

Retention of As (III), F⁻ and Microbes by Iron and Aluminum Oxide Coated Sand

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ABSTRACT: The capacity of adsorption of arsenic, fluoride and microbes on iron and aluminum-oxides-coated quartz sand has been studied. The adsorption process has been described as Freundlich and Langmuir isotherms. In all cases, Langmuir equation yields better fits than Freundlich equation. The covering quartz particles with Fe and Al oxides provide a high capacity adsorption and immobilization of As, F⁻ and microbes from groundwaters. Also, columns have been studied by using Fe and Al-oxides-coated quartz sand to examine the removal of AS (III), fluoride and microbes spiked to required concentrations in tap water. Performance observed by breakthrough cycles shows that Fe and Al oxides particles provide an excellent material for construction of As, F⁻ and microbes removal system for groundwaters. The characteristics of this material would allow the design of a complementary filtration system to reduce As, F⁻ and microbes levels in the effluent, reducing contamination risks.

Keywords: Retention, Aluminum Oxide, Iron Oxide, Quartz, Multimedia.

INTRODUCTION

Providing safe and adequate drinking water supplies to the population is a challenging task faced by the governments in the developing countries. Generally, the microbiological quality of the drinking water is of greatest importance. The health risk due to toxic chemicals in drinking water differs from that caused by microbiological contaminants. The problem arises primarily from their ability to cause adverse effects after prolonged period of exposure. The problems of particular concern are cumulative poisons and carcinogens.

Arsenic is a toxic and carcinogenic metalloid, which is ubiquitous in rock, soil and water. Drinking arsenic-rich water over a long period is unsafe and in some countries around the world the health, effects are well known. The adverse health effects of arsenic are well documented in the literature (Karim, 1999). The major pathway for human exposure to arsenic is drinking polluted ground water. In order to minimize the health effects of arsenic, the World Health Organization (WHO), the US Environmental Protection Agency (USEPA) and the European Commission have proposed a new guideline for arsenic in water (10 µg/L). In India, as per BIS 10500 (1991), a maximum arsenic level of 50 µg/L has been permitted in groundwater supplies for drinking purposes.

Fluoride in minute quantity is an essential component for normal mineralization of bones and formation of

dental enamel (Bell, M.C. *et al.*, 1970). However, its excessive intake may result in slow, progressive crippling scourge known as fluorosis. There are more than 20 developed and developing nations that are endemic for fluorosis. These are Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Sri Lanka, Syria, India, etc. (Mameri, N. *et al.*, 1998). In India, it was first detected in Nellore district of Andhra Pradesh in 1937 (Shortt, W. E. 1937). At present, it has been estimated that fluorosis is prevalent in 17 states of India (Susheela A.K, 1999).

According to WHO report, 1.8 million people die every year from diarrhoeal diseases (including cholera); 90% are children under five, mostly in developing countries. 88% of diarrhoeal disease is attributed to unsafe water supply, inadequate sanitation and hygiene. While access to drinking water in India has increased over the past decade, the tremendous adverse impact of unsafe water on health continues. The World Bank estimates 21% of communicable diseases in India are water related. Of these diseases, diarrhoea alone killed over 700,000 Indians in 1999 (estimated)—over 1,600 deaths each day (Justin *et al.*, 2002).

A variety of methods have been used in the past for removal of arsenic, fluoride and microbes from water. Coagulation, Ion exchange, adsorption, filtration and

reverse osmosis process were help in removing such kind of impurities from water. Because of lack of fund above mentioned technology was proved less appropriate technology for rural water supply application in developing countries. Therefore, sorptive sand filtration using oxide-coated sand is a new approach for treating drinking water contaminated with toxic metal pollutants.

