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ARSENIC REMOVAL FROM WATER: A REVIEW

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ABSTRACT

The aim of this work is to analyze and study various methods of removing arsenic from drinking water. Arsenic is introduced into water through the dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition. Even at high concentrations, arsenic-contaminated water is translucent, tasteless, and odorless. The primary route of exposure to arsenic for humans is ingestion. Exposure via inhalation is considered minimal. The standard amount arsenic to be present in water is 10ppb and an amount greater than it, cause threat to human body. Excess amount of arsenic in drinking water causes respiratory effects, reproductive effects, lung and bladder cancer, cardiovascular diseases. Hence it became essential to treat drinking water in such a way that water is left with a minimal and non-effective amount of arsenic. Thus, it provides you with various new, common and most advantages methods for removing arsenic with proper detailing.

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INTRODUCTION

To Arsenic

Arsenic (atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in the seawater, and 12th in the human body. The term "elevated arsenic" refers to arsenic concentrations greater than the health standard of 10 µg/L. Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities. Arsenic is introduced into water through the dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition. It can enter drinking water through the ground or as runoff into surface water sources. Two forms are common in natural waters: arsenic (III) and arsenic (V). Pentavalent species predominate and are stable in oxygen rich aerobic environments. Trivalent arsenates predominate in moderately reducing anaerobic environments such as groundwater. Even at high concentrations, arsenic-contaminated water is translucent, tasteless, and odorless. The primary route of exposure to arsenic for humans is ingestion. Exposure via inhalation is considered minimal. The standard amount arsenic to be present in water is 10ppb and an amount greater than it, cause threat to human body.

Why should i be concerned about arsenic in my drinking water??

Although short-term exposures to high doses (about a thousand times higher than the drinking water standard) cause adverse effects in people, such exposures do not occur from public water supplies in the U.S. that comply with the arsenic MCL.

Some people who drink water containing arsenic in excess of EPA's standard over many years could experience skin damage or problems with their circulatory system, and may have an increased risk of getting cancer. Health effects might include:

- Thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, and liver effects;
- Cardiovascular, pulmonary, immunological, neurological (e.g., numbness and partial paralysis), reproductive, and endocrine (e.g., diabetes) effects;
- Cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate

Long term drinking water exposure causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea. This differs from acute poisoning, which typically causes vomiting, esophageal and abdominal pain, and bloody "rice water" diarrhea detection of arsenic in water.

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Effects of Arsenic on Human Body

Pregnancy Outcomes-The main findings concerning pregnancy outcomes relate to spontaneous abortion, stillbirths, reduced birth weight, and infant mortality

Reduced Birth Weight and Infant Mortality-reductions in birth weight have been found in a low-arsenic-exposure study in Chile (<50 µg/L), and in higher-exposure studies in Taiwan and in Bangladesh.

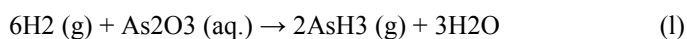
Childhood Cancer-Childhood cancer and much higher water arsenic concentrations in Northern Chile, up to 860 µg/L, were studied by Liaw et al.. No increases were detected for all cancers combined. However, childhood liver cancer mortality under age 20, which is normally extremely rare, was markedly increased for those who were young children when they would have experienced high water arsenic concentrations (RR = 10.6, 95% CI 2.9--39.2, $p < 0.001$)

Cardiovascular Disease-A large number of studies have considered cardiovascular effects of arsenic in drinking water, especially in Taiwan.

Arsenic in natural waters is a worldwide problem. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India. Population of Bangladesh followed by West Bengal in India is at maximum risk from this contaminated water.

Detection of Arsenic

There are currently a number of methods used to detect arsenic in water, ranging from simple methods such as the Gutzeit test to more sophisticated atomic spectrometric methods. **The Gutzeit test** is an old method of arsenic detection. It is a relatively cheap and simple test and can be used in the field. However, it is not very reliable or accurate and it produces toxic arsine gas:



The concentration of arsenic is determined by observing the color on a strip of paper that has been exposed to the arsine gas. As the color on the paper changes from white to yellow to reddish-brown, this indicates increasing concentrations of arsenic due to formation of AsH_2HgBr .

More accurate and reliable detection methods are atomic spectrometric techniques such as inductively coupled plasma mass spectrometry (**ICP-MS**), inductively coupled plasma atomic emission spectroscopy (**ICP-AES**), atomic absorption spectrometry with hydride generation (**AAS-HG**) and graphite furnace atomic absorption spectroscopy (**AAS-GF**). However, those methods involve the use of sophisticated and expensive laboratory-based instruments. They require water samples to be collected and then brought to the laboratory where a trained chemist analyses them. With over 6 million wells spread across Bangladesh, using such methods is not only highly expensive but also time-consuming.

There is thus a desperate need for a method that is more accurate and reliable than the Gutzeit test but cheaper, faster and requiring fewer infrastructures than the AAS or ICP methods. The aim of current research is to investigate the

possible use of a portable digital voltammeter as a field-based method for arsenic detection in groundwater and soil.

Anodic stripping voltammetry (ASV), is a historical method that uses reduction to deposit ions (such as arsenic ions) in the solution onto an electrode and then requires an oxidation step to strip the ions back into solution. The number of electrons being produced as a current, which is related to the concentration of ions in solution, is measured, giving a voltammogram. The exact position of the voltammogram peak is different for each ionic species. For example, for arsenic ions, the peak occurs at around 125 mV. The instrument that was chosen for the development of a field-based voltammetric arsenic detection method was the PDV6000+ (Cogent Environmental) portable voltammetric analyzer, which is capable of performing either as a stand-alone unit or in conjunction with a laptop computer. The apparatus basically consists of the electrochemical cell with three electrodes (working electrode, reference electrode and counter electrode) and a handheld controller.

