Arsenic Remediation by Synthetic and Natural Adsorbents

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Abstract

The contagion of toxic metals in water is a serious environmental and health concern and threatening problem worldwide. Particularly arsenic contamination in ground water has became great dilemma in the earlier decades. With advent in research for arsenic remediation, standard of drinking water is improving and now reduced to few parts per million (ppm) level of arsenic in drinking water sources. However, due to continuous enhancement in environmental pollution, remediation techniques are still needed to achieve the drinking water quality standard. Development of novel and economically feasible removal techniques or materials for selective separation of this toxic specie has been the main focus of research. Several arsenic removal techniques, including membrane separation, coagulation, precipitation, anion exchange have been developed. The aim of this article is to review briefly arsenic chemistry and previous and current available technologies that have been reported various low-cost adsorbents for arsenic removal.

Keywords: Arsenic removal, Metal toxicity, Water purification, Removal techniques, Low cost adsorbents

Introduction

Metals toxicity is serious health concern due to their chronic and acute toxicity, specifically heavy metals have tendency to aggravate the different cancers. Among heavy metals arsenic (As) is naturally occurring hazardous element found at trace levels in air, water, soil, and food [1-6]. The elevated level of arsenic in ground water increase due to the anthropological activities as well as natural phenomena has posed serious health issues [7-9]. As exposure in food and water poses serious health effects in humans, it may cause non-cancer effects (hyper- and hypo-pigmentation, keratos is, black foot disease, hypertension, cardiovascular diseases and diabetes), and/or carcinogenic such as typical skin, lung and bladder cancers [1, 3, 4, 10-17]. According to the World Health Organization (WHO) classification, arsenic has been label as a first group carcinogenic substance [18]. However, arsenic has been recognized as one of the most noxious element as extensive but just its cumulative role as a toxin of water has expanded attention of scientists throughout the world. It is because of their increasing concentration in water through geothermal dissolution of reserves and mineral ores [19]. Mining of coal or other rocks, fossil fuel burning and casting of non-iron metals has been found the main industrial methods that contribute to anthropogenic As impurities in water [20]. Study showed that about 70 % of Arsenic production is due to copper chrome arsenate (CCA) used timber treatment where as 22% is produced in agricultural chemicals other may be in glass, non-ferrous alloys and pharmaceuticals [21]. The oxidation state and toxicity of arsenic varies
from organic or inorganic in the terminology of the oxidation state. Arsenic occurs in four forms which are arsenic (0), arsenite As(III), arsine As(III) and arsenate As (V). Among these four oxidation states the inorganic arsenite and arsenate is commonly found in the water, these are the most prevalent forms of the arsenic [22]. Due to the slow transformation of the redox, arsenite and arsenate both are oxidized and reduced in the environment [23]. Under the anoxic reduction reaction (e.g., reduced sediments, subsurface waters) mostly arsenic occurs as arsenite, however the arsenate is prevalent in aerobic oxidation condition such as surface water [24]. The pH plays a key role while determining the state of arsenic, the solubility of arsenic is very low at neutral or slightly acidic conditions, but it may increase drastically both at very low pH (below 2.0) and at very high pH (above 9.0). 2. The maximal amounts of arsenic that might be released from soils in extremely acidic (pH<2) or extremely alkaline (pH>9) conditions depend on the total arsenic concentration. [25-28]. The As(III) is about more than 60 times toxic then As(V), it may be due to higher cellular uptake [22, 29, 30]. Due to its toxicity about 130 million people in 2001 were affected and a considerable increase was observed in the number of people affected by arsenic [31]. Hence the high and worst contamination of arsenic in ground water is observed and reported in Asian countries, mainly in India, Pakistan, Bangladesh and West Bengal, [32-34]. It has been reported that about 60–100 million people in India and Bangladesh are currently at risk, due to arsenic-contaminated drinking waters [6, 31, 35, 36]. In these both areas the drinking resources to the population are water supply and tube-wells and 79.9 million and 42.7 million natives are using the contaminated water which has arsenic concentrations above then 50 µg/L [37, 38]. Likewise, the concentration of arsenic in the underground water of some area is as high as 4730 µg/L [39]. According to the WHO and US-EPA, the maximum concentration of arsenic is allowed in drinking water is 10 µg/L [40]. But for different countries the permissible limit is vary due to high arsenic contaminated waters, listed in Table 1. For the past three decades, a number of studies showed that arsenic- contaminated water is one of the principle threats for the human health [41, 42]. Arsenic enters in the human body from different sources like, digestion, breathing and skin absorption. It is distributed in different large number of living organs like liver, lungs, kidney and skin [43]. Erythrocyte contain about 95 - 99 % of arsenic which is bound to hemoglobin and it is transported to all body parts. It is reported that about 70% arsenic level is excreted through urine. The form of Arsenic which is excreted in urine is mainly in methylated form which is less toxic. The levels of arsenic appears in skin are counted lower than 60 times toxic then arsenic. Chronic exposure of inorganic arsenic in concentrations above 50 µg/L in drinking water, can cause diverse skin lesion such as hyper pigmentation, hyperkeratosis and cancers including skin, lung, kidney, bladder, the disease cause by arsenic termed as arsenicosis [30].

