

Arsenic and Fluoride Problems of Groundwater in West Bengal and Available Technologies for Remediation

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ABSTRACT : India is a subcontinent country with large amount of resources, though many places in India people uses Ground water as only source for drinking and domestic purpose. But ground water is not safe in most of the places. Arsenic and Fluoride can be taken care of major concern of ground water pollution in these days. Arsenic and fluoride contamination is found in many places in India and as well as in West Bengal also. There are lots of promising technology available for arsenic and fluoride removal but considering all the technologies it was found that using Electro-coagulation and activated alumina are convenient and suitable for removal. In West Bengal Baruipur is a place where both arsenic and fluoride is found. So adopting appropriate technology can remove both arsenic and fluoride at same time. Further experimental analysis need to be done for both the cases laboratory and field based.

KEY WORDS: Arsenic, Fluoride, Activated Alumina, Removal Technology, West Bengal, Groundwater, ARP

I. INTRODUCTION

The 85 % of rural population of the country uses ground water for drinking and domestic purposes. In West Bengal the arsenic concentration in drinking water is about 60 to 3700 $\mu\text{g/l}$ and about 40 million people are affected from it. In middle Ganga plain, Bihar, 206 tube wells (95% of total) were analyzed for arsenic content and showed that 56.8% tube wells have exceeded arsenic concentration of 50 $\mu\text{g/l}$ and 19.9% have more than 300 $\mu\text{g/l}$. In exposer of the arsenic level about 750 to 800 $\mu\text{g/l}$, which caused several skin and lung disease and arsenic concentration in well water used for drinking purpose were 10-1800 $\mu\text{g/l}$ and a peripheral vascular disease called "Black foot disease" is a common disease among the living population due to arsenicism. High concentration of fluoride in ground water beyond the permissible limit of 1.5 mg/l poses the health problem. World Health Organization (WHO) guideline value and the permissible limit of fluoride as per Bureau of Indian Standard (BIS) is 1.5 mg/L. Excessive fluoride in drinking water causes dental and skeletal fluorosis, which is encountered in endemic proportions in several parts of the world. In small doses it has remarkable influence on the dental system by inhibiting dental caries, while in higher doses, it causes dental and skeletal fluorosis. In India 62 million people including 6 million children are affected with fluoride related health diseases.

II.BACKGROUND

In West Bengal groundwater in 79 blocks (out of 341 blocks in the state) in the district of Malda (7 out of 15 blocks), Murshidabad (19 out of 26 blocks), Nadia (17 out of 17 blocks), North 24-Parganas (19 out of 22 blocks), South 24-Parganas (9 out of 29 blocks), Howrah (2 out of 14 blocks), Hooghly (1 out of 18 blocks) and Barddhaman (5 out of 31 blocks) is under the risk of Arsenic contamination. The problem of high fluoride concentration in groundwater resources has become one of the most important toxicological and geo-environmental issues in India. About 20 states of India, including 225 villages in 43 blocks of 7 districts were found to contain fluoride in ground water beyond permissible limit of West Bengal (Including 7 districts Birbaum, Bankura, Malda, Purulia, 24 South Parganas, Dakshin Dinajpur, Uttar Dinajpur), were identified as endemic for fluorosis and people in these regions are at risk of fluoride contamination.

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II. SCOPE OF RESEARCH

It was reported that in West Bengal at South 24 pargana, Baruipur is a place where both arsenic and fluoride has found in ground water (from Central Ground Water Board ministry of water resources Government of India, "Bhu-Jal News", Quarterly Journal Volume No.24 , Number 1, Jan-March 2009). This could be a major concern for both the aspect. A suitable technology must be incorporate so that the remediation can be done simultaneously for arsenic and fluoride contaminated water. This is the place where a future scope of work may be done.

