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## DESORPTION AND STABILITY STUDIES ON As (V) LOADED FERRIC HYDROXIDE

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TCLP

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## ABSTRACT

Arsenic is a commonly occurring toxic metal in natural systems and the root cause of many diseases and disorders. Mainly iron oxides/hydroxides and alumina are considered as efficient adsorbents for arsenic removal. As(V) on iron based oxides/hydroxides from effluents and drinking water contaminated with arsenic have been widely reported. However, most of the reported work is devoted to the adsorption of arsenic while desorption characteristics of arsenic from the loaded surfaces before discarding the solids is much less studied. In the present work desorption and stability studies on As(V) loaded ferric hydroxide are reported. During desorption the effect of three parameters namely contact time, pH and presence of Ca<sup>2+</sup> ions were studied. The pH was varied in the range of 4.0 to 8.0 at 35°C over a period of 96 hr. TCLP (Toxicity Characteristic Leaching Procedure) tests were performed on loaded ferric hydroxide to estimate the stability of loaded solids. To reduce the solubility of As(V), the loaded ferric hydroxide was calcined at 200°C for 2hr. The TCLP test carried out on the calcined material showed that 200°C calcination temperature was enough to stabilize the loaded ferric hydroxide even if the new regulations of TCLP comes into force.

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## INTRODUCTION

Water is one of the major means of transport of arsenic in the environment. In the aquatic environment it is predominant in places with high geo-thermal activity. It is one of the most toxic elements in the environment and is of great interest in environmental studies (Siegeal 2002; Smedley and Kinniburgh, 2002). In India, states like Uttar Pradesh, Bihar, Jharkhand, West Bengal, Assam, Manipur, mainly in Ganga-Meghna-Brahmaputra (GMB) plain covering an area of about 569749 sq km with a population of over 500 million have reported serious illnesses due to presence of arsenic. Arsenic-enriched groundwater is also found in other parts of world, e.g. Bangladesh, USA (Arizona) and Korea (PHED, UNICEF, 1999). Arsenic occurs naturally in rocks and soil, water, air, and plants and animals. It can be further released into the environment through natural activities such as volcanic action, erosion of rocks and forest fires, or through human actions. Approximately 90 percent of industrial arsenic in the U.S. is currently used as a wood preservative, but arsenic is also used in paints, dyes, metals, drugs, soaps and semi-conductors. High arsenic levels can also come from certain fertilizers and animal feeding operations. Industry practices such as copper smelting, mining and coal burning also contribute to arsenic in our environment. Higher levels of arsenic tend to be found more in ground water sources than in surface water sources (*i.e.* lakes and rivers) of drinking water. The demand on ground water from municipal systems and private drinking water wells may cause water levels to drop and release arsenic from rock formations. Compared to the rest of the United States, western states have more systems with arsenic levels greater than EPA's standard of 10 parts per billion (ppb). Parts of the Midwest and New England have some systems whose current arsenic levels are greater than 10 ppb, but more systems with arsenic levels that range from 2-10 ppb. While many systems may not have detected arsenic in their drinking water above 10 ppb, there may be geographic "hot spots" with systems that may have higher levels of arsenic than the predicted occurrence for that area. On January 22, 2001 EPA adopted a new standard for arsenic in drinking water at 10 parts per billion (ppb), replacing the old standard of 50 ppb. The rule became effective on February 22, 2002. The date by which systems must comply with the new 10 ppb standard is January 23, 2006.

### Toxicity

Although arsenic is not the most toxic element especially in pentavalent state yet the same has drawn attention because of its notoriety as a poison both in history and popular literature. Important factors to be considered for a water source to be used for drinking purposes are its bacteriology quality and presence of certain inorganic constituent like fluoride and arsenic. The toxicity of arsenic varies greatly with its oxidation states as As(+3) is much more toxic and mobile than As(+5). Numerous recent investigations indicated that arsenic constitutes a serious health risk at different places and it was also confirmed by medical studies. Ingestion via food or water is the main pathway of this metalloid in the organism, where its absorption takes place in the stomach and intestines, followed by its release into the blood stream. It gets deposited on or bound to tissues. Arsenic is converted by the liver to less toxic form, which is eventually largely excreted in the urine. It was estimated that more than two lakh people in West Bengal have arsenic skin lesions. Arsenic toxicity develops insidiously after six to twenty months of drinking arsenic contaminated water. In the initial period the skin of the body or palm becomes dark (diffuse melanosis) followed by spotted melanosis usually on chest, back or limbs. Leucomelanosis is common in persons who stopped arsenic contaminated water, but had spotted melanosis earlier. The other symptoms are conjunctival congestion, non-pitting swelling of feet, complications like liver and spleen enlargement and fluid in abdomen. Prolonged use of arsenic contaminated water results in carcinoma affecting lungs, bladder and other sites.