The ASV method is currently at the stage of being validated using ICP-MS, which is one of the approved methods for arsenic detection in drinking water. So far, a small number of samples (four from Bangladesh and eight from Perth, Western Australia) have been analyzed using both voltammetric and ICP-MS methods and the results are encouraging. Plotting the ASV analyses against the ICP-MS analyses shows correlation with an R^2 value of 0.9.



The components of the PDV 6000+ instrument

Recently an instrument is designed, **Whole-cell arsenic biosensor** that is cheap, non-toxic and easy to use was designed to detect the presence of amount of arsenic in water with reference to 10ppb. Some species of bacteria are natural arsenic biosensors: in the presence of less than 10 parts per billion of arsenic, they initiate the production of enzymes and an efflux pump for the detoxification and removal of arsenic. For the sensor, the team will take the genes that detect arsenic and combine them with bacterial genes that produce coloured pigments. The modified bacteria will turn green when arsenic

levels are safe and purple when arsenic levels are unsafe. The test uses a harmless strain of the soil-dwelling bacterium *Bacillus subtilis*, which poses no threat to human health or the environment. The extremely simple visual output combined with the low cost (estimated at around \$0.50 per test) and the lack of need for any expensive monitoring equipment make the whole-cell arsenic biosensor ideal for use in the rural areas where arsenic contamination of drinking water is widespread.

Pre-Treatment of Arsenic Contaminated Water

Several pretreatment steps are followed in order to efficiently remove arsenic in form of As (V) from drinking water. Among several pre-treatment processes, most commonly used one are as follows:

Pre-treatment to remove iron

In Ohio, groundwater with elevated arsenic has elevated concentrations of iron, which can “foul” water-treatment systems by clogging up the pore spaces with small iron particles. If a home water softener is already in place, iron (or manganese) fouling should not be an issue for new arsenic removal systems. Oxidation/filtration is another pretreatment method that can remove iron.

Pre-oxidation to convert As (3) to As (5)

As (3) is harder to remove from water than As(5). Anion exchange systems remove only As (5), so a pre-oxidation step is required to convert As(3) to As(5). Adsorptive media and reverse osmosis remove both forms of arsenic, but the efficiency for removing As(3) is lower than for As(5), and a pre-oxidation step will improve the efficiency and lower operating costs, especially for whole-house systems. Manganese dioxide filters and chlorination are two methods that can be used to oxidize As (3) to As (5).

Pretreatment to Remove Iron

Methods used in removing iron is **water softener (cation exchange)**, it removes dissolved iron and manganese and is readily used and **oxidation/filtration**, it removes dissolved and particulate iron and manganese but sometimes uses chlorine that is needed to be avoided.

Pre-Treatment to Convert As (III) To As(V)

It is a method that helps in the conversion are named as **Manganese dioxide filter**, simple to operate and do not involve use of chemicals and **chlorination**, provides disinfection and is used in public water for a long time.

Treatment of Arsenic

Common household water-treatment methods, such as water softeners, activated carbon filters, and sediment filters are not effective for removing arsenic from water. Arsenic cannot be removed from water by boiling. Some treatment methods only remove As (5). Other methods can remove both types of arsenic, but are less effective at removing As (3). If arsenic concentrations are elevated, and a large percentage of the arsenic is As (3), an additional pretreatment may be needed to convert As(3) to As(5) which is generally known as pre-oxidation. Manganese dioxide filters and chlorination are two methods that can be used to oxidize As(3) to As(5). Water softener (cation exchangers) and oxidation/filtration are generally used methods for pretreatment which are generally used to soften the elevated arsenic in water. Basically, there are several laboratory methods to reduce the amount of arsenic from water. Among these I will be focusing on synthetic activated charcoal method, anion exchange method and precipitation method. A new method of chelating is being observed or under experiment in our college laboratory.

Single Tap			Point-of-use (POU) systems		
Method	Type of arsenic removed	Advantages	Disadvantages	Estimated costs*	
				Initial	Maintenance
POU Adsorptive	Can remove As(3) and As(5), but, capacity to remove As(3) is lower.	Produces very little wastewater. Spent media is non-hazardous and disposable.	The media can be expensive, especially without using additional pretreatment.	\$300–\$700	\$300 ~\$500 every 6 months ~ 1 year
Media	Pretreatment is usually needed.	Simple to install and operate.			
POU Reverse Osmosis	Removes about 95% As(5) and 50~60% As(3). Pretreatment is usually needed.	Requires little maintenance.	For each gallon of treated water, creates about 7~9 gallons of “reject” water.	\$300–\$1,500	\$100 ~\$200 every 1~2 years
POU Distillation	Removes both As(5) and As(3). Pretreatment is not required.	Simple to install and operate.	Slow process; uses a lot of electricity.	\$300 ~ \$1,200	~
WHOLE HOUSE			Point-of-entry (POE) systems		
Method	Type of arsenic removed	Advantages	Disadvantages	Estimated costs*	
				Initial	Maintenance
POE Adsorptive	Can remove As(3) and As(5), but capacity to remove As(3) is lower. Pretreatment is usually needed.	Produces very little wastewater. Spent media is non-hazardous and disposable.	The media can be expensive, especially without using additional pre-treatment.	\$2,400 ~ \$4,500	\$700 ~\$900 per year
Media	Pretreatment is usually needed.	Simple to install and operate.			
POE Reverse Osmosis	Removes about 95% As(5) and 50~60% As(3). Pretreatment is usually needed.	Requires little maintenance.	For each gallon of treated water, creates about 0.5 ~1 gallon of “reject” water.	\$5,000–\$12,000	\$250 ~\$500 every 1~2 years
POE Anion Exchange	Removes only As(5). Pretreatment is required to remove As(3).	Operation is similar to a water softener.	Without careful maintenance, an abrupt increase in arsenic in treated water could occur. Produces waste water with elevated arsenic.	\$1,800~\$2,500	\$700 ~\$900 every 8~10 years

More precisely this method has shown more efficient result in removing arsenic from portable water. Different methods to treat arsenic from drinking water either for single tap or whole house are required. These different methods include reverse osmosis, filtration techniques, using adsorptive media and anion exchange. All these methods with their advantages, disadvantages and economical feasibility are explained in below in tabulated form. Thus treating water at small scale is possible through these methods which can be very helpful in providing a suitable drinking water with reduced and safe amount of arsenic in it.