III. METHODOLOGY FOR ARSENIC REMOVAL

Many of ARP (Arsenic Removal Process) technologies can be reduced in scale and conveniently applied at household and community level, for the removal of arsenic from groundwater. For arsenic removal technics conventionally distinguished into:

A. SMALL-SCALE WATER TREATMENT:

a. A simpler and less expensive form of arsenic removal is known as the Sono arsenic filter, using 3 pitchers containing cast iron turnings and sand in the first pitcher and wood activated carbon and sand in the second. Plastic buckets can also be used as filter containers. b. In the United States small "under the sink" units have been used to remove arsenic from drinking water. This option is called "point of use" treatment. The most common types of domestic treatment use the technologies of adsorption (using media such as Bayoxide E33, GFH, or titanium dioxide) or reverse osmosis. Ion exchange and activated alumina have been considered but not commonly used. c. Using black colored tablet contains Fe^{3+} salt, an oxidizing agent and activated charcoal. After addition of the tablet to the arsenic contaminated water, water turns black due to presence of carbon and after filtration it is easy to know whether there is any leakage from the filter.

B. LARGE-SCALE WATER TREATMENT:

Some large utilities with multiple water supply wells could shut down those wells with high arsenic concentrations, and produce only from wells or surface water sources that meet the arsenic standard. Other utilities, however, especially small utilities with only a few wells, may have no available water supply that meets the arsenic standard

a. **Oxidation and filtration:** Oxidation of As (III) to As (V) by adding suitable oxidizing agent followed by coagulation, sedimentation and filtration. Oxidation and filtration normally refer to the processes that are designed to remove naturally occurring iron and manganese from water. If arsenic is present in the water, it is removed via two primary mechanisms: adsorption and co-precipitation. First, soluble iron and As (III) are oxidized. The As (V) then adsorbs onto the iron hydroxide precipitation that are ultimately filtered from solution. In general, the Fe: As mass ratio should be at least 20:1. These conditions customarily result in an arsenic removal efficiency of 80-95%.

b. **Co-precipitation:** The effectiveness of arsenic co-precipitation, with iron, is relatively independent of source water pH, in the range 5.5 to 8.5. This technology can typically reduce arsenic concentrations to less than 50 $\mu\text{g/L}$ and in some cases below 10 $\mu\text{g/L}$. In order to remove arsenic by co-precipitation, coagulant is to be added. Water treatment with coagulants, such as alum $[Al_2(SO_4)_3 \cdot 18H_2O]$, ferric chloride $[FeCl_3]$ and ferric sulfate $[Fe_2(SO_4)_3 \cdot 7H_2O]$, are effective in removing arsenic from water. Ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and effect over a wider range of pH. In both cases, pentavalent arsenic can be more effectively removed than trivalent arsenic.

c. **Adsorption:** Activated Alumina, Iron filings (zero valent iron) and hydrated iron oxide. The technology can reduce arsenic concentrations to less than 50 $\mu\text{g/L}$ in general and in some cases even below 10 $\mu\text{g/L}$. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics.

d. **Iron oxide adsorption** filters the water through a granular medium containing ferric oxide. Ferric oxide has a high affinity for adsorbing dissolved metals such as arsenic. The iron oxide medium eventually becomes saturated, and must be replaced.

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e. **Ion Exchange** has long been used as a water-softening process, although usually on a single-home basis. It can also be effective in removing arsenic with a net ionic charge. (Note that arsenic oxide, As_2O_3 , is a common form of arsenic in groundwater that is soluble, but has no net charge.)

f. Both **Reverse osmosis** and **electro dialysis** (also called *electrodialysis reversal*) can remove arsenic with a net ionic charge. (Note that arsenic oxide, As_2O_3 , is a common form of arsenic in groundwater that is soluble, but has no net charge.) Some utilities presently use one of these methods to reduce total dissolved solids and therefore improve taste. A problem with both methods is the production of high-salinity waste water, called brine, or concentrate, which then must be disposed of.