### Treatment methods

Various treatment methods have been adopted to remove arsenic from drinking water under both laboratory and field conditions. The major mode of removing arsenic from water is by physico-chemical treatment methods. Various treatment methods include:

- adsorption-co-precipitation using iron and aluminium salts (Chow, 1997; Harper and Kinghom, 1992; Raman and Sengupta, 1992)

- adsorption on activated alumina/activated carbon/activated bauxite (Elizalde, 2001; Gregor, 2001; Gupta and Chen, 1978 and Huang and Fu, 1984).

- Reverse osmosis

- Ion exchange (Clifford and Lin, 1991)

- Oxidation followed by filtration (Bellack, 1971)

Arsenic adsorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, presence of competing anions, and solid phase structural changes at the atomic level. As a result, arsenic may be present in a variety of redox states. Arsenic and arsenite are the two forms of arsenic commonly found in ground water. Currently, Al or Fe hydroxides are commonly used as adsorption agents in water treatment systems (Hering *et al.*, 1996). Activated alumina is another such adsorbent, which has a great affinity for various organic and inorganic pollutants. It has been reported that activated alumina has been effective for arsenic removal (Lin and Wu, 2001; Singh *et al.*, 2001). In an earlier investigation, it was observed that ferric hydroxide can adsorb ~ 15 mg of As(V)/g of material. The arsenic loaded oxides need to be safely disposed. The disposal of the arsenic-containing sludge has to be done in a way that does not lead to its remobilization. Since there is no systematic data available on stability of arsenic loaded ferric hydroxide this work has been taken up. The aim of this work is to evaluate the stability of As(V) loaded ferric hydroxide by carrying out studies on desorption of As(V) under different conditions.

## MATERIALS AND METHODS

### Preparation of Ferric hydroxide

250 mL of 1 M  $\text{Fe}(\text{NO}_3)_3$  solution was taken in a beaker. The solution was stirred using a magnetic stirrer and 10 M NaOH solution was added to that beaker drop wise till the solution pH became 7.0. Distilled water was added to the slurry to double its volume and kept for 2hr for aging. After that the slurry was filtered, the precipitate was washed with distilled water till the precipitate was free from nitrate, which was confirmed by brown ring test. The precipitate was then dried at 110°C for 24hr. The same procedure was repeated to obtain the bulk material for carrying out the studies.

The particle size and specific surface area of ferric hydroxide sample was determined using a Malvern Particle Size Analyzer.

### Preparation of As(V) loaded Ferric hydroxide

The As(V) loaded ferric hydroxide was prepared under the following conditions: quantity of ferric hydroxide = 0.10 g, volume of arsenic solution = 100 mL, concentration of arsenic solution = 20 mg/L, initial pH = 7.0, time = 1hr, temp. = ambient (~25°C). The adsorption capacity under the above mentioned conditions was found to be 14.79 mg/g of adsorbent. The bulk sample of As(V) loaded ferric hydroxide was prepared by taking 25 grams of ferric hydroxide and treating under the conditions mentioned above.

### Desorption studies

The desorption of arsenic from As(V) loaded ferric hydroxide at 35°C at different pH (4.0 – 8.0) was studied. The solution volume used in each experiment was 100 mL. 0.2g of arsenic loaded aluminic ferrihydrite was taken for each experiment. To maintain the pH (4.0 – 8.0) of solution, a suitable volume of HCl or sodium hydroxide was added. Samples were withdrawn at different time intervals and filtered. The filtrates were analyzed to determine the extent of As(V) desorption from loaded solids.

### US EPA TCLP test (Toxicity Characterisation Leaching Procedure)

The test solution was prepared by using 5.7 mL of glacial acetic acid and 64.3 mL of 1.0 M NaOH made up to 1L, at pH 4.93. One gram of As(V) loaded ferric hydroxide was taken in 20 mL of solution and agitated at 30 rpm for a period of 20hr in a horizontal shaker. The filtrate was analysed for As(V) to know the leachability.

## Calcination

The arsenic loaded ferric hydroxide was calcined at 200°C for 2h in a muffle furnace and the calcined samples was subjected to TCLP test.

## RESULTS AND DISCUSSION

### Surface area and particle size results

The results on particle size distribution and surface area are given in Table 1.

