

# Arsenic removal from water through adsorption-A Review

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## Abstract

Arsenic is a commonly occurring toxic metal in natural systems. It is a human carcinogen in water over a wide range of pH values, having harmful effects on both human health and environment, even at low concentration. Because of this effect, the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) set the arsenic standard for drinking water at 0.10 ppm to protect consumers served by public water systems. Occurrence of arsenic contaminated water is reported in several countries like USA, China, Bangladesh, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. The largest population at risk is in Bangladesh followed by India (West Bengal). There is no effective treatment for arsenic toxicity. Only the removal of arsenic from water can prevent the toxicity. A great deal of research over recent decades has been done to lower the concentration of arsenic in drinking water and still there is a need to develop low cost viable techniques. Existing major arsenic removal technologies include oxidation, adsorption, precipitation, coagulation and membrane separation. This paper presents the review of current status of research in the area of arsenic removal from contaminated water and comparison of all technologies available with more emphasis on adsorption.

**Keywords:** Arsenic, sorption, Adsorption, oxidation, precipitation technologies, Coagulation, electro-coagulation, co-precipitation,  $Fe_3O_4$ .

## INTRODUCTION

Arsenic 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 vapour pressure 1mm Hg at 372 °C. In almost all mining areas, hundreds of years of mining activities for gold, silver and metallic sulfide minerals left a considerable quantity of tailings, some of which have a high arsenic content. Owing to rain, wind and other natural effects, the arsenic dispersed into the nearest water courses or agricultural fields in the forms of arsenate ion ( $As(V)$ ) and arsenite ion ( $As(III)$ ), leading to a high arsenic concentration in the water courses around the mines. However, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts. Arsenic exists in the -3, 0, +3 and +5 oxidation states. Environmental forms include arsenious acids, arsenic acids, arsenites, arsenates, methyl arsenic acid, dimethyl arsenic acid, arsine, etc. Arsenic(III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, Arsenic(V) behaves like a soft acid, forming complexes with sulfides. Inorganic forms of arsenic most often exist in water supplies [4]. Occurrence of arsenic in groundwater above the permissible value ( $>10 \mu g/L$  WHO) is one of the wide spread problem owing to its toxicity and carcinogenicity. The third world countries such as India, Bangladesh, etc., that comprise the southern portion of Asian sub-continent are worst affected because the rural population of those areas are yet to

consume the groundwater as drinking water.

Countries affected by arsenic contamination and maximum with permissible limits for drinking water [5]

Country	Maximum permissible limits ( $\mu g/L$ )
Argentina	50
Bangladesh	50
China	50
Chile	50
India	10
Mexico	50
Nepal	50
New Zealand	10
Taiwan	10
USA	10
Vietnam	10

## Effect of Arsenic in India

In a survey it was found that, the maximum concentration of it is 0.05 ppm. Generally, West Bengal and Ganga basin regions are highly affected. In Bengal, Bihar and UP this contamination is known to have affected a population of about 50 million and an equal number in Bangladesh.

Arsenic in ground water have been reported in a range of 0.05-3.2 mg/l in shallow aquifers from 61 blocks in 8 districts of West Bengal namely Malda, Muzshirbad, Nadia, North and South 24 Pargana, Bardhaman, Howrah, and Hugli. In other countries where the population has had long-term exposure to arsenic in groundwater studies indicate that 1 in 10 people who drink water containing 500 mg/L of arsenic may ultimately die from cancers caused by arsenic, including lung, bladder and skin cancers.

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Table-1 Chemical composition of the high-arsenic water sample (Concentration in mg/l) [3]

Ca	SO <sup>2-</sup> 4	Mg	Na	K	Fe	Mn	As	Cl <sup>-</sup>	NO <sup>3-</sup>	HCO <sup>-</sup>	PO <sup>3-</sup> 4
566	1340	77	37	8.9	0.11	0.01	5.07	142	0.25	185	40.8

Table-2 Some properties of the high-arsenic water sample [3]

pH	Dissolved organic Carbon (mg/l)	Dissolved organic materials (mg/l)
7.62	60.5	121

Table 3. Main arsenic removal technologies [5]

