



Low Cost Adsorption, Phytoremediation and Sludge Management Technologies of Arsenic Remediation Adoptable in India: A Review

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ABSTRACT

Arsenic is an important element in today's groundwater pollution scenario. It is introduced into soil and groundwater because of weathering of rocks and minerals followed by subsequent leaching and runoff. In India, a number of States, namely; West Bengal, Jharkhand, Bihar, Uttar Pradesh, Assam, Manipur and Chhattisgarh have chronically been exposed to drinking arsenic contaminated hand tube-wells water above permissible limit of 0.05 mg/L. Arsenic causes serious health hazard such as skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea etc. Many treatment and technologies are available for arsenic remediation but any method suitable for a specific area should not be generalized for the other affected regions due to geographical and geomorphological variations, different socio-economic conditions, local availability, processing required and treatment conditions. The arsenic remediation capability of treatments and technologies vary, depending on the characteristics of the material used, concentration of arsenic, pH, temperature and contact time. Agricultural waste, Industrial waste, soil constituents, and biosorbents in natural or modified form are highly efficient for the removal of arsenic, and their potential availability in India provides hope for technology advancement at very low cost. Many of the technologies and treatments described in this paper are possibly adoptable in India which greatly helps for arsenic remediation.

INTRODUCTION

Arsenic is an important element in today's scenario of groundwater pollution. Its atomic number is 33 and comprising about 0.00005% of the earth's crust. Its concentration in most of the rocks ranges from 0.5 to 2.5 mg/kg. It is most abundantly found in finer grained argillaceous sediments and phosphorites (Mohan Dinesh & Charl 2007). It is introduced into soil and groundwater because of weathering of rocks and minerals followed by subsequent leaching and runoff. Many factors such as anthropogenic activities, biological action, and geochemical reactions help to mobilize arsenic into groundwaters. Soil erosion and leaching contribute around 612×10^8 and 2380×10^8 g/year of arsenic respectively in dissolved and suspended forms in the oceans. Mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides and crop desiccants and use of arsenic additives to livestock feed create additional impacts. The adsorption and desorption reactions, arsenic species, Eh, pH and solid-phase dissolutions and precipitations may vary from aquifer to aquifer that depend upon the geological settings, geochemistry and geo-environmental conditions of an aquifer. Therefore, rigorous geochemical investigation for adequate understanding of arsenic geochemistry under different hydro-geological and geo-environmental conditions of

aquifers is essentially required for evolving sustainable solutions. In terms of health hazard, arsenic causes skin, lung, bladder and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea. Occurrence of arsenic in natural waters is a worldwide problem. Arsenic pollution has been seriously reported in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India. The largest population at risk among the different countries with known groundwater arsenic contamination is in Bangladesh, followed by India. By considering arsenic health hazard, different countries have made different maximum permissible limits of arsenic for drinking water, which are given in Table 1.

In India, a number of States likely West Bengal, Jharkhand, Bihar, Uttar Pradesh, Assam, Manipur and Chhattisgarh are chronically exposed to drinking of arsenic contaminated water from hand tube-wells above permissible limit of 0.05 mg/L. Many more northeastern hill States in the flood plains are also suspected to have the possibility of arsenic in groundwater. Even with every additional survey, new arsenic affected villages and people suffering from arsenic related diseases are being reported. All the arsenic affected river plains have the river routes originated

Table 1: Countries affected by arsenic contamination with permissible limits for drinking water.

Country	Maximum permissible limits mg/L
Argentina	0.05
Bangladesh	0.05
China	0.05
Chile	0.05
India	0.01
Mexico	0.05
Nepal	0.05
New Zealand	0.01
Taiwan	0.01
USA	0.01
Vietnam	0.01

Table 2: Districts from which arsenic in excess of 0.05 mg/L has been reported.

Sr. No.	State	Parts of Districts having As > 0.05 mgL ⁻¹
1.	Assam	Dhemaji
2.	Bihar*	Begusarai, Bhagalpur, Bhojpur, Buxar, Darbhanga, Katihar, Khagaria, Kishanganj, Lakhiserai, Munger, Patna, Purnea, Samastipur, Saran, Vaishali
3.	Chhattisgarh	Rajnandgaon
4.	Uttar Pradesh	Agra, Aligarh, Balia, Balrampur, Gonda, Gorakhpur, LakhimpurKheri*, Mathura, Muradabad
5.	West Bengal*	Bardhaman, Hooghly, Howrah, Malda, Murshidabad, Nadia, North 24-Parganas, South 24-Parganas

*Source-CGWB (2010)

from the Himalayan region. Whether or not the source material has any bearing on the projections is a matter of research; however, over the years, the problem of groundwater arsenic contamination has been complicated, to a large variability at both the local and regional scale, by a number of unknown factors.