Synthetic Activated Charcoal

Activated carbons are produced by carbonization employing slow substrate heating in the absence of air below 600 °C. This removes volatiles. Then chemical or physical activation follows. Treatment with oxidizing agents (steam, carbon dioxide, or oxygen) at elevated temperature or with chemical activants (ZnCl₂, H₂PO₄, H₂SO₄, KOH, K₂S, KCNS, etc.) completes the activation. Chemical activants may promote cross linking forming a rigid, less volatile matrix with a smaller volume contraction going to high temperature. An **advantage of chemical activation** is the lower temperature required. Chemical activation gives higher global yields since char burn-off is not required. Post activation removes residual catalyst, which may be recovered and reused. As (V) and As(III) removal from water was studied using a char carbon (CC) derived from fly ash. Darco activated carbon [Darco S-51 (DC)] obtained from North Americas Inc and carbon produced by a graphite electric arc (AC). CC and AC adsorbents removed almost equal amounts of As(V) at optimum conditions; however, percent As(III) removal was more on CC than AC. DC sample was ineffective for both As(III) and As(V) removal. The maximum uptakes of As (V) were 34.5 mg/g (490 ppm, pH 2.2) for CC versus 30.5 mg/g (159 ppm, pH 7.5) for AC. Those of As (III) were 89.2(709 ppm and pH 2.2) for CC and 29.9 (992 ppm and pH 7.0) mg/g for AC. These sorbents contain different amounts of ash (28.4% for CC and 0.2% for AC). Since their specific surface areas are very similar, the ash contents alone did not greatly influence the adsorption of As (V). The efficiency of As (V) adsorption by activated carbon (AC) produced from oat hulls. Adsorption capacity decreased from 3.09 to 1.57 mg as g⁻¹ when the initial pH increased from 5 to 8. A modified linear driving force model coupled with the Langmuir isotherm described simultaneous rapid and slow kinetic process. The LDF model assumes that the uptake is linearly proportional to a driving force, defined as the difference between the surface concentration and the average adsorbed phase concentration. The simulation results indicate that the adsorption process is described well by the modified LDF model. Because the adsorbate is adsorbs easily on the surface (macro pore surface) of the adsorbent, rapid adsorption results. In the interior (or micro pore surface) of the adsorbent, the adsorbate would be adsorbed by a pore and surface diffusion mechanism, resulting in a slower adsorption. As (V) removal was strongly pH dependent. A two-monoprotic site-triple layer model described As (V) removal using two fitting parameters.

Anionic Exchange Resins

The adsorption of As(III) and As(V) can be done by titanium dioxide loaded onto an Amberlite XAD-7 resin. This resin was

prepared by impregnation of Ti (OC₂H₅)₄ followed by hydrolysis with ammonium hydroxide. The resin strongly adsorbed As (V) from pH 1 to 5 and As(III) from pH 5 to 10. Langmuir adsorption capacities of 0.063 mmol/g for As (V) at pH 4.0 and 0.13 mmol/g for As(III) at pH 7.0 were achieved. An anion exchanger (AE) prepared from coconut coir pith (CP) was used for the removal of As(V) from aqueous solutions. The adsorbent (CP-AE), carrying weakly basic dimethylaminohydroxypropyl functional groups, was synthesized by the reaction of CP with epichlorohydrin and dimethylamine followed by treatment of hydrochloric acid. Maximum removal of 99.2% was achieved for an initial concentration of 1 mg/L As (V) at pH 7.0 and an adsorbent dose of 2 g/L. This adsorbent was tested for As(V) remediation from simulated groundwater. Regeneration of the adsorbent was achieved using 0.1N HCl. Anionic exchange systems use a physical/chemical process to exchange ions between a resin bed and water passing through. These systems soften water; remove iron and manganese, and lower nitrate and arsenic levels. Specific contaminant removal is determined by the composition of the resin bed used. Anionic exchange systems are typically point-of-entry systems, meaning that they treat all water coming into the home.

These systems work by passing water through the resin bed, which is charged with chloride ions from dissolved salt. Arsenic molecules in the water replace these chloride ions by knocking them off and taking their place. This process continues until all of the sites on the resin are full. The resin is then backwashed with water that is super-saturated with dissolved salt. The chlorine ions in this backwash water strip the embedded arsenic molecules out of the resin and into the backwash wastewater. New chlorine ions replace the arsenic molecules, fully recharging the resin bed so that the process can be performed again.

Pros and Cons of Anionic Exchange

Advantages

1. Anionic exchange requires little maintenance; additional salt is added every few weeks.
2. Systems are typically installed to treat an entire house.

Disadvantages

1. Other constituents in water can compete with arsenic for the resin sites reducing the systems effectiveness. EPA recommends the influent water have less than 500 mg/L of total dissolved solids (TDS) and less than 25 mg/L of sulfate.
2. Treated water can have a very low (acidic) pH and high levels of chloride, which can cause corrosion control problems and high levels of lead and copper in the treated water.
3. If the system fails, all of the arsenic captured on the resin at that time can be released at once causing a large concentration of arsenic in the treated water.