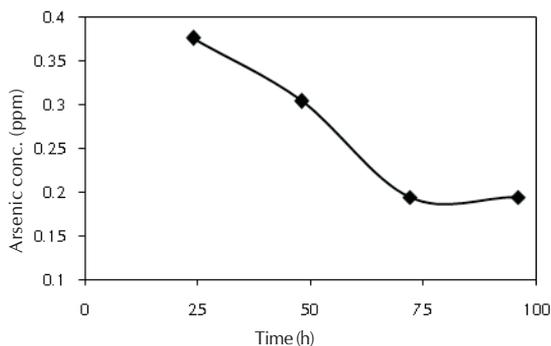
### Desorption studies on As(V) loaded Ferric hydroxide at 35°C

The desorption of arsenic from arsenic loaded ferric hydroxide was carried out at different pH (6.0, 7.0 and 8.0) while keeping the temperature as 35°C and varying desorption time from 24 to 96 hr. The effect of time

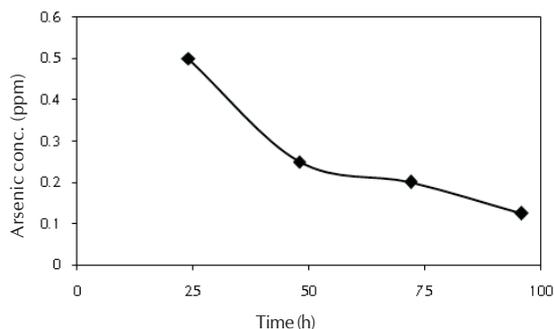
**Table 1: Data on Ferric Hydroxide**

Elements	Quantitative value
Specific Surface Area (m <sup>2</sup> /c.c.)	0.3498
Particle size (mm) (50%) d <sub>50</sub>	32.56
Particle size (mm) (90%) d <sub>90</sub>	72.58

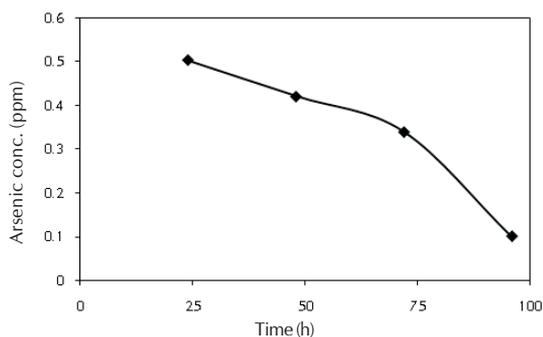
at various pH on desorption is shown in Fig. 1 to 3. The results shows that maximum desorption takes place at a pH of 8 at 24 hr (Fig. 3). The arsenic concentration at that point was 0.5ppm (mg/L). At all pH values, it is observed that with the increase in desorption time, the arsenic in solution decreased, indicating that first desorption takes place and then again the dissolved arsenic has a tendency to get re-adsorbed on the surface.



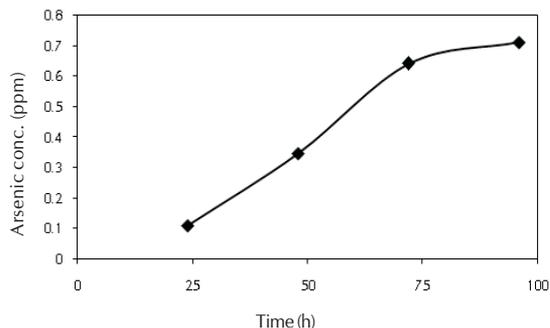
**Figure 1: Desorption of arsenic from As(V) loaded ferric hydroxide at pH-6.0 at 35°C**



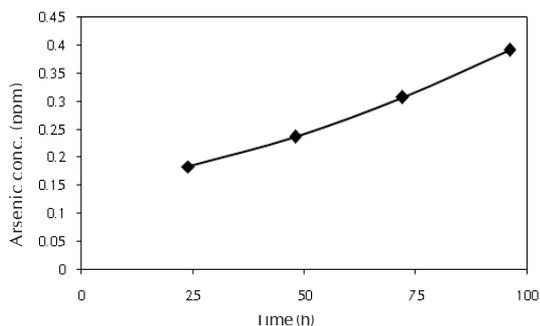
**Figure 2: Desorption of arsenic from As(V) loaded ferric hydroxide at pH-7.0 at 35°C**



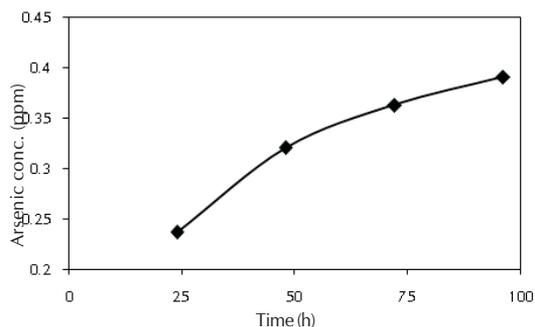
**Figure 3: Desorption of arsenic from As(V) loaded ferric hydroxide at pH-8.0 at 35°C**