Table 1. Countries affected by arsenic contamination and WHO permissible limits for drinking water.

<table>
<thead>
<tr>
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<th>WHO Limit in (µg/L)</th>
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<td>[70-71]</td>
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Conventional Techniques

Several techniques are available for the removal of arsenic from contaminated water like as oxidation- precipitation [100-106], adsorption [107], coagulation-flocculation filtration [108], ion exchange and membrane filtration like reverse osmosis [109] and nanofiltration [110]. Each of the above technique has its own advantages and disadvantages it make very difficult to choose an appropriate method. There are many drawback of conventional techniques such as cost (oxidation, coagulation–flocculation–filtration and nanofiltration), high slurry production (electrochemical
Adsorption Method

The adsorption is known as one of the popular method used to eliminate arsenic from aqueous solution. Adsorption method is said as most economic and efficient method for the treatment of water and process is similar to ion-exchange. The cost of process depends upon the cost of adsorbent [40]. Some known adsorbents used for the removal of arsenic are hydrous titanium dioxide (TiO₂) [112, 113], various iron oxides/hydroxides [114], synthetic zeolites [115, 116], activated carbon [117], and activated alumina [118]. For the removal of arsenic different biological origins, wastes and industrial by products are also used [112]. Due to toxic nature of arsenic scientists are seriously working for the development of new adsorbent methods which must be more rapid and cost effective than reported methods [115]. The development of nano-size adsorbents are taking great concentration in this regard due to their high surface area and high tendency to adsorb arsenic from water. Synthesis of nano particles have been employed from respective metal and metal oxides e.g. gold, titanium oxide, cupric oxide, metal oxide nanomaterials, nano-iron, impregnated granulated activated carbon, synthetic nanostructured Fe(III)–Cr(III) mixed oxides [119-123]. For the removal of arsenic few papers h arsenic been reported. The cupric oxide nanoparticles have been used as adsorbent for the removal of As(III) and (V). These researchers have studied the different parameters such as pH effect, equilibrium behavior, temperature, and turbulence [124]. They have used the Langmuir and Freundlich isotherm model to check the equilibrium behavior of the system, the main advantage of this technique is the reuse of adsorbent material. It is reported that this method is highly pH dependent so effect of different species may alter the require pH. This is time consuming method takes about 1 g/L adsorb in 5 hours. The efficiency of adsorbent decreases in time intervals and the presence of different ions such as sulfate and phosphate ions reduces adsorbent efficiency by 10 to 20%, respectively [120].

Natural adsorbents

Different cost effective adsorbents have been used for the removal of arsenic such as iron oxide coated fungal biomass [125], methylated yeast biomass [126], modified fungal biomass, residue rice polish [127], acid-washed crab shells [128], modified fungal biomass [129,130], modified coconut coir pith [131], modified cotton cellulose [132], bone char [133], shrimp shells [134], saw dust of spruce (Picea abies) that is chemically modified [135], HDTMA modified zeolite [136], iron-coated zeolite [137] and surfactant-modified zeolite [138]. Different chemically or physically modified materials are used but their performance was found to be poor towards lower concentrations.

Waste of pomegranate fruit

The waste of pomegranate fruit as a bio-adsorbent has been used for decontamination of As(III) in water. Bio-adsorbent was prepared by acid treatment and loaded with Fe(III) to check the adsorption efficiency for the As [139]. Many factors including pH, initial arsenic level, adsorbent dose and contact time on adsorption of As(III) onto Fe-CPW were examined. The optimum pH 9 was best suited for 70.7% removal of As(III) at 2 hours equilibrium time for the adsorption of As(III) onto Fe-CPW. The main advantage of this method is low cost bio adsorbent prepared from pomegranate waste has been investigated for the removal of As(III) from water [139]. However, the adsorption of As(III) was found to be strongly dependent upon pH of the solution and it takes longer time during experiment [139].