Pine Leaves

In order to find out more economical and efficient adsorbents, the present study was carried out to explore the adsorption characteristics of leaves of *Pinus roxburghii*, commonly known as Chir. *P. roxburghii* is a pine native to the Himalaya,

commonly found in northern Pakistan (Khyber Pakhtunkhwa and Azad Kashmir), northern India, Nepal, and Bhutan. It generally occurs at lower altitudes than other pines in the Himalaya. *P. roxburghii* is a large tree (30–50 m) with a trunk diameter of up to 2 m. It has thick, red–brown bark that is deeply fissured at the base of the trunk. The yellowish green, needle-like leaves are slender and are 20–35 cm long. During the study, effect of various process conditions such as the amount of adsorbent, pH and time of interaction were studied. Besides, various isotherm models were used to explain the phenomenon.

Preparation of adsorbent

Fresh leaves of *P. roxburghii* were collected from Balakot, Pakistan (34833/N: 73821/E), situated at an altitude of 1400 m above sea level. Later, leaves were washed with distilled water and subsequently dried in an incubator at 70 °C until all the moisture had evaporated (nearly took 8 h). The material was ground to a fine powder in a laboratory grinder and was sieved in the particle size range of 100–150 μ m. The processed material was stored in airtight plastic containers.

Chemicals, equipment and apparatus

High purity chemicals and reagents, purchased from Sigma–Aldrich, Inc., were used during the study. The glassware was thoroughly washed with chromic acid, caustic soda, soda ash, tap water, distilled water, in that order, and dried in an oven prior to use. Double distilled water was used throughout the research. Batch experiments were performed in 250 ml conical flasks on top of orbital shaker (Optima, OS-752). The pH was adjusted with 0.1 mol/L solutions of either NaOH or HCl using a digital pH meter (inoLab, pH 720). The concentrations of the arsenic in water were determined with an inductively coupled plasma technique (Perkin–Elmer ICPOES Optima 2100) using standard working conditions.

Stock solutions and standards

Stock solution of As(V) (1000 mg/L) was prepared by dissolving appropriate quantity of sodium arsenate heptahydrate. Solutions of the desired concentrations were obtained by proper dilutions of the stock solution with double distilled water.

Batch experiments

To evaluate optimum working conditions, batch mode experiments were performed in conical flasks placed on an orbital shaker with 50 mL of As(V) solution having initial concentration 10 mg/L. To study the effect of adsorbent dose in the range (0.2–2.0 g/50 ml) 4–40 g/L at room temperature (25 °C), pH was adjusted to 7.0, and contents were agitated for 30 min at a speed of 100 rpm. Afterwards, suspensions were filtered to remove adsorbent and filtrates were subjected to analysis on ICP-OES to find out the remaining amount of sorbate in aqueous phase with arsenic standards, drawing regression line to interpolate samples' concentration. In the next experiment, most favorable adsorbent dose was added according to the findings of previous trial, while pH was changed from 1.0 to 10.0 with speed of agitation 100 rpm, time of contact 30 min and temperature 25 °C. Likewise, in studying the effect of contact time, adsorbent dose and pH were selected optimally in accordance with the findings of previous trials,

while time of contact was changed in the range 5–50 min at 25 °C, shaking the contents at 100 rpm. In the same way, next experiment was to study the effect of agitation speed in the range 25–250 rpm.

Adsorption isotherms and kinetics

Isotherm studies were performed in six 250 ml Erlenmeyer flasks. Each flask was filled with 50 ml of As(V) solutions of different initial concentrations (5–30 mg/L) and pH was adjusted to 4.0. To each flask, 1.0 g of adsorbent was added, and solutions were agitated at a speed of 100 rpm for 35 min. Later, the solutions were filtered and analyzed. Langmuir (Eq. (1)), Freundlich (Eq. (2)), Temkin (Eq. (3)), Elovich (Eq. (4)), Dubinin–Radushkevich (Eq. (5)), and Flory–Huggins (Eq. (6)) isotherms were plotted and the respective parameters were evaluated.

In the same way, batch studies were conducted in a temperature-controlled shaker (25 °C) using 50 ml of adsorbate solution and a fixed adsorbent dosage of 1.0 g at pH 4.0. The agitation speed of the shaker was 100 rpm. The samples at different time intervals (0–30 min) were taken and analyzed. Then, pseudo first order (Eq. (7)) and pseudo second order (Eq. (8)) models were plotted and the corresponding parameters were calculated.

Precautionary measures

Since arsenic and its compounds have highly toxic character, it was mandatory to act appropriately to avoid any accident. Solutions were not pipetted by mouth but by rubber suckers. Disposable gloves were used when dealing with spent sorbent or arsenic solutions. The residuals (contaminated powder of leaves) were placed in a container marked as “hazardous waste” and sent to external treatment. Old arsenic solutions were passed through ion exchangers/RO membranes ahead of final disposal to sewage.

Electrocoagulation

It is also termed as ECAR i.e. electro coagulation arsenic removal. It is known wastewater technology. During coagulation and filtration, arsenic is removed through three main mechanisms:

- **precipitation:** the formation of the insoluble compounds $\text{Al}(\text{AsO}_4)$ or $\text{Fe}(\text{AsO}_4)$
- **co-precipitation:** the incorporation of soluble arsenic species into a growing metal hydroxide phase
- **Adsorption:** the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

There are series of three distinct processes that completes electro-coagulation and are described as follows:

- **Dosing:** Formation of arsenic binding corrosion products (ABCP) through electrochemical dissolution of iron electrodes.
- **Mixing:** Coagulation of ABCP with arsenic
- **Filtration:** Mechanical removal of the arsenic-laden ABCP.

This system is community based center with full cost recovery which encourages local participation, scalable, replicable and is sustainable with built-in incentives for maintenance.