Several studies have been demonstrated that arsenic; fluoride and microbes removal can be achieved by various technologies. (Kall *et al.*, 2005, Stahl *et al.*, 1991, Benjamin *et al.*, Dharmendra *et al.*, 2007, 2008) Namely, activated alumina sorption, polymeric anion exchange, sorption by iron oxide-coated sand, coagulation with ferric chloride, pressurized granulated iron particles, manganese dioxide-coated sand, polymeric ligand exchange, and zero-valent iron, and these have been tried in the laboratory and/or in the field. Among these technologies, adsorption on iron oxide-coated sand is considered an emerging technology for arsenic, fluoride as well as microbes removal. Studies (Vaishya *et al.*, 2003, 2004) have shown that iron oxide coated sand and iron impregnated sand can reduce the contaminants at desirable concentration. Very few researchers have worked with contaminated adsorption on aluminum hydroxide coated sand. Aluminum hydroxide coated sand has been used to eliminate selenium IV and VI from water (Kuan *et al.*, 1998). Sand coated with iron or aluminum oxihydroxide have been used to retain microorganisms (AFFSA, 2005). In a study of aluminum hydroxide coated sand for bacterial removal from waste water (Scott, 2002) found three fourths of aluminum originally coated on sand was still present after three months of continuous flushing and reported that iron and aluminum concentrations in the effluents of filtration columns containing coated media were below the detection limit (0.01 ppm for Al).

The adsorption of contaminants by oxide-coated sand has not received proper attention despite few good studies in the area so far. Therefore, a concerted effort is required to explore the possibility of employing the coated sand for the treatment of contaminated water. Since both iron and aluminum are abundantly available at cheap rate in all part of world, therefore, this innovative media become popular media of future for removal of arsenic, fluoride and microbes from drinking water on cost comparison basis.

MATERIALS AND METHODS

Chemicals

The entire chemicals used in the study were of high purity analytical grade and double distilled water was

used in the preparation of all the solutions. All the experiments were carried out at room temperature and atmospheric pressure. Sodium arsenite (Na AsO_2) and Sodium fluoride (NaF) were used as the source of As (III) and F^- respectively. A stock solution of As (III) and F^- (100 mg/L) were prepared in distilled water by dissolving 0.1734 g of sodium arsenite and 0.221 g Sodium fluoride in 1000 ml volumetric flask up to the mark. Microbes were prepared from supernatants of sewage.

COATING PROCEDURE

Iron Oxide Coated Sand

This media was prepared by taking sand and ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ten percent of the sand mixed with water at the rate of 30 percent by weight of the sand in an iron frying pan. The frying pan heated over gas stove and continuously stir until completely dried. After cooling to room temperature, the coated sand was washed with tap water until washings were clear. The washed coated sand was dried in oven at 75°C . The coated sand cooled and stored in plastic jar for further use.

Aluminum Oxide Coated Sand

This media was prepared by dissolving 25 g aluminum chloride (AlCl_3) in 150 ml distilled water. Then in this solution, 500 g sand (size = $547.72 \mu\text{m}$) was poured and was heated over gas stove into the Aluminum frying pan, and continuously stirred by Aluminum spoon. After reaching to the boiling point, lowering to gas flame and continuously stir until completely dried (approx 60 minute required in this process). The media is cooled at room temperature. Again the media is mixed with 3 N (240 ml of ammonia solution to one liter distilled water) ammonium hydroxide solution and heated on gas stove with continuously stir till completely dried (approx 10 minute required in this process). The coated sand washed with tap water until washing were clear, also washed with distilled water. The washed coated sand is dried in oven at 75°C . The coated sand cooled and stored in plastic jar for further use.

EXPERIMENTS

Batch Studies

To evaluate the feasibility of arsenic and fluoride removal by IOCS and AOCS were used as adsorbents with a dose of 20 g/L and solution pH was 7 ± 0.1 . The parameters of reaction at room temperature (31°C) and revolution per minute of shaker were controlled at

38 rpm. The adsorption time was set at 8 h for all adsorption isotherm experiments. Isotherm studies were conducted with varying initial As (III) and F⁻ concentration (1 mg/L to 8 mg/L). Batch sorption experiments were conducted to obtain sorption capacity of IOCS and AOCS using 300 ml BOD bottle kept at room temperature; an end-to-end shaker was used to agitate the solution. The reaction mixture consisted of 100 ml As (III) solution of known concentration and the adsorbent was weighed and added to the solution. Each bottle was removed after the required reaction time and the solution was filtered through whatman No. 40 filter paper. The measured arsenic and fluoride data were statistically analyzed for the fitting of isotherm models of both the Langmuir and Freundlich.