Since groundwater arsenic contamination was first reported in year 1983 from 33 affected villages in four districts of West Bengal, number has been increased up to 79 blocks in 8 districts having arsenic beyond the permissible limit of 0.05 mg/L till 2010. The most affected areas are on the eastern side of Bhagirathi River in the districts of Malda, Murshidabad, Nadia, North 24-Parganas, South 24-Parganas, and western side of the districts of Howrah, Hugli and Bardhaman. Apart from West Bengal, arsenic contamination in groundwater has also been found in the States of Bihar, Uttar Pradesh, Assam and Chhattisgarh. Arsenic in groundwater has been reported in 57 blocks in 15 districts of Bihar, 45 blocks in 9 districts of Uttar Pradesh, 1 block of Chhattisgarh and 3 blocks in Assam. The arsenic occurred in the States of Bihar, West Bengal and Uttar Pradesh was in

the alluvial formations but in the State of Chhattisgarh, it occurred in the volcanic rocks exclusively confined to N-S trending Dongargarh-Kotri ancient rift zone. It has also been reported in Dhemaji district of Assam. Table 2 and Fig. 1 show the list of districts in which arsenic exceeds more than 0.05 mg/L. Table 3 gives most affected areas of arsenic in India.

TECHNOLOGIES AND MATERIALS FOR ARSENIC REMEDIATION

Remediation Technologies

Arsenic preservation and mobility in surface water and groundwater are of great concern because of their toxic effects in the environment. There are many technologies developed for the removal arsenic from water but each method depends upon different criteria such as local availability, processing required and treatment conditions and availability of funds and other criteria. Currently, maximum remediation technologies are costly thus, in current natural and any lowering of the standard will put increased economic pressure on rural communities with high levels of arsenic in their daily water. Therefore, we focus only those methods that are practicable according to readily available natural resources, industrial wastes and agricultural wastes which reduce high levels of arsenic.

Adsorption

Adsorption is a process that uses solids for removing substances from either gaseous or liquid solutions. Adsorption phenomenon is functioning in most natural physical, biological and chemical systems. Adsorption operations employing solids such as activated carbon, metal hydrides and synthetic resins are used widely in industrial applications for purification of waters and wastewaters. Activated carbon is also commonly used as the material in arsenic treatment. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Physical adsorption is caused mainly by van der Waal's forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, etc. Many activated carbons are available but few are selective. These are expensive as well. Therefore, the research thirst over the years is leading to find improved and tailor-made materials, which will meet several requirements such as regeneration capability, easy availability, cost effectiveness, etc. Consequently, low-cost adsorbents have drawn attention to many researchers and characteristics as well as application of many such

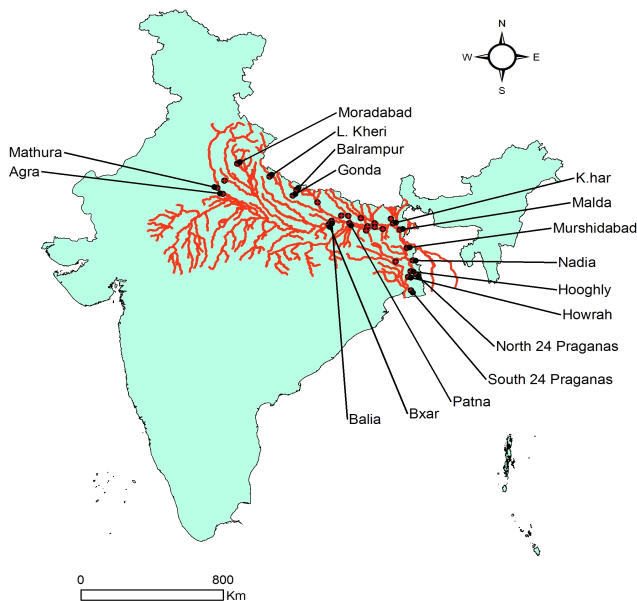


Fig. 1: Most affected districts in India.

adsorbents are reported.