Principal Challenges

Design

- Provide **energy** in off-grid rural communities
- Design an efficient, robust, and simple flow-reactor

From scratch

Lab Testing

Target and characterize **key parameters** to facilitate fine-tuning during field testing

Implementation

Meet the low willingness to pay of \$0.04/person-day.

Adapt to local culture

Design Principles

Demand technical requirements

- Serve at least 10 households per system at >500 L/day
- Removal effectiveness of <10 ppb
- Turbidity of <1 NTU.

Design choice

- Lab friendly and easily scalable at 10 to 100 L/h.
- Focus on critical dosing process after initial design iterations.
- Allow for a 12 V car battery input and gravity flow.
- Optimal “HOT” zone: 150 C/L and 1.1 mA/cm².

Experimental Settling

Synthesized Bangladeshi groundwater

- Replicate pH, DO, principal interfering ions with 600 ppb arsenic.
- 3 hours required per 8 L batch
 - Controlled flow (valve) and current (galvanostat)
 - Batch mixing with magnetic stirrers
 - Batch vacuum filtration with 0.1 micrometer membrane
 - Quick test (QT) and ICPMS (more accurate test) results now available.

Optimization Needed

- Higher current density of about 1.1 mA/cm² is to consistently meet WHO standards.
- Slightly higher flow rate may be possible.
- Minimum mixing time of about 30 minutes.
- Allow bigger particles to form and facilitate filtration.
- Find optimal mixing speed
- Adapt to local field conditions

Advantages of Community Based Model with Full Cost Recovery

- Provides maintenance and quality control through trained staff
- Provides electricity through lease or rent
- Sustainable and replicable turnkey solution

- Encourages local participation
- Proven success with Water Health International.

Pros

- Low cost
- Scalable
- Produces less waste
- Highly effective in testing
- Low level supply chain

Cons

- Requires electricity
- Uncertainty (younger technology)

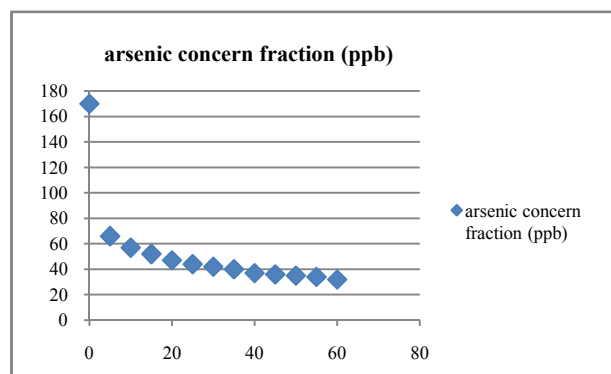
Bottom Ash

Bottom ash is one of the methods used to remove arsenic from contaminated drinking water in rural Bangladesh. It is named as ARUBA abbreviated for Arsenic Removal Using Bottom Ash. It uses bottom ash, waste from coal-fire power plants and coated with rust (ferric hydroxide). The salient features of process are as follows:

- Simple process operated at atmospheric pressure and room temperature.
- Inexpensive, readily available chemicals like NaOH and Fe₂SO₄.
- Large surface to volume ratio minimizes the media required and waste.
- Waste are approved for disposal in municipal landfill
- Bottom ash cost \$4/ton.

Laboratory results show that the arsenic removal capacity of the process is 0.96 mg As/g of bottom ash. But the field results show that it is just 0.03-0.16 mg As/g of bottom ash. Thus an important task is to improve the arsenic removal capacity which is done by one of the three methods as follows:

- Understanding ARUBA kinetics



- Fractionated dosing

It is defined as dosing of a fraction of arsenic and the removing it in two conditions of solvent.

- Water storage before treatment

It is shown that ARUBA treatment reduces the arsenic concentration from the water at very fast rate which is much better than the filtration or any other methods.

Community scale implementation increases the feasibility of capacity improving methods. In 2003 World Bank study, 72%

of the Bangladeshi villagers interviewed preferred a community safe water source to household filters. It is popular among the villagers because of following advantages:

- Is convenient to users
- Facilitates waste management
- Allows implementation of capacity-improving methods
- Ensures water quality can be monitored
- Increases feasibility of local water management.

Pros

- Low cost
- Scalable
- Doesn't require electricity
- Proven in Bangladesh
- Easy to use

Cons

- Produce more waste
- Significant supply waste
- Less effective at removing As(III)
- Ions such as silicate and phosphate compete for adsorption site.

Future Aspects: (Under Experiments)

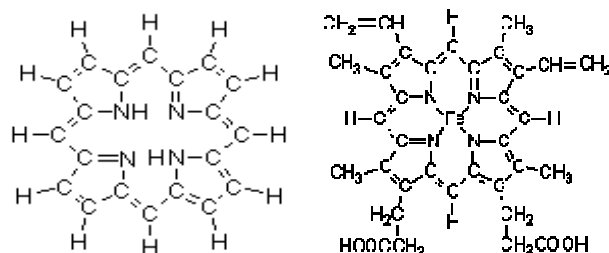
Chelation

Chelation describes a particular way that ions and molecules bind metal ions. According to the International Union of Pure and Applied Chemistry (IUPAC), Chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom. Usually these ligands are organic compounds, and are called chelants, Chelators, chelating agents, or sequestering agents.