Orange peel

Orange peel is used as bio absorbent to reduce the concentration of arsenic below the standard level form the aqueous media. Orange peel is used without any chemical modification for the removal of arsenic from real samples [140]. However, this method is laborious and time
consuming. According to literature survey this method is selective at particular pH and shaking speed is also selective for the desired adsorbent capacity [138, 140].

**Raw rice husk**

Rice husk is an agro waste and abundantly available at low cost. The potential of rice husks as an adsorbent has been used for the removal of As(V) from groundwater [141]. Rice husk is considered as low cost agro waste. Furthermore, various factors including, adsorbent dose flow rate, particle size of adsorbent, metal concentration and column diameter for the maximum removal of arsenic was explored to investigate the potential of raw rice husk as adsorbent as well as performance of fixed bed column [142], the reported method rely on the surface of column, pH specific for the As(V).

**Tea waste**

The tea waste, straw and microbial biomass have been used generally as an inexpensive adsorbent [143-152]. Earlier reported that tea waste is more capable to trap the metals owing its insoluble cell and highly porous structure [153-157]. The present functional groups in tea waste also enhanced trapping action. Therefore the adsorption capacity of As are investigated extensively in comparison to recommend an inexpensive alternative to activated carbon. This method is time consuming and it is also reagent dependent [158].

**Bone char**

Bone char is derived from the crushed animal bones through the carbonization by heating over 500–700 °C in iron retort in the absence of air for 4–6 h. The composition of bone charcoal is calcium carbonate (7–9 wt%), carbon content (9–11 wt%) and calcium hydroxyapatite (CaHAP) (70–76 wt%) etc. The bone char is used for the removal of As(V) has been done as a function of pH, contact time and dosage of adsorbent [159]. The kinetics study resulted that the adsorbent of As(V) was rapid in the first 30 min however equilibrium time was not dependent of initial As(V) concentration. According to Fourier transform infrared (FTIR) spectra of bone char the Ca–OH functional group plays a key role for the adsorption of As(V) ion before and after adsorption. The mechanisms of the As(V) adsorption on bone char was complex where both ion exchange and co-precipitation mechanisms were followed. The arsenic removal was strongly dependent on pH and dosage of adsorbent this method is only applicable for the adsorption of As(V) ion [160].

**Banana Peel**

The waste of plant material is alternative to chemical method for the sorption of metal ions [161, 162]. There are number of reported methods for the removal of arsenic which are either costly or not easily available in Pakistan [163]. However, the banana peel has been used owing its low cost and easily available in our area. The banana peel was used for the adsorption of arsenic species from the ground water. The adsorption of arsenic species on banana peel was observed pH independent. Besides the advantages of this method its process gets slower with passage of time [164].

**Acid-washed crab shells (AWCS)**

During the last few years the advanced knowledge of biosorption relatively low costs, high adsorption capacities and regenerability of natural bio adsorbent materials [165, 166]. Some of them have the efficient capacities for the removal of arsenate as a biosorption [167,168]. However different challenges rising biosorbents with low cost and high uptake as well as sympathetic the bio adsorbent mechanism still remain. Current results proved that acid-washed crab shells (AWCS) have a capably for binding anionic metal species such as chromate cyanide, gold and vanadate [169]. Fourier transform infrared analysis (FTIR) is used for the study of the biosorption mechanism of arsenate. This method is strongly pH dependent and time consuming process [170].

**Synthetic adsorbents**

**Surfactant-modified zeolite**

Natural zeolites are synthesized from amino–silicate materials which are effective for the
exchange of cations [171], but having low capability towards anions, such as Arsenite. Unmodified clinoptilolite is a type of natural zeolite the which has also been reported and show the adsorption capacity up to 1.5 μg/g at equilibrium time was attain at 60 min as compare to modified clinoptilolite it is very low capacity of adsorption it is time consuming process [172].

