

# Sustainability of in Situ Treatment of Underground Water Containing Arsenic

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**Abstract:** A laboratory setup for studying the in situ process of removing arsenic from underground water is prepared. The experiments were performed with a varying ratio of arsenic and iron, the latter acting as an adsorbing agent. The arsenic concentration of each of the solution is measured after a span of time. The change in concentration of arsenic is then used as a parameter to analyze the performance of adsorbent and for the qualitative analysis of the sand-bed.

**Keywords:** Arsenic, in situ technique, adsorption, sand-bed, arsenic kit

## 1. Introduction

Exposure to contaminated groundwater has been a major public health problem in India, USA, Bangladesh, Taiwan, Mexico, Mongolia, Argentina and Chile. More than 100 million people worldwide have been estimated to be chronically exposed to arsenic from drinking water containing high arsenic levels (Oddin and Huda, 2011). The situation is devastating in West Bengal and Bangladesh. The groundwater has Arsenic content as high as 200 ppb, whereas the WHO permissible limit is 10 ppb only.

To curb the problem, many Arsenic removal methods have been undertaken worldwide. Conventional arsenic remediation strategies primarily involve above-ground or ex-situ technologies. The ex-situ techniques include:

a) Oxidation: Arsenate (As<sup>5+</sup>) being less mobile than arsenite (As<sup>3+</sup>), it tends to co-precipitate with metallic cations or get adsorbed onto solid surfaces. The process can be carried out in three ways:

- 1) Air Oxidation
- 2) Chemical Oxidation
- 3) Biological Oxidation

b) Coagulation: Hydrolysing metal salts have been found effective for arsenic removal, out of which ferric chloride was found to be the best [1]. But it is observed that oxidation of As (III) to As (V) is necessary to achieve effective removal of As (III) during coagulation with FeCl<sub>3</sub>. Also, disposal of arsenic containing sludge is a cause of concern.

c) Membrane Method: Contaminants are removed by applying pressure on the feed water to direct it through a semi permeable membrane. Reverse osmosis and Nano-filtration have been found to be quite effective with high removal efficiencies of As (III) [2]. The high capital and running cost of this technique prevents its large scale use.

d) Adsorption: It is a surface phenomenon, so greater the surface area of the medium, greater its capacity to accumulate material. Various adsorbents effectively used for arsenic removal are iron hydroxide [3], activated carbon [4], activated alumina [5] etc. Activated alumina was found to be

the best in removal of As, but As (III) was less effectively removed than As (V) [4]. But activated alumina exhibits slow adsorption kinetics. The waste stream from regeneration of spent activated alumina is quite toxic and needs proper disposal [6].

An overview of the above ex-situ techniques revealed major disadvantages associated with them. First of them being high operational and running cost. Many techniques discussed above have high operational costs, i.e. the cost involved in setting up the plant to start the process. Others have high running costs like the Membrane Method where change of membranes is required at frequent interval or the adsorption method where the adsorbent becomes useless after some time and needs to be changed. Second major issue is the problem of disposal of sludge material containing high arsenic content.

The latter point poses serious concern for environmental health. On one hand it is highly carcinogenic for the biomass, while on other, there are high chances of Arsenic seeping into the groundwater again, making the whole process go in vain [7]. These concerns urged people to look for techniques which could avoid these problems, and henceforth the in situ techniques were brought into action.

In the in situ technique, arsenic is effectively immobilized within the aquifer using ions like Fe<sup>2+</sup>, Mn<sup>2+</sup> etc. A plant consisting of two wells is alternatively used for pumping or infiltrating water enriched with reactive chemicals like Iron Chloride or Iron Sulphate [8]. At first, As (III) is oxidized to As (V) & Fe<sup>2+</sup> to Fe<sup>3+</sup> and then to iron hydroxide on which these ions get adsorbed [9]. The in situ method has low operational cost and avoids the problem of sludge disposal as no sludge is generated in the process, thus being advantageous over their ex situ counterparts.

The in situ techniques currently being employed involve adsorption and/or precipitation of ions in the sub surface layers. These affect the porosity of the aquifer and the usability of the adsorption site. In times ahead, there is a possibility of aquifers being clogged or arsenic being released from the adsorbent into the aquifer again, making the whole process go in vain. The overall objective of our

project is to approach these problems and analyze the situation using experimental simulations.

The specific objectives of our project includes analyzing the effect of adsorption and precipitation on the porosity of the media and the adsorption sites.

## 2. Literature Review

Various in situ technologies have been in use since many years to serve different purposes like extraction of oil from underground oil reserves, remediation of hazardous substances present in soil etc. Some of the underlying technologies for the latter include Soil Flushing, Vapor Extraction, Bio-treatment, Landfilling and Incineration (U.S. Environmental Protection Agency under Contract Number 68-W-03-038). Further, the in situ techniques were also applied to remediate the groundwater, contaminated with metal ions like  $Fe^{2+}$ . Oxygenated water is injected into the aquifer which oxidizes the ferrous ions in the pore space and forms ferric oxy-hydroxide precipitate. During pumping this ferrous ion is sorbed from groundwater on the exchange/adsorption site. In situ iron removal has proved to be a useful technique for reducing iron concentration in groundwater [10].