C. EMERGING METHODS

Besides the conventional methods mentioned above several new methods have been studied recently. Some interesting methods are shortly described below.

a. **Fe-Mn-Oxidation:** Conventional iron and manganese removal can result in significant arsenic removal, through coprecipitation and sorption onto ferric or manganic hydroxides. Most low-cost methods for arsenic and manganese removal rely on aeration and filtration through porous media such as sand and gravel. Any method that effectively removes iron and manganese could be evaluated to see if arsenic is also removed effectively.

b. **Green sand filtration:** Greensand is a granular material composed of the mineral glaucite, which has been coated with manganese oxide. It is a natural zeolite (microporous mineral), and has strong ion exchange properties, and will remove iron, manganese, arsenic, sulphide, and many other anions (Water & Wastes, 2003). Like manganese dioxide coated sand, greensand surface is strongly oxidizing, and is thus able to remove both arsenite and arsenate. This method is especially interesting to utilities where Fe and Mn are already being removed using a manganese greensand filter. It is possible that a small pH adjustment from 8+ to 6.5 may be all that is required to bring the facility into compliance.

c. **Coagulation assisted Microfiltration:** In coagulation assisted microfiltration technology, microfiltration is used in a manner similar to a conventional gravity filter. The advantages of MF over conventional filtration are a more effective microorganism barrier, removal of smaller floc sizes and an increased plant capacity (EPA, 2000). The microfiltration membrane system works to remove arsenic from water by the addition of an iron-based coagulant, such as ferric chloride, to the water. The arsenic is adsorbed onto positively charged ferric hydroxide particles, which are then removed by micro-filtration. In pilot studies, the removal of arsenic to below 2 $\mu\text{g/l}$ is reported in waters with a pH between 6 and 7.

d. **In situ (sub-surface) arsenic immobilization:** When arsenic is mobilized in groundwater under reducing conditions, it is also possible to immobilize the arsenic by creating oxidized conditions in the subsurface. In Germany, in order to remediate an aquifer containing high arsenite, high ferrous iron, low-pH groundwater, potassium permanganate was injected directly into contaminated wells, oxidizing arsenite, which coprecipitated with ferric oxides as ferric arsenate. Arsenic concentrations were reduced by over 99%, from 13,600 to 60 $\mu\text{g/l}$.

e. **Enhanced coagulation (aka electrocoagulation, electroflotation):** With enhanced coagulation, aka electrocoagulation or electroflotation, soluble anodes made from iron or aluminum are used. Reported advantages mentioned in laboratory studies are the in-situ oxidation of As (III) to As (V), and better removal efficiencies than with classical coagulation. Also organic arsenic, fluoride and dissolved metals are removed by this method. Final As concentrations in groundwater are below 10 $\mu\text{g/l}$, even with high initial concentrations. An additional advantage of enhanced coagulation is the reported removal of natural organic matter (NOM).

f. **Biological arsenic removal:** Arsenic in water can be removed by microbiological processes (Rahman and Ravenscroft, 2003). Two main types of metal-microbe interactions can be potentially used for the removal of arsenic from ground water. They are (a) microbial oxidation of arsenic (III) to arsenic (V) to facilitate its removal by conventional arsenic removal processes, and (b) bioaccumulation of arsenic by microbial biomass.

g. **Phytoremediation:** Some aquatic plants have capacity to accumulate arsenic. Among these aquatic plants, Azolla and Spirodella (duckweed) species have the highest efficiency of arsenic absorption. In study it was revealed that

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Spirodella polyrhiza species was found to absorb arsenic very efficiently. The results indicated that a complete cover of *Spirodella polyrhiza* could accumulate about 175 g of arsenic from a pond of one hectare area per day.

h. Electrokinetic treatment: Electrokinetic treatment is an emerging remediation method designed to remove heavy metal contaminants from soil and groundwater. The method is most applicable to soil with small particle sizes, such as clay. A current passed between electrodes is intended to cause water, ions, and particulates to move through the soil, waste, and water. Components arriving at the electrodes can be removed by means of electroplating or electrode position, precipitation or coprecipitation, adsorption, complexing with ion exchange resins, or by pumping of water (or other fluid) near the electrode (EPA, 2002).