Low Cost Adsorbents for Removing Arsenic from Water

In the adsorption process activated carbon is the most popular and widely used adsorbent in wastewater treatment throughout the world, but the high cost and regeneration cost of activated carbon limits its large scale use for the removal of inorganic and organic pollutants, which has encouraged researchers to look for low cost adsorbing materials. Recently, adsorption of arsenic using natural materials or the waste 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 such as dry plants, red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides and various bioadsorbents

Agricultural products and horticultural by-products: Rice hulls: Rice hulls (or rice husks) are the hard protecting coverings of grains of rice. Rice husk is an agricultural residue which is abundantly available in India. The annual rice husk production in India is approximately 24 million tons. Maximum adsorption capacity of rice husk occurred at 0.01 mol/L of HNO_3 , HCl , H_2SO_4 and HClO_4 using 1.0 g of adsorbent for 5.97×10^{-3} mol/L of arsenic for 5 min. The Freundlich isotherm was followed over concentration range from 8.69×10^{-5} to 1.73×10^{-3} mol/L of arsenic ($1/n = 0.83$ and $K = 4.43$ mmol/g) and increased with increasing temperature (Nasir et al. 1998).

Untreated rice husk was utilized for aqueous arsenic remediation. Complete removal (using rice husk columns) of both As(III) and As(V) was achieved under the following conditions: initial As concentration, 100 $\mu\text{g/L}$; rice husk amount, 6 g; average particle size, 780 and 510 μm ; flow rate, 6.7 and 1.7 mL/min; and pH, 6.5 and 6.0, respectively. Desorption (71-96%) was also achieved with 1 M KOH.

As(III) is more toxic and more difficult to be removed from water by adsorption on activated alumina (Nasir et al. 1998). Immobilization (adsorption) of As(III) by quaternized rice husk was examined. Batch adsorption test showed that extent of adsorption was dependent on pH, As (III) concentration, contact time and rice husk dose. Maximum adsorption occurred at pH 7-8, and equilibrium adsorption was attained in 2 h. Equilibrium adsorption data were described by the Langmuir and Freundlich isotherm models. According to the Langmuir isotherm, adsorption capacity of quaternized rice husk is 0.775 mg As(III)/g, which is 4.3 times higher than that (0.180 mg As(III)/g) of activated alumina. Quaternized rice husk is a potentially useful adsorbent for removing arsenic from groundwater.

Lemon juice: Cornejo et al. (2008) have presented an *in situ* arsenic removal method applicable to highly contaminated water based on zero valent iron (steel wool), lemon juice and solar radiation. Response surface method analysis was used to optimize the amount of zero valent iron and the citrate concentration (lemon juice) to be used. The optimal conditions when using solar radiation to remove arsenic from natural water are 1.3 g/L of steel wool and one drop (0.04 mL) of lemon juice. Under these conditions, removal percentage is higher than 99.5% and the final arsenic concentration is below 10 $\mu\text{g/L}$. The authors reported that the method is highly effective in removing arsenic and easy to use and inexpensive to be implemented.

Orange juice: As(III) and As(V) removal using orange juice residue and phosphorylated crosslinked orange waste has been considered (Ghimire et al. 2002, 2003). Orange waste contains cellulose, pectins, hemicellulose, chlorophyll pigments and other low molecular weight compounds like limonene. The active binding sites for metals are thought to be the carboxylic groups of the pectins. The carboxylic group content of the original orange waste did not bind sufficient iron (III) to adsorb arsenic. Thus, the waste's cellulose content was phosphorylated in order to convert its abundant hydroxyl groups into phosphoric acid groups which have a high affinity for ferric iron. The resulting phosphorylated gel was further loaded with Fe(III) (iron loading capacity of 3.7 mol/kg). Batch and column adsorption studies on this adsorbent found maximum adsorption capacities for As(V) and As(III) of 0.94 and 0.91 mol/kg at their optimum pH

Table 3: Selective most affected areas of arsenic and its value.

Sr. No.	State	District	Block	Arsenic Value(mg/L)
1	Bihar	Bhojpur	Shahpur	1.630
2	Bihar	Purnea	Kasba	1.810
3	West Bengal	Murshidabad	Bhagwangola-I	3.000
4	West Bengal	North 24 Parganas	Habra-II	3.773
5	West Bengal	South 24 Parganas	Sonarpur	2.715
6	Assam	Dhemaji	Dhemaji	0.147
7	Chhattisgarh	Rajanandgaon	AmbagarhChouki	1.890
8	Uttar Pradesh	Balia	Belhari (Rajpur Ekauna)	1.31
9	Uttar Pradesh	Balia	Reoti (Gaighat)	0.30
10	Uttar Pradesh	Siar	Haldi Rampur	0.35

values of 3.1 and 10.0, respectively (Ghimire et al. 2002).