Based on similar lines, many experimental studies were done to see the effectiveness of this technique in removal of Arsenic from the underground water. The experiments yielded positive results and were successful in reducing the arsenic concentration of aquifers. The working of an in situ plant is explained further.

The process of in-situ oxidation of groundwater virtually transfers the oxidation and filtration process of the conventional above ground water treatment plants into the aquifer. The underground aquifer is used as a natural biochemical reactor. In the treatment method, the aerated tube well water is stored in feed water tanks and released back into the aquifers through the tube. The dissolved oxygen in aerated water oxidizes arsenite ( $As^{3+}$ ) to less-mobile arsenate ( $As^{5+}$ ), the ferrous iron to ferric iron and Manganese(II) to Manganese(III), followed by adsorption of arsenate on  $Fe(III)$  and manganese(III) resulting in a reduction of the arsenic content in tube well water. The in situ method is a very cost effective and eco-friendly process for arsenic removal. The greatest advantage of this process is that there is no need for sludge handling.

Thus, this technology has been replicated on large scales to set up a full operational plant in many parts of the world. Major ones includes Bengal Delta (West Bengal and Bangladesh), Carson Valley, Douglas County, Nevada and Northern Germany.

Despite being successful in achieving lower concentration of Arsenic in aquifers, the above listed projects and papers fail to analyze the further effect of these treatments on aquifers and adsorption sites, eg. reduction in porosity, clogging, etc. Studies have been done to get optimized result for other

factors like pH, contact time, temperature and best iron to arsenic ratio. But, no study or experiment has been done to probe these issues and hence the question of the time of usability of a site and the volume it can filtrate, remains still unanswered. The objective of our project is to analyze and find answers to these issues.

## 3. Materials and Methods

### 3.1 Materials

The major equipment used throughout the process were Arsenic Kit, pH meter, micropipette, and weighing Balance. The chemicals required were Sodium Arsenite, ferric chloride, acetone and sand.

### 3.2 Methods

#### 3.2.1. Preparation of Solutions

- Arsenic stock solution (0.01 mg/l): prepared using sodium arsenite
- Ferric chloride stock solution (1mg/ml): diluted to required concentrations.

#### 3.2.2. Cleaning of Sand

The sand being used is washed first using acetone and then several times using de-ionized water. The pH is checked every time after washing to get a final pH value less than 8.

#### 3.2.3. Experimental Procedure

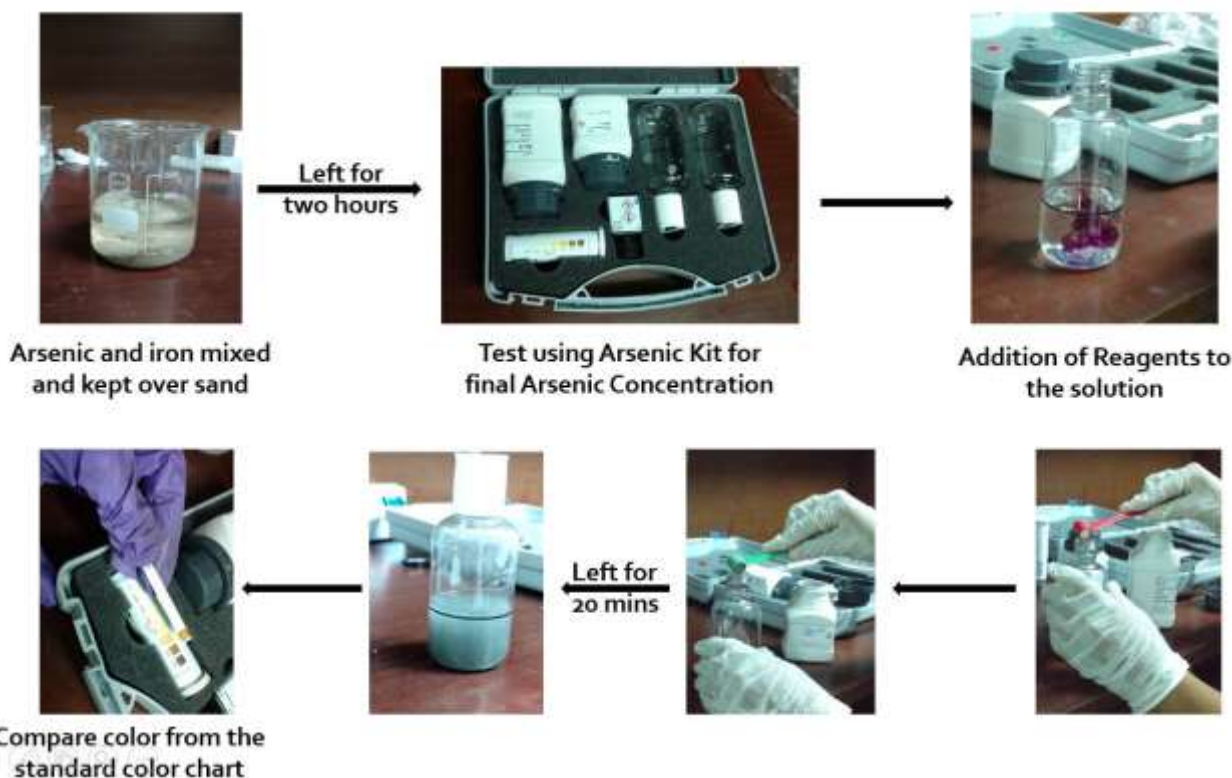
For testing and verification of Arsenic Kit, standard solutions of two different arsenic concentrations were prepared and then tested using the kit.