Methods	Advantages	Disadvantages
<b>Major oxidation/precipitation technologies</b>		
• Air oxidation	Relatively simple, low-cost but slow process; <i>in situ</i> arsenic removal; also oxidizes other inorganic and organic constituents in water.	Mainly removes arsenic(V) and accelerate the oxidation process.
• Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass.	Efficient control of the pH and oxidation step is needed
<b>Coagulation/electro- coagulation/co precipitation:</b>		
• Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; effective over a wide range of pH.	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required.
• Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weight basis.	Medium removal of As(III); Sedimentation and filtration needed.
• Lime softening	Chemicals are available commercially.	Readjustment of pH is required.
<b>Major sorption and ion-exchange technologies</b>		
<b>Adsorption</b>		
• Activated alumina/carbon	Relatively well known and commercially available.	Needs replacement after 4 to 5 regeneration.
• Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V).	Not standardized; produces toxic solid waste.
• Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic.	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; life of resins
<b>Major membrane technologies</b>		
• Nano-filtration	Well-defined and high-removal efficiency.	Very high-capital and running cost, pre-conditioning; high water rejection.
• Reverse osmosis	No toxic solid waste is produced.	High tech operation and maintenance.
• Electro-dialysis	Capable of removal of other contaminants.	Toxic wastewater produced.

Although all the above technologies have been utilised by different researchers but it is felt that adsorption is an effective and low cost method of treatment for arsenic removal.

**Adsorption**

In water treatment, adsorption has been proved as an efficient removal technique for a multiplicity of solutes. Here, molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces which are characterized by active, energy-rich sites that are able to interact with solutes in the adjacent aqueous phase due to their specific electronic and spatial properties. Typically, the surface is energetically heterogeneous

**Some absorbents and methods used for arsenic removal in different studies are as under**

**Activated carbons**

Activated carbon is a highly porous, crude form of graphite having structure with broad range of pore sizes. Active carbons are prepared from petroleum coke, coconut shells, wood char, bone-char, rice hulls, sugar, fertilizer waste, sawdust, carbon black, waste rubber tire, etc. They are produced by carbonization below 600°C. They are activated by treatment with oxidizing agents like steam, carbon dioxide, or oxygen at elevated temperature or with chemical activators like ZnCl<sub>2</sub>, H<sub>2</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>S, etc. Activated carbons have been extensively used for As(III) and As(V) adsorption from water [5]. Some activated carbons impregnated with metallic silver and copper have also been used for arsenic removal.

**Ferrihydrite/granular ferric hydroxide**

Ferrihydrite has been found to consist of nano size crystals, formerly ascribed the formula Fe<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O. The particle size of ferrihydrite (5 nm) gives it a large surface area (200-500 m<sup>2</sup>/g), ideal for adsorbing a range of either anions or cations from aqueous solutions.

**Arsenic adsorption on iron oxides (magnetite/haematite)**

It is known as Iron (II, III) Oxide or Ferrous-Ferric Oxide. It has the formula FeO.Fe<sub>2</sub>O<sub>3</sub> but it is generally known as Fe<sub>3</sub>O<sub>4</sub>. It is formed by chemical combination of Iron (II) Oxide with Iron (III) Oxide. It has a special property different from the other 2 oxides, as it exhibits magnetism. It exists naturally in the Earth in form of Magnetite (or Lodestone) mineral.

As a sorbent its magnetite powder efficiently removes arsenic (III) and arsenic (V) from water, the efficiency of which increases ~200 times when the magnetite particle size decreases from 300 to 12 nm particle which is more than expected from simple considerations of surface area. These magnetic particles are gaining importance as these can be used as effective adsorbents with an additional advantage of easy magnetic separation of the loaded adsorbent. Chowdhury and Yanful (2010) reported arsenic and chromium adsorption on a commercial grade nano-size magnetite from different water samples including a ground water sample. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were added into 25 mL of As(III & V) solution different concentration (mg/L), and shaken for 3-5 h at room temperature. After shaking, the mixtures were placed under an

external magnetic field and Fe<sub>3</sub>O<sub>4</sub> sample was separated from solution.

### Magnetic separations

Magnetic separations are performed with a magnetic field column separator consisting of a stainless steel column which is packed with stainless steel wool (about 80µm wire diameter), with a packing volume of (50g stainless-steel wool). A magnetic field is applied, and then a sample is passed through the column. The particles are retained in the column as the solvent passed through.

### Arsenic adsorption on akaganéite

A few studies have been reported related to arsenic (V) adsorption on akaganéite (Deliyanni et al., 2003) Synthesized akaganéite was used in two forms, i.e., in fine powder (of crystals) and in the form of grains (as granular). Granular akaganéite was less effective when compared to the fine powder. Guo et al. (2007) prepared a new adsorbent by loading iron oxyhydroxide (b-FeOOH) on bead cellulose. To get an insight into the mechanism of the adsorption process, the extended X-ray absorption fine structure spectra of arsenite and arsenate adsorbed onto the adsorbent with different surface coverages were taken. Both arsenite and arsenate were strongly and specifically adsorbed by akaganéite [13]. Both arsenite and arsenate were strongly adsorbed by akaganéite by an inner-sphere mechanism.