The hexadecyltrimethyl ammonium bromide (HDTMA) adsorbent materials are used as the surfactant for the modification of fly ash based commercial zeolites [173-175]. These are called surfactant-modified zeolite (SMZ) adsorbents. The SMZ forms active sites for anions adsorption due to the presence of amino group [176]. This modification of natural zeolite has enhanced the capability of arsenite removal due to its chemical as well as surface charge modification. The SMZ is an adsorbent used for the removal of arsenate from aqueous media. Many researchers have reported that sulfate, selenite and hydrogen chromate is used for the adsorption of anion on SMZ [174,177,178]. The absorption of polyhexamethylene guanidine-chloride on zeolite for the removal of As (V) using SMZ. According to him the adsorption capacity was about 6 mg/g at a concentration of 1000 mg/L at equilibrium. The drawback of this method was that the effect of pH and temperature on adsorbing capacity has not been investigated systematically. This method only attributed to aqueous solutions and favors on specific temperature [179].

Iron containing high surface area compounds

The iron containing (Iron Oxides) are known efficient adsorbing material due to their economic value, efficiency and strong affinity for the removal of As [180]. The reported method was modified for the preparation of magnetite (an iron ore) [181], that has increased the adsorption capabilities of As(III & V) to 2237 and 26 times respectively [182,183]. The addition of FeCl₃ supplementary to raw material used in conventional method formed the amorphous structure and enhanced the surface area of compound. The dispersion of hydrated iron oxide particles which behave as colloidal solution in addition with Amberlite XAD-2 resin (macro porous ion exchange resins) activate the hybrid sorbent material and gives efficiency up to 90% removal of As(V) [184]. It was proved that iron oxide such as zero valent iron particles (modified and unmodified) are considered as pretty useful adsorbents [185-188]. The goethite nanoparticles (α-FeOOH) synthesized from hydrazine sulfate through a wet-chemical method is known as good adsorbent for arsenic. This study suggested that the dose of 6g/L α-FeOOH adsorbent is enough for the elimination of As (V) upto 99% from water with 50mg/L concentration of As (V) [188]. The mesoporous lepidocrocites (γ-FeOOH) heat treated adsorbent showed 94% removal efficiency for As (III) and >99% for As(V) as reported [189]. The ultrafine α-Fe₂O₃ nanoparticles are more efficient than γ-FeOOH because of their smaller size and high surface area, they are more capable for removal of As (III) from the aqueous media [190]. Besides these advantages, there are some drawbacks of iron oxides due to powdery form it is difficult to separate from treated water. So researchers are working on the modification of iron compounds in the regard of economic value and adsorbent capacity.

Magnetite

The magnetite is a form of iron oxide which is remarkable functional material in different fields like magnetic, catalyst, adsorption, and separation. It is efficient adsorbent for As(III) and As(V) [19], nowadays magnetites are developed by precipitation solvothermal and sol-gel hydrothermal methods [192,193]. Among these the precipitation method is preferred due to simple operation and cheap material. Conditions for this method can be set at desired purposes. The main drawback of this method is that the solution of magnetite can only be prepared in low dielectric solvent and/or aqueous [194].

Non-ferrous compounds and nano-clusters

The inorganic nanoparticles are 5 to 10 times more efficient then micro size particles due to their chemical characteristics, high surface to mass ratio, and surface reactivity [195]. Most recent studies showed that the aluminum nanoclusters are widely used for such applications
[196], it has been reported that the main constituent in the coagulant polyaluminium chloride (PACL) is aluminum nanoclusters which is used for the remediation of water. The aluminum nanoparticles have specific surface charge and contain large number of OH group due to their ability to deprotonate over a wide pH range. For the increase in adsorption efficiency PACL is added to arsenic contaminated water in granulated or powdery form in conventional method. This method relies at specific pH range. Co-precipitates with Al flocks above pH 7 lowers the efficiency for the adsorption of As(III) [196].

After complete review we have compile all the adsorbent reported for arsenic removal and their adsorption capacity in tabulated and graphical form. Table 2 and 3 represents the different adsorbents reported in literature for As(V) and As(III). The bar graphs showed in figure 1 and 2 represents the adsorption capacity of all adsorbents which are mention in Table 2 and 3 respectively.

![Bar Graph](image)

**Figure 1.** Adsorption capacity of different adsorbents reported for arsenic (V)

**Table 2.** Comparative evaluation among different adsorbents for Arsenic (V).

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<td>[164]</td>
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</table>

**Figure 2.** Adsorption capacity of different adsorbents reported for arsenic (III)
Table 3. Comparative evaluation among different adsorbents for Arsenic (III).

