava, and M. M. Srivastava, Arsenic removal from the aqueous system using plant biomass: a bioremediation approach J. Indus. Microbiol. Biotechnol., 2005, 32(11-12), 521-526.
61. Amin, M. N., T. Kaneco, A. Kitagawa, H. Begum, T. Katsumata, K. Suzuk, and Ohta, Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. Indus, Eng. Chem Res., 2006, 45(24), 8105-8110.
62. Biplob, J. Hazard. Mat, Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product., 2006, 154, 1066-1074.
63. Memon, S. Q, M. I. Bhangar and J.-Ur-R. Memon, Evaluation of banana peel for treatment of arsenic contaminated water, Proc. First Tech. Meeting Muslim Water Res Coope., 2008, 104-109 .
64. Israt, J. M., A. M. Lotin, M. Moniuzzaman, and M. A. Sadullah, Arsenic removal from water using activated carbon obtained from chemical activation of jute stick. Indian J. Chem. Technol., 2008, 15, 413-416.
65. Ranjana D., Talat M., and Hasana S. H., Biosorption of arsenic from aqueous solution using agricultural residue rice polish. J. Hazard. Mater., 2008, 166(2-3), 1050-1059 .
66. Lorenzen L, van Deventer JSJ, Landi WM, Factor affecting the mechanism of the adsorption of arsenic species on activated carbon. Miner. Eng., 1995, 8, 557-569.
67. Guo X., Chen F., Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater, Environ. Sci. Technol., 2005, 39(17), 6808-6818 .
68. Zhu X., Jyo A., Removal of arsenic(V) by zirconium(IV) loaded phosphoric acid chelating resin, Sep. Sci. Technol., 2001, 36(14), 3175-3189.
69. Kundu S., Gupta A.K., Adsorptive removal of As (III) from aqueous solution using iron oxide coated cement (IOCC), evaluation of kinetic, equilibrium and thermodynamic models, Sep. Purif. Technol., 2006, 52(2), 165-172.

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