### Aluminium-based adsorbents

Adsorbents based on aluminium include activated alumina, gibbsite (mineral Al(OH)<sub>3</sub>), aluminium hydroxide precipitated from aluminium salts, and layered double hydroxides. Pigna et al. (2006) followed the kinetics of adsorption-desorption of various iron/aluminium oxides/hydroxides and reported that the order of rates of adsorption of arsenic(V) was ferrihydrite > goethite > non-crystalline Al(OH)<sub>x</sub> > gibbsite. Iron hydroxide has better selectivity towards arsenic(V) in the presence of other anions (especially phosphate) than aluminium hydroxide (Jeong et al., 2007). Arsenic (V) has long been known to be strongly adsorbed by aluminium hydroxides. Gregor (2001) tracked arsenic (V) and arsenic (III) through a conventional drinking-water treatment plant based on alum and a synthetic flocculent aid. Arsenic (III) was passed through the system until a final chlorination step in which it was converted into arsenic (V) and adsorbed.

### Iron Oxide Mixed with Calcinated Laterite [15]

Iron oxide (Fe<sub>3</sub>O<sub>4</sub>) particles were synthesized by novel ageing process. Then calcination of laterite was carried at 400°C for 4 hours. The laterite was crushed and sieved to obtain powder laterite with a particle size of less than 75µm and washed with deionized water. In the final step, prepared nano-dimensional particles were mixed with denatured laterite in a grinder for about ten minutes to create new high performance adsorption materials. The mixing ratio of these two materials was 1:1 ratio. 50 ml of arsenic contaminated water was taken into a beaker and different adsorbent dosage were added for different batches on the magnetic stirrer. The adsorption process parameters were 0.03g, 0.05g, 0.07g adsorbent dosage and 20min, 40min, 60min, and 80 min adsorption time for the initial

arsenic concentration about 0.3ppm. Testing with 0.05g dosage for initial arsenic concentration 0.03ppm was also examined.

### Red mud[13]

Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. Bayer process plant generate about 1–2 tonnes of red mud per ton of alumina produced [5]. Red mud is only about 25% iron oxide and contains similar amounts of alumina and silica along with smaller amounts of natural components such as titanium oxide, and soluble components. The As (III) adsorption was exothermic, whereas As (V) adsorption was endothermic.

### Ferric and manganese binary oxides (FMBO)[6]

FMBO are prepared through the reaction between KMnO<sub>4</sub> and FeSO<sub>4</sub>. Hydrated manganese oxide (HMO) is obtained from the reaction between equivalent amount of KMnO<sub>4</sub> and MnSO<sub>4</sub>. Hydrated ferric precipitate (HFO) is formed after FeCl<sub>3</sub> hydrolyzation. Batch experiments were conducted in capped flasks with continuous rotary shaking (125 r/min) at 20±1 °C for 60 min. The UF membrane filter was prepared with natural manganese ores. Samples were filtered through 0.20-µm membrane filters before analysing the arsenic concentrations.

### Graphene oxide (GO)[7]

Graphene oxide is synthesized from natural graphite (crystalline) which removes arsenic to a larger extent. Graphite and NaNO<sub>3</sub> are mixed with H<sub>2</sub>SO<sub>4</sub> in a flask. The mixture is stirred in ice bath. While maintaining vigorous stirring, potassium permanganate is added. The rate of addition is carefully controlled to keep the reaction temperature lower. The ice bath is then removed and the mixture is stirred at room temperature overnight. As the reaction progresses, the mixture gradually becomes pasty and the colour is turned into light brownish. At the end, H<sub>2</sub>O is slowly added to the paste with vigorous agitation. The reaction temperature is rapidly increased with effervescence, and the colour changed into yellow. The diluted suspension is stirred and H<sub>2</sub>O<sub>2</sub> is added to the mixture after purification, filtration and drying under vacuum GO is obtained as grey powder.