Nearly complete removal of arsenate and chromate from solutions containing more than 100 mg/L was achieved in the presence of competing anions under a variety of conditions. Anion loading was more than 120 mg (anion)/g of adsorbent. A binding mechanism based on computer modeling was also proposed. First, Cu(II) ions bonded to ethylenediamine ligands to form surface octahedral complexes on the mesoporous silica. This gave rise to positively charged hosts with three-fold symmetry that match the geometry of tetrahedral anions. The anion binding involved initial electrostatic coordination, followed by displacement of one ligand and direct binding with the Cu (II) centre. Highly ordered mesoporous silica, SBA-15 impregnated with iron, aluminum, and zinc oxides were used for arsenic removal. A 10 wt. % aluminum-impregnated sample (designated to Al10SBA-15) had 1.9–2.7 times greater arsenate adsorption

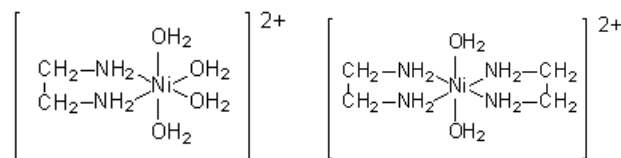
Capacities over a wide range of initial arsenate concentrations and a 15 times greater initial sorption rate at pH 7.2 than activated alumina. Fe(III)-Octolig-21 composite was prepared from dried Octolig-21 and used for arsenic remediation [300]. Octolig-21 is an immobilized ligand containing (polyethylene amino) groups bound to a silane that is covalently bound to silica gel. A stream of ingoing water containing 50 ppb as over

a 1 kg composite might last for months before column would lose effectiveness at the flow rate of 5 L/h.



Porphine

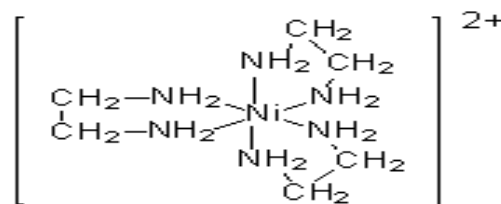
Heme



chelate with one ethylenediamine ligand

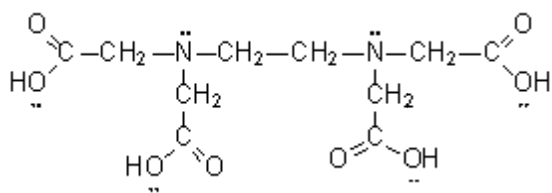
chelate with two ethylenediamine ligands

Porphine is a chelating agent similar to ethylenediamine in that it forms bonds to a metal ion through nitrogen atoms. Each of the four nitrogen atoms in the center of the molecule can form a bond to a metal ion. Porphine is the simplest of a group of chelating agents called porphyrin. Porphyrins have a structure derived from Porphine by replacing some of the hydrogen atoms around the outside with other groups of atoms. One important porphyrin chelate is **Heme**, the central component of hemoglobin, which carries oxygen through the blood from the lungs to the tissues. Heme contains a porphyrin chelating agent bonded to an iron(II) ion. Iron, like nickel, can form six bonds. Four of these bonds tie it to the porphyrin. One of iron's two remaining bonds holds an oxygen molecule as it is transported through the blood. Chlorophyll is another porphyrin chelate. In chlorophyll, the metal at the center of the chelate is a magnesium ion. Chlorophyll, which is responsible for the green color of plant leaves, absorbs the light energy that is converted to chemical energy in the process of photosynthesis. Another biologically significant chelate is **vitamin B-12**. It is the only vitamin that contains a metal, a cobalt (II) ion bonded to a porphyrin-like chelating agent. As far as is known, it is required in the diet of all higher animals. It is not synthesized by either higher plants or animals, but only by certain bacteria and molds. These are the sources of the B-12 found in animal products. Because vitamin B-12 is not found in higher plants, vegetarians must take care to include in their diets foods or supplements that contain the vitamin.



chelate with three ethylenediamine ligands

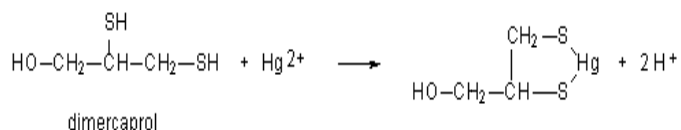
A chelating agent of particular economic significance is ethylenediaminetetraacetic acid (EDTA).



Ethylenediaminetetraacetic acid (EDTA)

EDTA is a versatile chelating agent. It can form four or six bonds with a metal ion, and it forms chelates with both transition-metal ions and main-group ions. In other applications, EDTA dissolves the CaCO_3 scale deposited from hard water without the use of corrosive acid. EDTA is used in the separation of the rare earth elements from each other.

Dimercaprol (2,3-dimercapto-1-propanol) is an effective chelating agent for heavy metals such as arsenic, mercury, antimony, and gold. These heavy metals form particularly strong bonds to the sulfur atoms in dimercaprol.

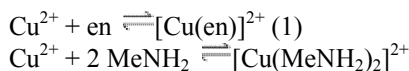


Dimercaprol was originally employed to treat the toxic effects of an arsenic-containing mustard gas called Lewisite [dichloro (2-chlorovinyl) arsine], which was used in World War I. The chelated metal cannot enter living cells and is rapidly excreted from the body. Since dimercaprol is water insoluble, it is dissolved in an oil base (often peanut oil) and injected intramuscularly.

Chelate Effect

The chelate effect describes the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar non-chelating (monodentate) ligands for the same metal.

Consider the two equilibria, in aqueous solution, between the copper (II) ion, Cu^{2+} and ethylenediamine (en) on the one hand and methylamine, MeNH_2 on the other.



In the bidentate ligand ethylene diamine forms a chelate complex with the copper ion. Chelation results in the formation of a five-membered ring. In (2) the bidentate ligand is replaced by two monodentate methylamine ligands of approximately the same donor power, meaning that the enthalpy of formation of Cu—N bonds is approximately the same in the two reactions. Under conditions of equal copper concentrations and when the concentration of methylamine is twice the concentration of ethylenediamine, the concentration of the complex (1) will be greater than the concentration of the complex. The effect increases with the number of chelate rings so the concentration of the EDTA complex, which has six chelate rings, is much higher than a corresponding complex with two monodentate nitrogen donor ligands and four monodentate carboxylate ligands. Thus, the phenomenon of the chelate effect is a firmly established empirical fact.