Figure 1: Testing of arsenic kit with a standard solution of 40 ug/L



Figure 2: Testing of arsenic kit with a standard solution of 200 ug/L



**Figure 3:** Step by step procedure for using an arsenic kit to determine arsenic concentration in the solution

For the main experiment and procedure of testing, 50-100 mL volume of sand is first cleaned and then kept in a beaker. 100 mL of arsenic solution and 100 mL of ferric chloride solution is added to it. The setup is left for 2 hours. The final arsenic concentration of the solution is measured using the arsenic kit. The entire procedure has been illustrated in Figure 3.

#### 4. Results and Discussion

First trial was an arsenic solution in absence of iron and sand-bed with an initial concentration of 100ug/L and pH of 7.0. The solution was left for 2 hours. For this particular setup, no change in arsenic concentration was observed (See Figure 4). Thus, ferric chloride solution is added to see if it can cause decrease in concentration of arsenic by adsorption over sand-bed.



**Figure 4:** Result for an arsenic solution in absence of iron and sand-bed

Addition of iron in the arsenic solution with As: Fe ratio of 1:5, an initial arsenic concentration of 100ug/L and pH of 7.0, second experiment was carried out. In one case, the solution is left for 2 hours, while in other case it was left for 18 hrs. Both of them showed a slight increase in concentration of arsenic, though increase in contact time creates no difference (See Figure 5 & 6). To check if extra arsenic was from sand, next experiment was done in its absence.



**Figure 5:** Result for an arsenic solution with As:Fe ratio 1:5 left for 2 hours

The next experiment has Arsenic and iron solution in the ratio of 1:5 in absence of sand. Initial arsenic concentration in the solution was 100ug/L with a pH of 7.0. The solution was left for 2 hrs. A slight decrease in concentration of arsenic was observed (See Figure 7).



**Figure 7:** Result for an arsenic solution with As:Fe ratio 1:5 in absence of sand-bed



**Figure 9:** Result for arsenic solution with As:Fe ratio of 1:20 and pH 7

To confirm whether the release of arsenic was from sand, water with no arsenic and just sand-bed with a pH of 7.0 was taken. The solution is left for 2 hrs. In this experiment, arsenic concentration observed thus verifying release of arsenic from sand (See Figure 8).



**Figure 8:** Result for arsenic concentration for water with no arsenic and just sand-bed



**Figure 10:** Result for arsenic solution with As:Fe ratio of 1:20 and pH 6

In the series of experiment, the arsenic to iron ration in the arsenic solution is increased to 1:20 with an expectation of increased adsorption. Initial arsenic concentration of the solution was 100 ug/L and pH was 7.0. The solution was left for 2 hours. Even in this case, only a slight decrease in arsenic concentration was observed (See Figure 9).



**Figure 6:** Result for an arsenic solution with As:Fe ratio 1:5 left for 18 hours

Decreasing the pH of solution to 6 with other factors being constant shows a significant decrease (up to 50ug/L) in arsenic concentration (See Figure 10).

## 5. Conclusion

Performing experiment without using sand or iron with the water shows no decrease in arsenic concentration. This indicates that there is no adsorption on glass wares. Whereas, experiment on sand-bed with Fe:As ratio as 5:1 with solution left for 2 hours showed slight increase in concentration of arsenic. By increasing the contact time to 18 hours for same experimental condition as previous one creates no difference in adsorption of arsenic. After thus another experiment without sand-bed with Fe:As ratio as 5:1 with solution left for 2 hours was performed. This showed a slight decrease in arsenic concentration in the water. The overall experiment gives us an idea that an increase in concentration of arsenic observed in previous experiment might be due to release of arsenic from sand.

An additional test of water over sand-bed without addition of arsenic solution showing arsenic concentration around 25ug/L confirming presence of arsenic in sand. The last experiment with Fe:As ratio increased from 5:1 to 20:1 was expected to enhance adsorption. Yet again only slight decrease in concentration was observed, conforming the release of arsenic from sand.

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