### Nanostructured iron (III)–cerium (IV) mixed oxide (NICMO)[8]

It is synthesized by mixing (with vigorous stirring) equal volumes of 0.1 M ammonium cerium(IV) nitrate solution (ACN) in 0.1 M HCl and 0.1 M ferric chloride solutions in 0.1 M HCl. 5 M NaOH solution is also added drop wise with continuous stirring to raise pH to 9.3 (±0.3). The gel-like precipitate that appears subsequently is allowed to stand for two days with the mother liquid without disturbing. Decanting off the mother liquid from the solid mass, the gel-like precipitate is washed three times with distilled water and dried at 100 (±2)°C in an air oven. The dried product is treated with distilled water and carefully grounded using mortar and pestle followed by sieving to separate the agglomerates having dimension in the range 140–290 nm. The agglomerates are homogenized at pH 7.0 before its further use in the experiments. For estimating the drying temperature effect on NICMO, the material was calcined for 1 h separately at 100°C, 150°C, 200°C, 250°C, 300°C, 350°C, 400°C

and 500°C. Batch adsorption experiments were conducted by mechanical agitation. Here, 0.1 g of NICMO was mixed with 50 ml of As(III) or As(V) solution ( $C_0$ ,  $\text{mg l}^{-1}$ ) into 250 ml polythene vials and capped properly. The reaction mixture was agitated (speed:  $300 \pm 10$  rpm) using a thermo-stated shaker at an adjusted temperature. The desired pH of the test solutions was adjusted using 0.1 M HCl and/or 0.1 M NaOH as required.

#### Ascorbic acid-coated $\text{Fe}_3\text{O}_4$ nanoparticles [9]

1 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is dissolved in 40 ml distilled water under vigorous magnetic stirring to form a clear solution, followed by the addition of 3 mmol of ascorbic acid and 5 ml of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (50% v/v). Then the solution is transferred into Teflon-lined stainless steel autoclave, heated at 180 °C for 8 h, and then cooled to room temperature naturally. The precipitate is collected by centrifugation and washed with deionized water and absolute ethanol several times and dried under vacuum at 60 °C for 6 h.  $\text{NaAsO}_2$  and  $\text{NaAsO}_4 \cdot 12\text{H}_2\text{O}$  were used as the sources of As (III) and As (V), respectively, and the pH values of the solution were adjusted using NaOH or HCl. Ascorbic acid-coated  $\text{Fe}_3\text{O}_4$  nanoparticles were added into 25 mL of As(III) solution (0.10 mg/L), sealed and shaken for 24 h with 60 rpm at room temperature. After shaking, the mixtures were placed under an external magnetic field and  $\text{Fe}_3\text{O}_4$  sample was separated from solution. Arsenic concentration in the supernatant solution was measured, by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The adsorption capacity was roughly estimated by following formula:

$$q_e = (C_0 - C)V/W$$

where  $q_e$  (mg/g) is the adsorption capacity,  $C_0$  (mg/L) is the initial concentration of the arsenic solution,  $C$  (mg/L) is the equilibrium concentration of arsenic ions,  $V$  (L) is the initial volume of the arsenic solution, and  $W$  (g) is the weight of the adsorbent.

#### Aluminum-coated pumice (ACP) [10]

Prior to the coating of alum on the surface of the pumice stone, it is crushed, treated with HCl, washed and dried. In order to coat the particles with alum, a solution of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  is prepared. Afterwards, pumice particles with alum solution are taken in a beaker and pH is adjusted by adding NaOH solution drop by drop while stirring for few min. Thereafter, the beaker is placed in a static and stable state at laboratory temperature ( $25 \pm 1^\circ\text{C}$ ) for 72 h, and is dried at 110°C in the oven for 14 h. All experiments were conducted in batch mode and in a series of 250 mL conical flasks. Parameters studied were pH (3-11), adsorbent doses (2.5- 60g/L) and initial As (V) concentrations (50  $\mu\text{g/L}$ , 250  $\mu\text{g/L}$  and 2000  $\mu\text{g/L}$ ) as well as contact time (0-200 min).

The conical flasks containing As (V) solution and the various doses of adsorbent were mixed by orbital shaker at 200 rpm in constant temperature ( $25 \pm 1^\circ\text{C}$ ). At the end of the adsorption process, the samples were filtered through 0.45  $\mu\text{m}$  membrane filter, centrifuged at 3000 rpm and analyzed by atomic adsorption spectrophotometer.

#### Fe(III)/Cr(III) hydroxide waste

Chromium (VI) compounds are used as corrosion inhibitors in

cooling water systems in industries. Fe(II), generated electrolytic ally, reduces chromium(VI) in the wastewater to Cr(III) under acidic conditions. The Fe(III)/Cr(III) ions produced in solution are precipitated as Fe(III)/Cr(III) hydroxide by the use of lime. The resultant sludge is discarded as waste. Namasivayam and Senthilkumar [11] adsorbed As(V) from water onto a Fe(III)/Cr(III). As(V) concentration, agitation time, adsorbent dosage, adsorbent particle size, temperature and pH were studied.