$\text{Cu}(\text{II})$ ions bonded to ethylenediamine ligands to form surface octahedral complexes on the mesoporous silica. This gave rise to positively charged hosts with three-fold symmetry that match the geometry of tetrahedral anions. The anion binding involved initial electrostatic coordination, followed by displacement of one ligand and direct binding with the $\text{Cu}(\text{II})$ center. Highly ordered mesoporous silica, SBA-15 impregnated with iron, aluminum, and zinc oxides were used for arsenic removal.

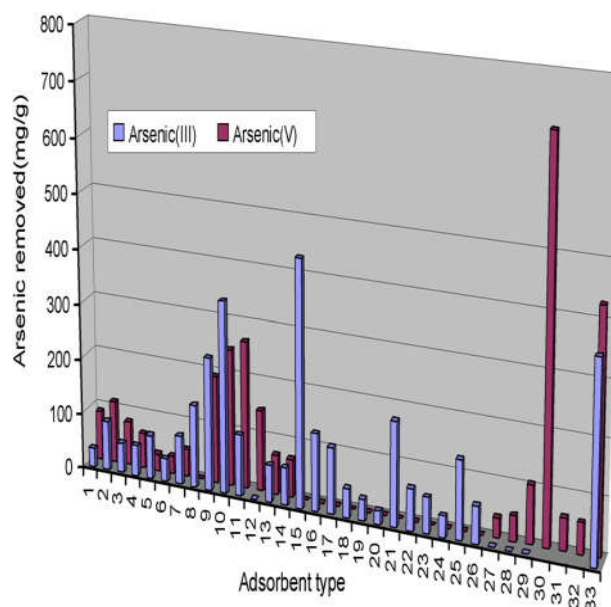
Applications

Chelators are used in producing nutritional supplements, fertilizers, chemical analysis, as water softeners, commercial products such as shampoos and food preservatives, medicine, heavy metal detox, and industrial applications.

In 2010, the Asia-Pacific region was the largest outlet, generating about 45% of worldwide demand for chelating agents. The region was followed by Western Europe and North America. The global chelating agents market is expected to reach more than 5 million tonnes in 2018.

Separation of Arsenic

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. We have a number of adsorbent to separate arsenic from sorbent and all these are listed and explained with their efficiencies as follows:



Sequentially, the adsorbents are Char carbon, Monoclinic hydrous zirconium oxide, Zr resin, Iron(III)-loaded chelating resin, Iron(III) oxide-loaded melted slag, TiO_2 , Zirconium(IV)-loaded chelating resin, Zirconium(IV)-loaded phosphoric chelate, Oxisol, Gibbsite, Ferrihydrite, Coconut husk carbon, Orange juice residue, Phosphorylated cross linked orange waste (POW), Goethite, Calcined mesoporous silica, Fe/NN-MCM-41, Co/NN-MCM-41, Ni/NN-MCM-41,

Cu/NN-MCM-41, Fe/NN-MCM-48, Co/NN-MCM-48, Ni/NN-MCM-48, Cu/NN-MCM-48, Alkaganeite, Shirasu-zeolite, *Penicillium purpurogenum*, *Lessonia nigrescens*, Synthetic hydrotalcite, Immobilized biomass, Mycan/HDTMA, Mycan/magnafloc, Basic yttrium carbonate. The graph shows that immobilized biomass is more efficient in separating As(5) rather than any other adsorbent and goethite can efficiently remove As(3).

Results vary from study to study depending on the Arsenic chemistry involved. Thus, it is very difficult to generalize the solidification/stabilization process. More work is needed to establish a commercial process for use on a large scale. Hydrated Fe(III) oxide (HFO) dispersed on a polymeric exchanger capable of removing As(III) and As(V) was regenerated using 10% NaOH. As (V) adsorbed on a Zr(VI)-

The properties of the above-described chelating agents are summarised in Table 3.

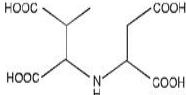
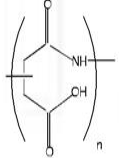
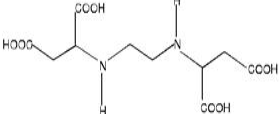
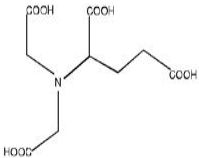
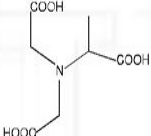
Name	Schematic structure	Physicochemical characteristic
IDS N-(1,2-dicarboxyethylene)-D,L-asparagine acid		molecular weight: 337.1 appearance: colourless to light yellow pH: 10.3-11.4 density: 1.32-1.35 g/mL solubility in H ₂ O: in any ratio biodegradability: > 80%
DS polyaspartic acid		molecular weight: [C ₄ H ₄ NO ₃ Na] _x appearance: clear reddish pH: 9.5-10.5 density: 1.3 g/mL solubility in H ₂ O: in any ratio biodegradability: > 60%
EDDS ethylenediamine-disuccinic acid		molecular weight: 358.1 appearance: colourless to yellowish pH: 9.2 density: 1.26 g/mL solubility in H ₂ O: in any ratio biodegradability: > 60%
GLDA N,N-bis(carboxymethyl)-L-glutamic acid		molecular weight: 351.1 appearance: colourless to yellowish pH: 13.5 density: 1.38 g/mL solubility in H ₂ O: in any ratio biodegradability: > 83%
MGDA methylglycine-diacetic acid		molecular weight: 271.0 appearance: clear yellowish pH: 11.0 density: 1.31 g/mL solubility in H ₂ O: in any ratio biodegradability: > 68%

Table 3. Physicochemical properties of IDS, DS, EDDS, GLDA and MGDA.