Ghimire et al. (2003) have also phosphorylated both cellulose and orange wastes. The chemically modified adsorbents were then loaded with iron(III) in order to create a medium for arsenate and arsenite chelation. The Fe(III) loading capacity on the gel from orange waste was 1.21 mmol/g compared with 0.96 mmol/g for the gel prepared from cellulose. Arsenite removal was favoured under alkaline conditions for both the gels. The orange waste gel showed some removal capability even at pH 7.0. Conversely, arsenate removal took place under acidic conditions at pH 2-3 and 2-6 for the cellulose gel and orange waste gel, respectively. The higher Fe(III) loading on the orange waste gel led to greater arsenic removal. Arsenite or arsenates are adsorbed by liquid exchange on the immobilized Fe(III) centers of the Fe(III)-loaded phosphorylated cellulose and phosphorylated orange wastes. The ligands involved in such an exchange process may be hydroxyl ions (mechanism 1) or neutral water molecules (mechanism 2) present in the Fe(III) coordination sphere. Other gels, prepared by the phosphorylation of orange juice residue exhibited 2.68 and 4.96 mol of phosphorus/kg dry gel, respectively. The latter, when loaded with ferric iron, exhibited higher adsorption capacities for the removal of oxo anions such as arsenic and selenium. These gels exhibited maximum As(V) adsorption capacities of 0.53 and 0.94 mol/kg dry gel after they were loaded with Fe(III).

Industrial by-products/wastes: Chars and coals: Lignite, peat chars, bonechar use in wastewater treatment has received increasing interest in biochar. They may be good substitutes for activated carbons. They are plentiful, inexpensive and locally available. As(V) removal from aqueous solution by mixture of synthetic hydroxylapatite and baryte or bonechar was carried out in the concentration range of 4-100 mg/L. Although the hydroxylapatite and baryte mixture had a small influence on arsenic concentrations, bone-char was found to be a very effective sorbing agent for As(V) in the pH range of 2-5 (Mohan Dinesh & Charl 2007).

Biochar by-products from fast wood/bark pyrolysis were investigated as adsorbents for the removal of the As^{3+} , Cd^{2+} and Pb^{2+} from water. Oak bark, pine bark, oak wood, and pine wood chars were obtained from fast pyrolysis at 400 and 450°C in an auger-fed reactor and characterized. Sorption studies were performed at different temperatures, pHs and solid to liquid ratios in the batch mode. Maximum adsorption occurred over a pH range of 3-4 for arsenic and 4-5 for lead and cadmium. The equilibrium data were modelled with the help of Langmuir and Freundlich equations. Overall, the data were well fitted with both the models, with a slight advantage for Langmuir model. As(III) removal followed the order: pine wood char (1.20 µg/g) < oak wood char (5.85 µg/g) < oak bark char (12.1 µg/g) < pine bark char (12.15 µg/g). This study shows that by-product chars from bio-oil production might be used as plentiful inexpensive adsorbents for water treatment (arsenic remediation) at a value above their pure fuel value. Further studies of such chars, both untreated and after activation, seem warranted as part of the efforts to generate by-product value from biorefineries (Mohan Dinesh & Charl 2007).

Red mud: Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. A typical Bayer process plant generates 1-2 tonnes of red mud per ton of alumina produced. Red mud has been explored as an alternate adsorbent for arsenic. 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 µmol/g at the pH of 9.5 for As(III) and 5.07 µmol/g 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). Adsorption followed a first-order rate expression and fit the Langmuir isotherm well. Isotherms were used to obtain the thermodynamic parameters. The As(III) adsorption was exothermic, whereas As(V) adsorption was endothermic. As(V) removal by using