#### Iron oxide hydroxide [16]

Hydrated ferric sulphate [ $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  ( $x = 5$ )] is taken in a beaker and dissolved in double distilled water. The beaker is placed on a magnetic stirrer and the solution is heated till the temperature of the same is attained 60°C. The solution is allowed to stir at 60°C for 30 min, and then 250 ml of 5.0(M) urea solution is added drop wise to the solution in the beaker within 3.5 h. During addition of urea to the solution, temperature is maintained at 70 °C for complete reaction. After complete addition of urea, the solution temperature is increased to 80°C and maintained till the volume of the solution is reduced to the half of the initial volume. Brown precipitate is formed after cooling the solution at room temperature (25°C). The precipitate is washed repeatedly to remove the alkalinity of the solution and finally oven dried at 70°C for 4 h to obtain brown powder.

Standard arsenic (III) stock solution of 1000 mg  $\text{L}^{-1}$  was prepared by dissolving 1.32 g of arsenic (III) oxide with distilled water. 100 ml of different concentration of arsenic(III) standard solution was taken in 250 ml conical flask and known weight of adsorbent material was added into it. The contents in the flask were shaken for 3 h on a mechanical shaker. The solution was centrifuged and the mother liquor was analysed for residual arsenic concentration by Atomic Absorption Spectrophotometer. All adsorption experiments were conducted at room temperature (25 °C). Batch adsorption experiments were conducted to investigate the effect of various parameters like adsorbent dose, initial concentration, presence of interfering ions, pH, etc. The effect of solution pH on arsenic removal was studied by adjusting the pH of the solution either by using 0.1 N HCl or 0.1 N NaOH in acidic as well as basic pH. After adsorption the solid was separated by filtration and dried in air. The dried adsorbent was repeatedly subjected to the arsenic removal/adsorption experiments in order to examine the extent of reusability.

#### $\text{Fe}_3\text{O}_4$ nanoparticle-coated boron nitride nanotubes (BNNTs) [17]

Pure BNNTs are synthesized at a high yield with boron and metal oxides. A mixture of MgO, SnO, and boron powder is used as the precursor and  $\text{NH}_3$  is used as the nitrogen source. Annealing at 1900 °C in an  $\text{N}_2$  atmosphere is performed in order to remove the possible impurities in the BNNTs. The purified samples typically contain nanotubes.  $\text{Fe}_3\text{O}_4$  /BNNT nano-composites are obtained. All batch tests were executed in 50 mL of polyethylene centrifuge tubes by taking 50 mg of  $\text{Fe}_3\text{O}_4$ /BNNT nano composites. In order to properly evaluate the arsenic adsorption under conditions suitable for practical applications, batch sorption experiments were conducted at neutral pH (6.9) and room temperature (25 °C). The adsorption proceeded for 24 h in a water thermostat. Samples were taken at certain intervals and filtered through a 0.45  $\mu\text{m}$  membrane filter to measure the residual As(V) concentration by ICP-AES. Isotherm experiments were performed in arsenic solutions with various initial concentrations (1, 5, 10, 20, 30, and 40 mg/L) and pH varied from 1

to13, to determine the equilibrium capacity and adsorption intensity.

#### Activated alumina: S. Kuriakose (2004)

Activated alumina (AA) is prepared by thermal dehydration of aluminium hydroxide, has a high surface area. Arsenic (V) sorption occurs best mostly between pH 6.0 and 8.0 where AA surfaces are positively charged. As (III) adsorption is strongly pH dependent and it exhibits a high affinity towards AA at pH 7.6 . More than 85% of the adsorbed arsenic desorbed in less than 1 h using 0.05M NaOH.

#### Fly ash

Coal combustion produces a huge amount of by-product fly ash, whose disposal requires large quantities of land and water. Resource recovery from coal fly ash is one of the most important issues in waste management worldwide. Since the major chemical compounds contained in fly ash are alumina silicate, intensive efforts have been recently made to utilize this material as an adsorbent. Fly ash obtained from coal power stations was examined for As(V) removal from water and to restrict As(V) migration in the solid wastes or the soil [5]. Removal at pH 4 was significantly higher than that at pH 7 or 10.

#### Oxidation of arsenic (III) to arsenic (V)[13]

Arsenic (V) is generally the main arsenic species in oxygen-rich surface waters and arsenic (III) usually predominates in groundwater. Arsenic (III) is usually more difficult to adsorb and it desorbs more readily than arsenic (V). Further, arsenite remaining at trace levels after treatment is more toxic than arsenate, therefore, steps are commonly taken to oxidise arsenic (III) before or during adsorption. Apart from the oxidation that occurs naturally by aeration, approaches to oxidize arsenic (III) include use of iron, hydrogen peroxide, chlorine, hypochlorite, and manganese.