**Figure 4: Desorption of arsenic from As(V) loaded ferric hydroxide at pH-6.0 at 35°C in presence of Ca<sup>2+</sup>**



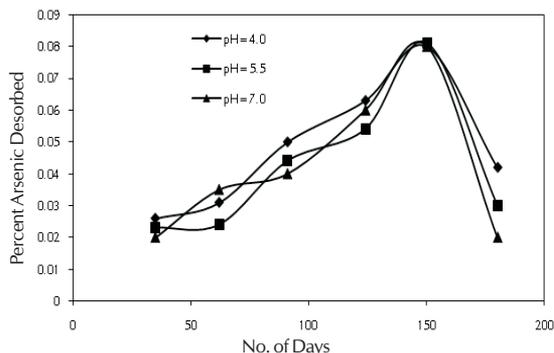
**Figure 5:** Desorption of arsenic from As(V) loaded ferric hydroxide at pH-7.0 at 35°C in presence of 10 ppm Ca<sup>2+</sup>



**Figure 6:** Desorption of arsenic from As(V) loaded ferric hydroxide at pH-8.0 at 35°C in presence of 10 ppm Ca<sup>2+</sup>

**Desorption studies on As(V) loaded Ferric Hydroxide in Presence of 10 ppm Ca<sup>2+</sup> at 35°C**

The desorption of arsenic from arsenic loaded ferric hydroxide was carried out at different pH (6.0, 7.0 and 8.0) in the presence of 10 ppm Ca<sup>2+</sup> while keeping the temperature as 35°C and varying desorption time from 24 to 96 hr. The effect of time at various pH values are shown in Figs. 4 to 6. The results are very interesting. In the presence of Ca<sup>2+</sup>, at all pH values desorption increases with the increase in time. From these results it is seen that maximum desorption takes place at a pH of 6 at 96 hr (Fig. 4). The arsenic concentration at that point was 0.77 ppm (mg/L). When these results are compared to the ones where no Ca<sup>2+</sup> ions were added, at all pH values, after 12 hr, the extent of desorption is less in the presence of Ca<sup>2+</sup> but with the increase in time, though desorption decreases in absence of Ca<sup>2+</sup> but it increases in its presence.



**Figure 7:** Long term desorption of arsenic from As(V) loaded ferric hydroxide at different pH at room temperature

**TCLP (Toxicity Characteristics Leaching Procedures) Tests [US EPA Method 1311]**

The desorption studies showed that depending on the pH, at 35°C in 24 to 96 hr the desorption was quite low indicating the solids to be quite stable. Further, TCLP test was carried out on loaded ferric hydroxide. After TCLP test, the concentration of the arsenic in the leach solution was found to be 1.06 ppm (Table 2). According to Environmental Health and Safety, the maximum allowable arsenic concentration in leachate for toxicity characteristic is 5.0 ppm for arsenic. As per the present norms, the loaded solids can be regarded safe for disposal. It is expected that the new regulations would project the arsenic in leachate after TCLP tests as 1.0 ppm. Our studies show that the uncalcined loaded ferric hydroxide will be considered as marginally safe if the revised concentrations are followed, therefore, the arsenic loaded samples was heated at 200°C for 6hr and the samples was subjected to TCLP test. It is observed that by calcining the loaded solid to 200°C for 6 hr, the soluble arsenic decreased to 0.24 ppm which will fall within the limits even the new regulations come into force.

**Long Duration Desorption Test**

With a view to observe the long duration affect on desorption of As (V) from loaded ferric hydroxide, the desorption was carried out by keeping the solids at room temperature at a pH varying between 4 to 7. The

**Table 2: TCLP Test results for ferric hydroxide**

Name of Samples	Temperature(°C)	Hour (h)	As concentration (ppm)
Ferric hydroxide	-----	-----	1.06
	200	6	0.24

results presented in Fig. 7 shows that the % As(V) desorption goes through a maxima at 150 days with 0.8% (0.16 ppm) desorption and then decrease to 0.02 to 0.04 % at 160 days. These values are much less than the ones obtained for a period of 96 hr. The present studies have indicated that the loaded ferric hydroxide can be disposed safely under the present regulations.

### CONCLUSION

- (i) Desorption studies were carried out on As (V) loaded ferric hydroxide
- (ii) Effect of time on desorption was studied at different pH and 35°C temperature. After 96hr, the maximum desorption gave 0.5 ppm at a pH 6.0.
- (iii) In presence of 10ppm Ca<sup>+2</sup>, the effect of time on desorption was also studied at different pH and at 35°C temperature. Maximum desorption gave 0.77 ppm at a pH 6.0 at 96hr.
- (iv) Loaded ferric hydroxide passed through the TCLP test as per the old norms (5 ppm) and after calcination at 200°C for 6hr, it would pass through the new expected norm of 1 ppm As in the leachate.
- (v) Long duration test on desorption showed the As(V) loaded solid to be quite stable as only 0.08% arsenic desorption took place.

### ACKNOWLEDGEMENT

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