liquid phase of red mud (LPRM) was also reported. Authors suggested that it is advantageous to use a waste material of red mud liquid phase in the treatment of arsenical wastewater, possibly conjunction with red mud solids as adsorbent. Seawater-neutralized red muds (bauxsol), bauxsol activated by acid treatment, and by combined acid and heat treatment, and bauxsol with added ferric sulphate or aluminium sulphate, activated bauxsol (AB), and chemically modified and activated bauxsol (AB)-coated sand were all applied to arsenic removal. Seawater-neutralized red mud (not activated) was prepared by suspending the red mud in the seawater solution and stirring until equilibrium pH was achieved. Adsorption increased with decreasing pH (i.e., ligand-like adsorption), higher adsorbent dosages, and lower initial arsenate concentrations. Arsenate adsorption decreased in the presence of HCO_3^- , while Cl^- had little effect and Ca^{2+} increased arsenic adsorption. Water quality assessment after treatment with bauxsol indicated that none of the trace elements tested were released from the adsorbent. A TCLP leaching test also revealed that the adsorbent was not toxic. The sorption capacity of this bauxsol was $14.43 \mu\text{mol/g}$. The acid treatment alone, as well as in combination with heat treatment, increased arsenic removal efficiency. Combined acid/heat treatment provided best removal. Addition of ferric sulphate or aluminium sulphate suppressed arsenic removal. The activated bauxsol (AB), produced using combined acid and heat treatment, removed roughly 100% of the arsenate (at pH 4.5) with or without the presence of competing anions (i.e., phosphate, bicarbonate, sulphate) at an initial arsenate concentration of 2 mg/L. Combined acid and heat treatments were performed by refluxing bauxsol in HCl, adding ammonia for complete precipitation, filtering, washing with distilled water (DIW), and calcining at 500°C for 2 h. The optimal pH for As(V) and As(III) adsorption was 4.5 and 8.5, respectively. The adsorption data fitted the linear form of the Langmuir isotherm. The FITEQL and PHREEQC models were used to predict As(V) adsorption at various pH values (based on diffuse double layer models). The kinetics followed a pseudofirst-order rate expression. Chemically modified bauxsol and activated bauxsol (AB)-coated sand were also investigated to remove As(V) from water. Bauxsol-coated sand (BCS) and AB-coated sand (ABCS) were prepared by mixing bauxsol or AB with wet sand and drying. The adsorption capacities of 3.32 and 1.64 mg/g at pH 4.5 and 7.1, respectively for BCS and of 2.14 mg/g for ABCS at pH 7.1 were reported (Mohan Dinesh & Charl 2007).

Fly ash: Fly ash is one of the residues generated in the combustion of coal. It is generally captured from the chimneys of power generation facilities. The availability of fly ash is so high that at many places its disposal is a prob-

lem. As such, a number of workers have attempted to use it as an adsorbent in pollution control. Removal of arsenate at pH 4 was reported higher than that at pH 7 or 10 by using fly ash collected from coal power stations (Mohan Dinesh & Charl 2007).

Blast furnace slag: Steel plants generate a large volume of granular blast furnace slag. It is being used as filler or in the production of slag cement. Recently, it was converted into an effective and economical scavenger and utilized for the remediation of aqueous arsenic (Mohan Dinesh & Charl 2007).

Soils and constituents: Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Owing to their low cost, abundance, high adsorption properties and potential for ion-exchange, clay materials are a strong candidate as adsorbents. There are several types of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite. The adsorption capabilities of clays generally result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positive charged species. In recent years, there has been an increasing interest in utilizing clay 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 (Mohan Dinesh & Charl 2007).

Biosorbents: Several biological materials have been found for removal of toxic ions from aqueous solutions. However, only a limited number of studies have investigated the use of bioadsorbents e.g., bio-char, methylated yeast biomass, fungal biomass, chicken feathers and alginate to remove arsenic from aqueous solution. It is noteworthy that biological materials represent a potential source of abundant low cost adsorbents and there is no environmental or technical reason which impedes the preparation of adsorbents by using those materials. Besides these, various other materials such as wood, peat, clay, kaolin, goethite, humic acid, human hair, hematite or feldspar, pine needles, cactus leaves, polymer materials, tea leaves, tree fern, leather waste, orange juice residue, coconut coir pith, ferruginous manganese ore, etc. have also been explored as low cost adsorbents (Mohan Dinesh & Charl 2007).

Human hair: Wasiuddin et al. (2002) examined the ability of human hairs to adsorb arsenic from contaminated drinking water. Both static and dynamic tests along with the numerical modelling have been carried out to test human hairs as an adsorbent. The maximum adsorption capacity of $12.4 \mu\text{g/g}$ was reported at an arsenic concentration of $360 \mu\text{g/L}$.

Chitin and chitosan: Chitosan, one of the common bioadsorbents, is produced from chitin, which is the struc-

tural element in the exoskeleton of crustaceans (shrimp, crabs, shellfish, etc.). Chitin, a long-chain polysaccharide, is the most widely occurring natural carbohydrate polymer next to cellulose. Various researches on chitosan have been done in recent years and it can be concluded that chitosan is a good adsorbent for all heavy metals (Mohan Dinesh & Charl 2007).