#### Oxidation by iron

Many oxidation procedures are based on the use of iron (0), iron (II) and iron (VI). When the arsenic (III) and the iron (0) and/or (II) are oxidised, the iron (III) hydroxide formed serves as an adsorbent for the contaminating arsenic species. Contact with iron (0) brings about oxidation of arsenic (III) through rapid oxidation of iron on surface to release iron (II) which catalyses oxidation by hydrogen peroxide. Iron (II) catalyses the oxidation of arsenic (III) by hydrogen peroxide to give arsenic (V) for adsorption.

#### Oxidation by manganese (IV) and manganese (VII)

Manganese (IV) and manganese (VII), often in conjunction with iron, have been used to oxidise arsenic (III) either in preparation for adsorption or coincident with it.

#### Oxidation by chlorine and hypochlorite

Chlorine, including available chlorine as hypochlorite, has lost favour as an oxidant for remediation of drinking water as the products of the reaction of chlorine with organic contaminants have been found to be carcinogenic or otherwise toxic.

#### Application of Arsenic

It's better to use the removed Arsenic rather than disposing it off because it's disposal may create other environmental issues so it can be extracted back to take in further use in various fields like

**Agriculture-** Roxarsone – For nutritional supplements for chickens. Mono-sodium methyl arsenate and disodium methyl arsenate are used as insecticides.

**Medical Use-** Arsphenamine is used to treat syphilis and arsenic trioxides – for treatment of cancer.

**Alloys-** Alloying with lead (used in car batteries) to reduce dezincification by adding arsenic. Gallium arsenide is used as semiconductor material (LASER diodes).

**Military-** Lewisite ( $\text{ClCH}=\text{CHAsCl}_2$ ) is used as chemical weapon.

**Other Uses** – Copper aceto-arsenite is used as a green pigment (colouring agent) in sweets. For bronzing: Up to 2% of arsenic is used for manufacture of bullets and shots. Also used in optical glass and glass manufacturing.

#### Arsenic desorption/sorbent regeneration

Once the sorbent becomes exhausted, the metals must be recovered and the sorbent regenerated. Desorption and sorbent regeneration is a critical consideration and contributor to process costs and metal(s) recovery in a concentrated form. A successful desorption process must restore the sorbent close to its initial properties for effective reuse. Desorption can be improved by gaining insight into the metal sorption mechanism. In most of the arsenic sorption studies discussed earlier, desorption/regeneration was not discussed. Very few desorption studies were found in literature. Furthermore, once arsenic is recovered in the concentrated form, the problem of how to dispose of this concentrated arsenic product must be addressed. This is a difficult task. Few attempts have been made in the literature to address the handling of concentrated arsenic wastes. Various disposal options and their advantages and disadvantages were reviewed by Leist et al. [12]. The methods frequently used for other metals and organics include combustion or recovery and purification for resale. These options are not feasible for arsenic due to the following reasons Leist et al. [12]

1. Incineration is not practically feasible because arsenic oxides are volatile and can easily escape.
2. Recovery and purification of arsenic is not cost effective because arsenic has limited markets.

One attractive option for treating arsenic concentrates is encapsulation through solidification/stabilization followed by disposal of treated wastes in secure landfills. Solidification/stabilization transforms potentially hazardous liquid/solid wastes into less hazardous or non-hazardous solids before entombing these solids in secure landfills. Few researchers have studied the arsenic desorption to regenerate the exhausted sorbent. Desorption has been achieved using several eluents. Sodium hydroxide and strong acids are most

commonly used to elute both tri- and penta-valent arsenic. Selection of eluent depends on the arsenic adsorption mechanism and nature of the adsorbent.

A few representative desorption/regeneration studies are discussed below

As(V) desorption from aluminium loaded Shirasu-zeolite was successfully achieved with 40 mM NaOH solution. This adsorbent was reused after regeneration. Bead cellulose loaded with iron oxyhydroxide was regenerated when elution is carried out with 2 M NaOH solution. The adsorbent was used through four cycles. Hydrated Fe(III) oxide (HFO) dispersed on a polymeric exchanger capable of removing As(III) and As(V) was regenerated using 10% NaOH [14].

## RESULTS AND DISCUSSIONS

**Activated charcoal** adsorbed 2.5 wt.% As(V) and 1.2 wt.% As(III) (based on the weight of carbon) at an equilibrium concentration. Three activated carbons with different ash contents were studied for As adsorption: coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5–6% ash. More As(V) was removed from water using carbon with a high ash content. Carbon pre-treatment with Cu (II) improved arsenic removal capacity. The optimum pH for arsenic adsorption by Cu-pre-treated carbon was ~6. Arsenic formed insoluble metal arsenates with the impregnated copper. Arsenic is also simultaneously adsorbed by carbon independently. Arsenic was desorbed using strongly acidic or alkaline solutions. Arsenic was adsorbed onto activated carbon impregnated with metallic silver and copper. A combination of granular activated carbon and carbon steel wool removed arsenic from water. The adsorption ability of the steel wool was due to iron–arsenic electrochemical reactions [5].