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<tbody>
<tr>
<td>1</td>
<td>Rice husk</td>
<td>8.00</td>
<td>Groundwater</td>
<td>[21, [72], 142]</td>
</tr>
<tr>
<td>2</td>
<td>cellulose sponge</td>
<td>4.5</td>
<td>Tap water</td>
<td>[127]</td>
</tr>
<tr>
<td>3</td>
<td>Rice Polish</td>
<td>7.00</td>
<td>Aqueous solution</td>
<td>[21]</td>
</tr>
<tr>
<td>4</td>
<td>Oyster shell</td>
<td>6.50</td>
<td>Groundwater</td>
<td>[127]</td>
</tr>
<tr>
<td>5</td>
<td>Copper-impregnated coconut husk carbon</td>
<td>6.50</td>
<td>Drinking Water</td>
<td>[129]</td>
</tr>
<tr>
<td>6</td>
<td>Sorghum biomass</td>
<td>5.00</td>
<td>Distill water</td>
<td>[76, 77]</td>
</tr>
<tr>
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<td>4.00</td>
<td>Tap water</td>
<td>[131]</td>
</tr>
<tr>
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<td>Allyl alcohol-treated chicken feathers</td>
<td>7.00</td>
<td>Synthetic water</td>
<td>[78]</td>
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<td>Natural siderite</td>
<td>7.31</td>
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<td>[82]</td>
</tr>
<tr>
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<td>7.00</td>
<td>Ground water</td>
<td>[83]</td>
</tr>
<tr>
<td>13</td>
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<td>7.00</td>
<td>Distill water</td>
<td>[24]</td>
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<td>Distill water</td>
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<td>[86]</td>
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<td>Drinking water</td>
<td>[132]</td>
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<tr>
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<td>10.00</td>
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<td>[181]</td>
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<tr>
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<tr>
<td>26</td>
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<tr>
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<td>Tap water</td>
<td>[92]</td>
</tr>
<tr>
<td>28</td>
<td>Fe₃O₄ nanoparticles</td>
<td>6.00</td>
<td>Drinking water</td>
<td>[95]</td>
</tr>
<tr>
<td>29</td>
<td>Magnetite nanoparticles</td>
<td>6.50</td>
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<td>[96]</td>
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<td>30</td>
<td>Fe₃O₄ nanoparticles</td>
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<td>Drinking water</td>
<td>[97]</td>
</tr>
<tr>
<td>31</td>
<td>Ceria nanoparticles</td>
<td>-</td>
<td>Drinking water</td>
<td>[98]</td>
</tr>
</tbody>
</table>

Advance materials as adsorbents for arsenic detoxification

Molecular imprinting technology (MIT)

Molecular Imprinting Technology (MIT) has been considered as viable technique to design and develop the molecular approach to recognize the material to able the mimic natural recognition entities, such as biological and antibodies receptors [197-205]. It is an important and dynamic area of research, molecular imprinting is one of the approach to produce materials with recognize the
ability as compare to the natural system. MIT is a versatile and up growing technique to use in both chemical and biological molecules such as proteins and amino acids [206-208], nucleotide derivatives [209], drugs and food [210, 211], pollutants [212, 213], separation, purification sciences [212, 214-219], catalysis [220], chemical sensors [221], drug delivery [222], biological antibodies and receptors system [206, 223, 224]. MIT is a simple technique, it is based on the complex between an analyte (template) and functional monomer in the presence of the cross-linking agent [225].