i. IOCS (iron oxide coated sand) & Memstill: UNESCO-IHE developed an arsenic removal method based on adsorption on iron oxide coated sand (IOCS). IOCS is a by-product from groundwater treatment plants and consequently very cheap. The Netherlands Organization of Applied Scientific Research (TNO) has developed a membrane based distillation concept which radically improves the economy and ecology of existing desalination technology for seawater and brackish water. This so-called "Memstill technology" combines multistage flash and multi-effect distillation modes into one membrane module.

j. Water Pyramid: Aqua-Aero Water Systems has developed the Water Pyramid concept for tropical, rural areas (Aqua-Aero Water systems, 2007). The Water Pyramid makes use of simple method to process clean drinking water out of salt, brackish or polluted water. One of the pollutants could be fluoride. Most of the energy needed to clean the water is derived from the sun.

k. Solar Dew Collector: Solar Dew purifies water uses a new porous membrane to purify water using solar energy (Solar Dew, 2007). The technique is similar to the Water Pyramid. Water sweats through the membrane, evaporates on the membrane's surface and increases the air humidity in the evaporation chamber. Based on a temperature difference, pure water condenses on the cooler surfaces of the system.

IV. METHODOLOGY FOR FLUORIDE REMOVAL

There are few technology available for fluoride removal. The unique potentiality of these different technological methodology is unique from one another.

a. Nalgonda Technique: In the Nalgonda Technique two chemicals (Dahi et al. 1996), alum (aluminum sulphate or kalium aluminum sulphate) and lime (calcium oxide) are added to and rapidly mixed with the fluoride contaminated water. Induced by a subsequent gentle stirring, flocs develop (aluminum hydroxides) and are subject to removal by simple settling. The main contents of the fluoride is removed along with the flocs, due to a combination of sorption and ion exchange with some of the produced hydroxide groups.

b. Precipitation methods: Fluoride removal by alum (Culp et al., 1958), a method studied for application alum dose. 225 ppm of alum in increments during rapid mixing and flocculation followed by settling and rapid sand filtration was verified. It was desired to reduce the raw water fluoride concentration from 3.6 to 1.0 ppm. Boruff's (1934) investigation, aluminum sulfate dosages of 8.5 ppm (0.5 gram) to 171 ppm (10 grams) per gallon were added to 2.5 liters of raw water containing known quantities of fluorides.

c. Activated alumina: Activated alumina is a granular, highly porous material consisting essentially of aluminum trihydrate. The use of activated alumina in a continuous flow fluidized system is an economical and efficient method for defluoridating (Kubli et. al. (1947), Ghorai et al. 2004) water supplies. The process could reduce the fluoride levels down to 0.1 mg/L. The operational, control and maintenance problems, mainly clogging of bed, may be averted in this method.

d. Electro coagulation (Electrochemical methods): Electro coagulation process with aluminum bipolar electrodes was used for defluoridation process. The influence of parameters such as inter-electrode distance, fluoride concentration, temperature and pH of the solution were investigated and optimized with synthetic water in batch mode.

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The basic principle (N. Mameri, et al. 1997) of the process is the adsorption of fluoride with freshly precipitated aluminum hydroxide, which is generated by the anodic dissolution of aluminum or its alloys, in an electrochemical cell. Constraints in the above technology: Electricity is the main raw material and hence wherever electricity is not available a suitable solar panel can be installed.

e. Bone Char: Bone char is simply ground animal bones charred to remove all organics. It consists essentially of tricalcium phosphate and carbon. It has been utilized by Scott et al. (1937) and Sorg et al. (1978) in full scale defluoridation plants. This material initially developed for decoloring cane syrup is more economical than bone. The ability to be regenerated by washing with caustic soda made bone char useful in fluoride removal processes.

f. Contact Precipitation: It is a technique by which fluoride is removed from the water through the addition of calcium and phosphate compounds and then bringing the water in contact with an already saturated bone charcoal medium.