As the adsorption capacity of the adsorbent varies with the initial arsenic concentration, solution pH and other experimental conditions, it may be difficult to compare the values directly. The adsorption capacity differences of arsenate ions uptake are ascribed to the properties of each adsorbent such as adsorbent structure, functional groups and surface areas because it depends on the nature of the system used (Mohan Dinesh & Charl 2007).

Biomass: Various properties of biomass have been reviewed by Mohan & Charles (2007). Microfungi have been recognized as promising low-cost adsorbents for heavy metal ion removal from aqueous solutions. A very few studies are reported on the removal of anionic metals including arsenic by fungal organisms. The surface charge of the fungal organisms is normally negative in a pH range of 3-10. The ability of *Garcinia cambogia*, an indigenous plant found in many parts of India, to remove trivalent arsenic from solution was assessed by Kamala et al. (2005). The As(III) removal capability of fresh and immobilized *G. cambogia* biomass was estimated. As(III) uptake was not greatly affected by pH with optimal biosorption occurred at around pH 6-8 (Mohan Dinesh & Charl 2007).

The tea fungus, a waste produced during black tea fermentation, has the capacity to sequester the metal ions from groundwater samples. Autoclaved tea fungal mats and autoclaved mats pretreated by FeCl_3 were exploited for As(III), As(V) and Fe(II) removal from groundwater samples collected from Kolkata, West Bengal, India. The FeCl_3 pretreated fungal mats removed 100% of As(III) and Fe(II) after a 30 min contact time. Moreover 77% of As(V) was removed after 90 min. Fungal mat without FeCl_3 was effective for Fe(II) removal from groundwater samples (Murugesan et al. 2006).

Sorghum moss was utilized for the remediation of arsenic from water. The effects of CaCl_2 , MgCl_2 , FeSO_4 , $\text{Fe}(\text{NO}_3)_3$ and humic substances on arsenic adsorption were evaluated. Iron slats increased arsenic removal while MgSO_4 decreased the removal by 21%. Arsenic adsorption on sorghum biomass (SB) was also investigated by Haque et al. (2007). Maximum adsorption was achieved at pH 5.0.

Phytoremediation

Phytoremediation is an *in situ* technology applicable to

contaminated soil and groundwater. It is designed to use plants to degrade, extract, contain or immobilize contaminants in soil, sediment or groundwater. Typically, trees with deep roots are applied to groundwater and other plants are used for shallow soil contamination. This technology tends to have low capital, operating and maintenance costs relative to other arsenic treatment technologies because it relies on the activity and growth of plants. The mechanisms of phytoremediation include phytoextraction (also known as phytoaccumulation, the uptake of contaminants by plant roots and the translocation/accumulation of contaminants into plant shoots and leaves), enhanced rhizosphere biodegradation (takes place in soil or groundwater immediately surrounding plant roots), phytodegradation (metabolism of contaminants within plant tissues), and phytostabilization (production of chemical compounds by plants to immobilize contaminants at the interface of roots and soil). Most applications of phytoremediation for arsenic removal include phytoextraction and phytostabilization. Experimental research into identifying appropriate plant species for phytoremediation is ongoing. It is generally applicable only to shallow soil or relatively shallow groundwater that can be reached by plant roots. In addition, the phytoremediating plants may accumulate high levels of arsenic during the phytoremediation process, and may require additional treatment prior to disposal. The selection of the phytoremediating species depends upon the species ability to treat the contaminants and the depth of contamination. Plants with shallow roots (e.g. grasses) are appropriate only for contamination near the surface, typically in shallow soil. Plants with deeper roots, (e.g. trees) may be capable of remediating deeper contaminants in soil or groundwater plumes. Examples of vegetation, used in phytoremediation, include sunflower, Indian mustard, corn and grasses (such as ryegrass and prairie grasses). Some plant species, known as hyperaccumulators, absorb and concentrate contaminants within the plant at levels greater than the concentration in the surrounding soil or groundwater. The ratio of contaminant concentration in the plant to that in the surrounding soil or groundwater is known as the bioconcentration factor. A hyperaccumulating fern (*Pteris vittata*) has been used in the remediation of arsenic-contaminated soil, waste and water. The fern can tolerate as much as 1,500 ppm of arsenic in soil, and can have a bioconcentration factor up to 265. The arsenic concentration in the plant can be as high as 2% (dry weight) (EPA 2001).

Waste Disposal/Sludge Management

Waste disposal is an important consideration in the treatment selection process. Arsenic removal technologies produce several different types of waste, including sludges,

brine streams, backwash slurries and spent media. These wastes have the potential for being classified as hazardous and can pose disposal problems. The arsenic-rich sludge should be disposed in a controlled manner.