**Granular ferric hydroxide (GFH)**, a typical porous iron adsorbent, is commercially available and frequently considered in evaluation of arsenic removal methods. GFH which is a combination of ferric hydroxide and poorly crystalline goethite is a highly porous adsorbent. [13].

**Iron oxides (magnetite/haematite):** the maximum arsenic adsorption occurred at pH 2 with values of 3.69 mg/g for arsenic (III) and 3.71 mg/g for arsenic (V) when the initial concentration was kept at 1.5 mg/L for both arsenic species. The results also showed the limitation of arsenic and chromium uptake by the nano-size magnetite-maghemite mixture in the presence of a competing anion such as phosphate. In natural groundwater containing more than 5 mg/L phosphate and 1.13 mg/L of arsenic, less than 60% arsenic uptake was achieved. It was anticipated that an optimum design with magnetite-maghemite particles may achieve high arsenic uptake in field applications. Recently Wang *et al.* (2010) showed that dissolved arsenic could be brought to well below the EPA maximum recommended concentration by simple filtration through a bed of iron (III) oxide coated on glass fibre. This was shown to be true whether the arsenic was present as arsenic (V) or as arsenic (III), and a pre-oxidation step was not required.

**Aluminium-based adsorbents:** arsenic (III) is considerably less readily adsorbed. Maximum adsorption of arsenic (V), on amorphous aluminium hydroxide, occurs at approximately 4–4.5 pH. Iron hydroxide is usually considered to be a superior arsenic adsorbent

when compared to aluminium hydroxide, but iron (III) hydroxide can release arsenic if its environment causes it to be reduced to soluble iron (II) hydroxide.

**Iron Oxide particles Mixed with Calcinated Laterite [15]:** Iron oxide ( $\text{Fe}_3\text{O}_4$ ) particles are prepared by novel ageing process with various parameters for examining which process can produce the smaller particle size. The changing of heating time is more important to the process. The arsenic removal efficiency of pure laterite is over 57% when used in small amounts. In the same condition, like laterite, Iron oxide ( $\text{Fe}_3\text{O}_4$ ) particles can remove about 61% toxic arsenic from aqueous solution. However the removal efficiency of the mixed adsorbent is 75% (at 0.3 ppm initial concentration) or 95% (at 0.03 ppm initial concentration). Because both laterite and iron were very effective materials for arsenic removal; the combination of these two materials is the best for arsenic removal.

**Red mud:** An alkaline aqueous medium (pH 9.5) favoured As (III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal. The capacities were  $4.31 \mu\text{mol g}^{-1}$  at the pH of 9.5 for As(III) and  $5.07 \mu\text{mol g}^{-1}$  at the pH of 3.2 for As(V). Heat and acid treatments on red mud increased its adsorptive capacity. Arsenic adsorption on acid and heat-treated red mud is also pH-dependent, with an optimum range of 5.8–7.5 for As(III) and 1.8–3.5 for As(V) [H.S. Altundogan 2002].

**FMBO** contributed to 98.8% of arsenic removal at a low dosage (4.6 mg/L). Comparatively, HMO (25 mg/L) and HFO (11.5 mg/L) resulted in lower arsenic removal as 69.3% and 75.4%, respectively. HMO exhibited the lowest adsorbing capability for arsenic among these three adsorbents.

**Graphene oxide (GO):** The weight ratio of iron to GO was increased stepwise in order to find the most efficient adsorbent. Because of the high adsorption capacity of the adsorbents, relatively high concentration of arsenate at 19.32 ppm, 39.73 ppm and 51.14 ppm had to be used to compare the relative efficiency of the different materials. Arsenate contaminated drinking water was prepared by dissolving  $\text{KH}_2\text{AsO}_4$  into DI water. All the tests were undertaken at room temperature (25 °C) with absorption time of 24 h. The percentage removal of arsenate increased with the amount of iron complex impregnated while fixing the starting arsenate concentration at 19.32 ppm. 100% removal of arsenate from the contaminated solutions was achieved by using GO–Fe-4 and GO–Fe-5 as adsorbent. Even GO–Fe-1 was able to absorb 80.4% of arsenate from the solution.