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. This solidified/ stabilized waste must satisfy leachability regulatory requirements prior to disposal. According to USEPA, a waste is deemed as hazardous material if the arsenic concentration in the Toxicity Characteristic Leaching Procedure (TCLP) leachate exceeds 5 mg/L. The solidification/stabilization process has not been fully optimized.

loaded phosphoric acid chelating resin (RGP) was quantitatively eluted with 0.4 mol/L sodium hydroxide with regeneration of the adsorbent.

Arsenic contamination of ground water- bangladesh story

In particular, a decision about 30 years ago by the United Nations (UN) and supported by its agencies the World Health Organization (WHO) and the UN Children's Fund (UNICEF) to switch people in Bangladesh from drinking bacteria-laden surface water to groundwater has now created the largest case of mass poisoning in the world. It is believed that the primary source of arsenic contamination in Bangladesh is the pyritic sedimentary rock laid down over millennia by the rivers that

run down from the Himalayas. The arsenic gets released into the groundwater mainly by the process of reductive dissolution of iron ox hydroxides, which contain high levels of arsenic and to a lesser extent by oxidation of arsenopyrite rocks. The latest reports (Ravenscroft, Brammer and Richards, 2009) show that contamination of groundwater is now more widespread, with people in 70 countries around the world now being exposed to toxic levels of arsenic in drinking water; the situation in Bangladesh is particularly alarming. The latest estimates in the World Bank's *World Development Report 2004* are that 'between 25 and 30 million people may be at risk in future' of arsenic poisoning. The British Geological Survey estimates that 35 million people are drinking water containing 50 ppb or more arsenic and in 2000, the WHO estimated that 35–77 million people were potentially exposed to high levels of arsenic in their drinking water. With over 1 million people (as reported in 2003 at the annual conference of the International Society for Environmental Epidemiology) have already being exposed to arsenic levels of 600 ppb and 90% of the Bangladeshi population of 125 million in 2000 getting their drinking water from groundwater which was contaminated by arsenic.

There is considerable research being done around the world to successfully treat contaminated groundwater and remove arsenic, or at least reduce its concentration to a safe level, particularly in Bangladesh. Currently, the only way to prevent Bangladeshi people's exposure to high levels is to test each tube well and identify wells that have high arsenic content and those that are safe (i.e. those with arsenic below 10 ppb). Wells that have arsenic levels above 10 ppb are painted red to prevent people from using them and those that are below 10 ppb are painted green.

It is imperative that people stop drinking from wells that contain water with high concentrations of arsenic. What is needed is a reliable, simple, fast, inexpensive and field-based method for arsenic detection Preliminary results on arsenic-contaminated groundwater samples from Perth and from Bangladesh indicate that the ASV method using the PDV6000+ instrument could be considered as an alternative method for field-based detection of arsenic in groundwater. This method thus provides a cheaper and accurate alternative to the currently used laboratory-based techniques. The World Bank is already interested in setting up a pilot project to evaluate the PDV6000+ instrument in Bangladesh.

Arsenic contamination of groundwater – under Observation in Kanpur:-

In global scenario, Kanpur is the top and famous for tannery industries. The Kanpur city is also known for their pollution in the world. The main reason of the pollution in Kanpur is due to the Tannery. Only about 20% of the chemicals used in the tanning process are absorbed by leather. Rest of these are released as waste, which is absorbed by bioaccumulation process in cultivated crops (1,2).The water of Kanpur is being tested in our college laboratory by our final year students under the guidance of HOD(Chemical Engineering) – Mr.S.R. Vidyarthi.

Arsenic contamination report of INDIA

As per observed in India, arsenic contamination is largely found in west Bengal. The threat of excess amount of arsenic in

water is increasing day to day basis. As there is a large need to make the situation in control and prevent other states to suffer from it. Here is the status of treatment of arsenic in West Bengal. In 2007, the **Public Health Engineering Department (PHED)** in West Bengal, India, began evaluating treatment processes to remove arsenic from drinking water supplies. The levels of arsenic in raw water supplies in this eastern India state frequently exceed the country's drinking water limit of 50 µg/l; some supplies contained arsenic levels of 1,000 µg/l. Just as the arsenic limit for drinking water in the United States was reduced in 2006 to 10 µg/l, so, too, might the limit in India be reduced to 10 µg/l in the future.

The West Bengal PHED set up an arsenic task force (ATF) to evaluate arsenic removal treatment technologies and processes that can reduce the arsenic to acceptable concentrations. The ATF guidelines required that any treatment process be capable of treating raw water with arsenic levels of 1,000 µg/l and must produce minimum quantities of sludge containing arsenic, which must be detoxified before disposal. Several technologies had been evaluated in recent years with varying degrees of success. One recent pilot study tested a system that promised to remove both arsenic and iron from raw water with the production of minimal quantities of sludge containing arsenic. Severn Trent Services installed a containerized **SORB 33®** arsenic demonstration unit at **Habra, West Bengal**, India. The unit was designed to treat 100 U.S. gallons per minute (378 litres per minute). The plant was commissioned on March 15, 2007 and operated six days per week until June 15, 2007, comprising a 90-day trial period.

Raw Water Quality at Habra

The raw water quality from the two tubewells available at Habra varied. The arsenic concentration ranged between 53 and 120 µg/l, and the average arsenic concentration during the trial was 82 µg/l. The raw water iron concentration also varied between 400 and 1,370 µg/l, and the average iron concentration during the trial was 860 µg/l

Treated Water Quality at Habra

SRL's arsenic sample results demonstrated that at the end of the trial the final treated water from the SORB 33 system contained arsenic below the limit of 10 µg/l and iron below the limit of 100 µg/l.

CONCLUSION

Estimation of techno-economic feasibility tells us about the best option. In other words, we can say that selection of the process according to the need of removal of a particular amount of arsenic is done by knowing the technical as well as the economic feasibility of all the methods possible.

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