According to the study conducted by AIH&PH, arsenic rich sludge may be disposed by the following methods:

- Disposal in on-site sanitation pits,
- Mixing with concrete in a controlled ratio,
- Mixing with clay for burning for brick manufacturing.

The adsorbed media rich in arsenic can also be mixed with concrete as an additional aggregate but in a controlled proportion. Liquid wastes must have lower concentrations than the toxicity characteristic in order for the waste to be classified as non-hazardous. The arsenic toxicity characteristic is 5.0 mg/L. Those liquid wastes that contain more than 5.0 mg/L of arsenic would, therefore, be classified as a hazardous waste. Many of the arsenic removal technologies also remove other constituents and, therefore, the liquid waste must also be analysed for other substances that may be present in concentrations above their respective toxicity characteristics. Because of the cost implications, on-site treatment or off-site disposal of hazardous waste is likely to be infeasible for small water systems. Indirect discharge through sewer to treatment plants may be viable option for waste disposal. There are five realistic methods for the disposal of arsenic wastes.

Landfill disposal: Historically, municipal solid waste landfills have been commonly used for the disposal of non-hazardous solid wastes emanating from treatment processes. However, the hazard potential of arsenic may limit the feasibility of this alternative. Dewatered sludge and spent media can be disposed in a municipal solid waste landfill if the waste passes both the paint filter liquids test (PFLT) and the toxicity characteristic leaching procedure (TCLP). The PFLT is used to verify that there is no free liquid residual associated with the waste. However, if the TCLP extract contains arsenic or any other contaminant (e.g., chromium) above the TC, the waste residuals must be disposed in a designated hazardous waste landfill. As such, the costs of disposal are relatively high. As with municipal solid waste landfill disposal, waste sludges must not contain free liquid residuals.

Direct discharge to surface waters: Direct discharge refers to the disposal of liquid wastes to nearby surface waters, which act to dilute and disperse the waste by-products. The primary advantage of direct discharge is to reduce capital and operations and maintenance costs due to the elimination of residuals treatment. The feasibility of this disposal method is subject to provisions of the guidelines for waste disposal. The allowable discharge is a function of the ability of the receiving water to assimilate the arsenic without ex-

ceeding water quality criteria established under the Govt. regulations. Different water quality criteria exist depending on the classification of the receiving water. For specific criteria, conditions and limits, the appropriate agency should be contacted, because the conditions and limits can vary according to the receiving water's particular characteristics.

Indirect discharge: The discharge of liquid wastes to a treatment plant is a potential disposal alternative. In this case, the wastes can be discharged to sewer systems. The arsenic limit is usually on the order of 50 to 10 µg/L. The technically based local limits (TBLLs) are computed for each publicly owned treatment works (POTW) to take into account the background levels of contaminants in the municipal wastewater. The background level will change because of the drinking water treatment process, which may lead to revised TBLLs. The revised TBLL can be used to determine if the liquid waste stream could be discharged to the POTW.

Land application: Land application of concentrated sludge may be allowed under certain conditions depending on the state law and regulations. As per United States Environmental Protection Agency (U.S.EPA) guidelines, sewage sludge (also called biosolids) containing <41 mg As/kg biosolids can be land-applied with no restrictions. Biosolids with arsenic concentrations between 41 and 75 mg/kg can be land-applied, but must track arsenic accumulation. The lifetime arsenic accumulation limit is 41 kg As/hectare of land.

On-site sewerage: Liquid wastes from reverse osmosis POU devices can suitably be disposed in on-site sewerage or septic system. Arsenic is concentrated in the RO retentate during normal process operation. However, eventually this retentate is combined with other domestic wastewaters in the septic tank. Because the amount of water consumed is small relative to the total flow entering the dwelling, the concentration of arsenic in the blended wastewater is nearly identical to that in the influent stream.

DISCUSSION

Cost assessment: The cost depends on local availability of materials, processing required and treatment conditions. These are not broadly and thoroughly discussed in any paper anywhere in the literature. The authors suggest these materials and technologies because the materials are abundantly present in India, and they can be used for removal of arsenic better than any other traditional methods.

Most researches reviewed in this paper have been limited to initial laboratory evaluations of adsorptive capacity and mechanism. Pilot-plant scale studies and cost evaluation

remain to be explored. In the growing literature on natural adsorbents for arsenic uptake, little literature exists containing full costs and application comparisons of various sorbents. In addition, different sorbents are difficult to compare because of inconsistencies in the data presentation. Thus, much work is necessary to demonstrate application costs at the single home village, municipal or industrial scales.