**Molecular imprinted polymers (MIPs)**

Imprinting polymers (IPs) are advanced state-of-art materials widely applied for the selective removal of molecule or ions characteristics to synthetic polymeric matrix. IPs are considered as an efficient system for the synthesis of promising materials are proficient to recognize targeted species [226, 227]. In typical procedure, at the first step the copolymerization occur between cross-linking and functional monomers during the imprinting process of targeted species. Initially the functional monomers form the complex with imprint species and then polymerization ensue. The functional monomers are fixed in polymeric matrix by cross linker. Successful removal of the imprinted specie left binding sites polymer network that is identical in shape and size to the targeted analyte. The targeted template design is then expert into the polymer network that enables it to rebound to analyte with more specificity and selectivity [228, 229]. For metal ions, the molecular imprint can be interpreted as ionic imprint. The functional monomer is allowed to self-assemble around molded ions in the ionic printing process, and followed by cross-linking as desired. The selectivity of the analyte is obtained with respect to the cavity polymers where the complexing ligands are organized so as to match the target ion size, charge, co-ordination geometry and coordination number [230]. The process activates ionic sites that are specific and specially targeted chemicals. Typically, the imprinting system is easily processed by bulk printing, where the imprinted polymers are prepared in large quantities and then post-processing method such as grinding and sieving are required. However, the creation of binding sites within the polymer volume and the issue of impeding the diffusion of adsorbate during template rejection limit imprinted polymers prepared for practical applications [231]. Thus, over the years, in new imprinting methodologies surface imprinting is one of the important imprinting methods. The polymer imprinted on the surface not only has high selectivity, but also avoids problems with mass transfer and shows a significant promise for industrial applications [232-239]. So far there are some polymers imprinted with metal ions, including U(VI) [233], Zr(IV) [234]. The imprinted polymers Ni(II)[235], Fe (III) [236] and Cd(II) [237-239] have been prepared by the surface imprinting technique causing the functional group to be immobilized on the surface of the silica gel for the selective separation of heavy metals from aqueous solution. However, few studies on the polymers printed with As (V) have been published. Recently, Chen et al., (2009) reported that 3-(2-aminoethylamino)propyltrimethoxysilane (AAPTS) has been modified As (V). The study shows that As (V) can be adsorbed by the modified mesoporous silica sorbet modified AAPTS by electrostatic effect because the compounds of As(III) are neutral in As the compounds of As(V) are negatively charged in the pH range 3-9 [240] whereas previous investigations show that AAPTS can be complexed with other heavy metal ions (such as Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)) by coordination bond. [241].

**Conclusion**

It is concluded from the detailed review of literature that water contamination due to arsenic, it is a major problem worldwide. The adsorption of arsenic from aqueous solution plays an important role in controlling water pollution. There is great interest in the use of low-cost adsorbents. But review of the literature, many researchers has tried to exploit natural materials as low-cost adsorbents for arsenic removal. The arsenic adsorption capacity of a low cost adsorption technology offered vary depending on the characteristics of the individual adsorbent, arsenic, pH, temperature and contact time. Adsorption technology, using natural materials and
agricultural waste either in natural form or modified form is highly effective for the removal of arsenic from aqueous solutions and offers a cost-effective alternative compared to traditional chemical and physical remediation and cleaning techniques. The interest is increasing to develop the knowledge about the polymers Metrix and the interaction of the template is very challenging process it could be employed in different industries such waste water treatment, drinking water treatment, drug delivery, biosensors and recycling of the different rare metals.

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References


https://nepis.epa.gov/Exe/ZyNET.exe/9100A OMS.TXT?ZyActionD16/i425

https://doi.org/10.1016/j.apgeochem.2007.01.004

doi:10.1017/S0022029904000640


doi:10.1016/S0048-9697(03)00056-1

doi:10.1002/cjen.201200466

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3184456/


doi:10.1016/j.chemosphere.2010.05.040

http://dx.doi.org/10.1080/02508060.2010.506275

doi:10.1126/science.1072375·Source: PubMed

doi:10.1021/st278-6915(99)00130-1

doi:10.1012/acs.estlett.6b00430


file:///C:/Users/Raqeeb%20Raja/Downloads/minerals-07-00099.pdf

http://dx.doi.org/10.1177/09603271830020110

doi:10.1144/geochem.1.1.23

doi:10.3390/w3010001

doi: 10.1016/0269-7491(94)00092-R

doi: 10.1012/es051271i

doi:10.1289/ehp.1509974


https://doi.org/10.1021/cr990099w

https://doi.org/10.1016/j.aca.2006.06.065

https://doi.org/10.1007/s00216-007-1362-4

https://doi.org/10.1021/ac070968e

doi: 10.1007/s00604-007-0870-4

https://doi.org/10.1016/j.aca.2006.06.049

https://doi.org/10.1016/j.talanta.2006.03.012

https://doi.org/10.1016/j.desal.2009.09.139

https://doi.org/10.1021/ac048570v

https://doi.org/10.1021/ac0347718

https://doi.org/10.1016/j.jhazmat.2008.09.022

doi:10.1023/A:1020799616387

https://doi.org/10.1016/S0927-7757(03)00138-9

https://doi.org/10.1016/j.jhazmat.2008.06.00

https://doi.org/10.1080/19443994.2012.734675

https://doi.org/10.1016/j.jenvman.2015.07.020