**Superparamagnetic high-surface-area  $\text{Fe}_3\text{O}_4$ :** The acidic pH range of 2–7, both arsenic(III) and arsenic(V) adsorption by the ascorbic acid-coated  $\text{Fe}_3\text{O}_4$  nanoparticles are not significantly affected by pH value, and the removal percentage of arsenic(III) and arsenic(V) basically remains constant at 45%. But when pH is adjusted to higher than 7, the removal percentage of arsenic (III) and arsenic (V) drops sharply less than 15%, which is similar to the result of arsenic removal by mixed magnetite-maghemite. The percentage of the removal increases markedly from 12.5% to 97.5% by increasing the concentration of the ascorbic acid-coated  $\text{Fe}_3\text{O}_4$  adsorbent from 5.67 to 200.13 mg/L.

**Aluminium-coated pumice: (ACP)** was an effective and

inexpensive adsorbent for As (V) removal; more than 98% of As (V) at an initial concentration of 250 µg/L was adsorbed by 10 g/L of it after 160 min contact time. The maximum ACP As (V) adsorption efficiency was obtained at pH = 7. One of the remarkable features of this adsorbent is that it performs very well in the pH range of the natural drinking water. The adsorption data of the adsorbent can be best fitted by Freundlich isotherm model which demonstrates the heterogeneous sites on the adsorbent surface.

**Iron oxide hydroxide:** The effect of pH on the efficiency of sorbent was studied at different pH from 2 to 11 keeping other parameters constant. The arsenic removal was found more than 95% at pH 7–8, whereas it was less than 85% at acidic pH. This result clearly showed that removal percentage of arsenic was slightly higher in basic pH compared to acidic one. Adsorption became slow and almost reached to equilibrium within 180 min. With further increase in contact time up to 9 h, no appreciable removal of arsenic takes place, indicating that complete adsorption occurred within 3 h.

**Fe<sub>3</sub>O<sub>4</sub> nanoparticle-coated boron nitride nanotubes (BNNT):** The experimental results showed a similar increasing trend in As (V) removal efficiency with the increasing surface area of BNNT, which indicated that using Fe<sub>3</sub>O<sub>4</sub> dose enhances the arsenic adsorption capability. Considering the advantages of lower cost and using fewer chemical reagents, for all further batch experiments, the BNNT was used. Arsenic adsorption was dependent on the initial solution pH. The optimal value for arsenic uptakes was recorded at pH 9, with a removal capacity of 0.96 mg/g. The removal ability slightly fluctuated in a pH range from 5 to 11, indicating that the functionalized BNNT could be used in a wide range of pH for As(V) adsorption and might be suitable for practical applications under standard conditions.

## CONCLUSION

Arsenic has been serious pollutants of water since Roman times and perhaps earlier. As arsenic in drinking water is having a major human impact in several locations many treatment technologies are available for arsenic removal but none of them is found to be completely applicable. Adsorption is a useful tool for controlling the extent of aqueous arsenic pollution.

Activated carbon has been studied extensively for arsenic removal. However, carbon only removes a few milligrams of metal ions per gram of activated carbon. Regeneration problems also exist. Thus, activated carbon use is expensive. Therefore, there is an urgent need for low-cost adsorbents, exhibiting superior adsorption capacities and also available locally. Activated alumina is very efficient and can be regenerated in situ to extend the useful life. However, sorption efficiency is highest only at low pH.

The removal efficiency of ion exchange resins are independent of water pH and the adsorbent and can also be regenerated in situ. However, sulphates, nitrates or dissolved solids reduce adsorption efficiency.

Clays, silica, sand, etc. are in fact low-cost adsorbents (and substrates). They are available worldwide. These can also be regenerated in situ. Unfortunately, they have lower adsorption efficiency than most of the other adsorbents.

Iron or iron compounds are the most widely used adsorbents, having higher removal efficiency at lower cost. However, their adsorption efficiency is highest only at low pH and they are not regenerable. Most of the commercially available adsorbents are

designed for application only within specific pH ranges.

Selection of a suitable sorbent media to supply arsenic free drinking water depends on (1) the range of initial arsenic concentrations, (2) other elements and their concentration in water, (3) optimization of adsorbent dose, (4) filtration of treated water, (5) adjustment of pH in water, (6) post treatment difficulties, (7) handling of waste and (8) proper operation and maintenance.

Adsorbent selection is a complex decision. The choice depends on the oxidation state of arsenic and the many other factors mentioned above. The technologies, successful in the laboratory, may fail in field conditions. Hence the criteria for best technology should include high removal efficiency, affordability, general geographic applicability, and compatibility with other water treatment processes, process transferability and process reliability.

This review would be helpful in initial screening of various sorbent media for setting up the treatment plants for removal of arsenic at the community level/ household levels.

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