g. Degreased and alkali treated bones : Degreased and alkali treated bones are effective in the removal of fluoride from initial fluoride concentration ranging from 3.5 mg fluoride/L to 10 mg fluoride/L to less than 0.2 mg fluoride/L.

h. Synthetic tri-calcium phosphate: The product is prepared by reacting phosphoric acid with lime. The medium is regenerated with 1% NaOH solution followed by a mild acid rinse. It has a capacity to remove 700 mg fluoride/L

i. Florex: A mixture of tri-calcium phosphate and Hydroxy-apatite, commercially called Florex, showed a fluoride removal capacity of 600 mg of fluoride per liter and is regenerated with 1.5% sodium hydroxide solution.

j. Activated Carbon & Lime: Most of the carbons prepared from different carbonaceous sources showed fluoride removal capacity after alum impregnation. High Fluoride removal capacities of various types of activated carbons had been reported. Scott et al (1937) and others showed that the decrease in fluoride concentration was a function of the amount of magnesium removed during the softening process. Upon a routine examination of raw and treated municipal water supplies, it was (Scott et al. 1937) reported that fluoride concentration in the effluents from lime softening plants showed a substantial reduction when compared to the fluoride in the raw water.

k. Ion Exchange Resins: Strong base exchange resins remove fluorides (Meenakshi et al. 2007). Cation exchange resins impregnated with alum solution have been found to act as defluoridation agents.

l. Magnesite & Serpentine: Investigations were conducted to study the usefulness of magnesite in fluoride removal. Crystalline magnesium hydroxide was obtained by reacting a magnesium salt with milk of lime. Serpentine is a mineral name, formula $Mg_3Si_2O_5(OH)_2$. The material is green or yellow and is available in Andhra Pradesh. To test the capacity of serpentine to remove fluorides from waters (Chidambaram et al. 2003), the green and yellow varieties were studied for their defluoridation capacity.

m. Lime stone, special soils and clay etc.: Recently limestone and heat-treated soil were tried for fluoride removal. Limestone was used in a two-column continuous flow system (limestone reactor) to reduce fluoride concentrations from wastewaters to below the MCL (Maximum contaminant level) of 4 mg/L. On the basis of experimental data a plausible mechanism of fluoride sorption by clay minerals is suggested. Removal of fluoride by adsorption on to low-cost materials like kaolinite, bentonite, charfines, and lignite seeds was investigated.

n. Fly Ash and natural minerals: The removal of fluoride was attempted using natural materials such as red soil, charcoal, brick, and fly-ash. The study reveals that red soil has good fluoride removal capacity followed by brick, fly-ash and charcoal.

In the report of "Fluoride in groundwater: Overview and evaluation of removal methods" & "Arsenic in groundwater: Overview and evaluation of removal methods" by International Groundwater Resources Assessment Centre (2008) based on available information. A promising emerging technique is Enhanced Coagulation (EC). With this technique a very efficient removal of As (III) and As (V) is possible to below the recommended WHO-value of 10 $\mu\text{g/l}$. With EC also the removal of fluoride, humic substances and other harmful or toxic matters is realized (metal hydroxides). For

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groundwater with high iron content, also conventional iron removal techniques, like aeration and filtration, can be used to remove arsenic at low costs. However the efficiency of these techniques for As-removal is not very high. The Nalgonda process, Bone charcoal and Calcined clay are low costs methods for domestic use. On a community scale, the Nalgonda process is also a low cost option. If a high fluoride removal is necessary then activated alumina, reverse osmosis and electrodialysis are preferred methods. For brackish water only reverse osmosis, electrodialysis and the Water Pyramid/Solar Dew method can be used.

V.CONCLUSION

Arsenic and fluoride contamination problems in groundwater is a major concern. Though these two affecting parameters are totally different from each other but critical situations and carcinogenic disease can be occurred for both cases. A typical situation like Baruipur, where arsenic and fluoride can be occurred at same time. Adopting appropriate technology can remove both arsenic and fluoride at same time. Further experimental analysis need to be done for both the cases laboratory and field based.

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