Abundance of adsorbent material and phytoremediating species in India: Every year approximately 120 million tonnes of paddy are produced in India. This gives around 24 million tons of rice husk and 4.4 million tons of rice husk ash every year. India is second largest producer of rice after China. In India, rice husk is used for cattle feeding, partition board manufacturing, etc. There are many small scale and industrial applications of rice husk, and rice husk ash is used in land filling. But these uses are not in a systematic manner and also rice husk has very low food value. Being fibrous, it can prove to be fatal for the cattle feeding. Therefore, rice husk will open up the door in India for prevention of arsenic contamination. India produces 2.06 million tonnes of lemon and 3.9 million tonnes of orange every year, with world's fifth largest lemon and orange producer in 2007. Therefore, citrus species with abundance in India which may be used for removing contamination of arsenic in water.

Yearly, India produces 588.5 million tonnes of coal, which contributes 5.6% of the total world's production and third largest coal producer in 2011. India ranks fifth in bauxite and eighth in aluminium in world's total production. India is a big aluminium producer in the world. It also houses a number of aluminium plants which include aluminium smelting plants, aluminium extrusion plants, alumina refineries, FRP plants, wire rod plants and aluminium foil plants. Yearly total ash generated around 131.09 million tonnes from 407.61 million tonnes of coal consumption in India, which boons the arsenic removal technology from industrial wastes.

The Lord Venkateshwara temple in Tirumala, Andhra Pradesh, tenth of its annual revenue comes from the sale of hair offered by devotees. Every year, thousands of people who visit the temple get tonsured to offer their hair to Lord Venkateshwara, in keeping with a centuries old tradition and in a world increasingly fascinated with pride. In 2011-12, the Tirumala temple earned nearly Rs. 200 crore out of its total revenue of Rs. 1,949 crore, from auctioning human hair. Therefore, India has enormous source of human hair, and it occurs at one place which is beneficial for arsenic removal. Other biosorbent materials like biochar, methylated yeast biomass, fungal biomass, chicken feathers, alginate and chitin are potentially found in India.

Phytoremediating species like sunflower, Indian mustard, corn, and grasses like ryegrass and prairie grasses, and fern are potentially found in India which can be grown on contaminated ground surfaces.

Waste disposal/sludge management: According to study conducted by The All India Institute of Hygiene & Public Health and method suggested by them as well as other methods suggested in this paper, a strong awareness is required amongst the people with their whole hearted participation. People must cooperate with government and other private agencies, which enormously work for controlling groundwater contamination.

CONCLUSIONS

Many treatment technologies are available for arsenic remediation. Methods suitable for a specific area should not be generalized for the other affected regions due to geographical and geomorphological variations, different socio-economic conditions, local availability of materials, processing required and treatment conditions.

The arsenic remediation capability of treatments and technologies vary, depending on the characteristics of the material used, concentration of arsenic, pH, temperature, and contact time. Agricultural waste, Industrial waste, soils and constituents, biosorbents either in natural form or modified form, are highly efficient for the removal of arsenic, and their potential availability in India provides hopes for technology advancement at very low cost. Many of the technologies and treatments described in this paper are possibly adoptable in India, which greatly helps for arsenic remediation.

Phytoremediation technology is a costless and imposing but it has its own disadvantages like:

1. It is generally slower than most other treatment methods and climate dependent.
2. In most cases, the contamination to be treated must be shallow.
3. It usually requires nutrient addition, and mass transfer is limited.
4. High metal and other contaminant concentrations can be toxic to the plants, although some plants have greater adaptation to toxicity than others.
5. Access to the site must be controlled, as the plants may be harmful to livestock and the general public.
6. The contaminants being treated by phytoremediation may be transferred across media (i.e., they may enter groundwater or may bioaccumulate in animals).
7. The site must be large enough to utilize agricultural

machinery for planting and harvesting. But it is easily possible to overcome from these disadvantages.

Waste disposal/sludge management will be successful if the people cooperate with the government and other private agencies which enormously work for controlling groundwater contamination. Awareness amongst people and their whole hearted participation is very much essential to achieve success at field level. Technologies found effective and safe for arsenic removal from contaminated water should be promoted for wider implementation in the acute arsenic problem areas to avoid ingestion of excessive arsenic through water. The arsenic removal technologies may improve further through adaptation in rural environment through people's participation.

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