Column Experiments

The experimental column was constructed with 22 mm ID borosilicate glass tube. Contaminants individual as well as combined effect were studied with multimedia arrangements 20 cm top AOCS & 20 cm bottom IOCS. The concentrations of As (III), F⁻ and microbes in influent were 1 mg/L, 3 mg/L and 300–500/100 ml respectively. The influent was pumped through the packed column at the target flow rate with a peristaltic pump. All the experiments were performed at room temperature. Portion of the effluent were collected at different time intervals for analysis for the same. Columns were run until the effluent concentration reached more than 95 percent of influent concentration.

RESULT AND DISCUSSION

Adsorption Isotherms

In general, adsorption isotherm is used to describe the equilibrium state of adsorbate, adsorbent and solute at a given temperature. Arsenic and fluoride adsorption isotherm experiments were carried out to compare their adsorption capacities under various conditions. Two adsorption models were proposed, Langmuir (Eqn. 1) and Freundlich (Eqn. 2) models, the equation of which are expressed as (J. Wiley & sons),

$$q_e = \frac{Q^{\circ}bc}{(1+bc)} \quad (\text{Langmuir equation}) \quad \dots (1)$$

$$\text{And } q_e = K_F C^{1/n} \quad (\text{Freundlich equation}) \quad \dots (2)$$

Where Q° and q_e represent saturated adsorption capacity at equilibrium concentration of adsorbate (C), respectively; b , K_F , and n stand for empirical constants.

The linearized form of Langmuir (Eqn. 3) and Freundlich (Eqn. 4), which are expressed below, respectively were used for obtaining the respective empirical constants,

$$\frac{1}{q_e} = \left(\frac{1}{bQ^{\circ}} \right) \left(\frac{1}{C} \right) + \frac{1}{Q^{\circ}} \quad \dots (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C \quad \dots (4)$$

Where,

K_F = Sorption capacity. Unit is $\text{mg}^{n-1/n} \text{g}^{-1} \text{L}^{1/n}$

$1/n$ = Adsorption intensity.

Table 1: Langmuir and Freundlich Isotherm Parameters for As (III) and F⁻

| Sl. No. | Name of Adsorbent | Langmuir Parameters | | | Freundlich Parameters | | |
|---------|-------------------|---------------------|-----------|-------|--|-------|-------|
| | | Q_0 (mg/g) | b (L/g) | R^2 | K_F ($\text{mg}^{n-1/n} \text{g}^{-1} \text{L}^{1/n}$) | $1/n$ | R^2 |
| 1. | IOCS | 0.202 | 2.16 | 0.99 | 1.13 | 0.039 | 0.95 |
| 2. | AOCS | 0.39 | 0.57 | 0.96 | 1.18 | 0.098 | 0.89 |

COLUMN STUDY

Group I Test

Arsenic removal by multimedia with IOCS-I & AOCS with As-III concentration 1 mg/L and flow rate 15 ml/minute ($2.36 \text{ m}^3/\text{m}^2/\text{hr}$). Media arrangements 20 cm top AOCS & 20 cm bottom IOCS. As Figure 1 depicts, breakthrough was observed six hours.

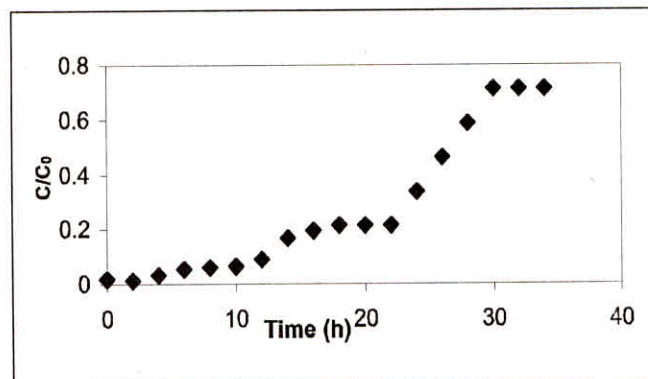


Fig. 1: Breakthrough curve for adsorption of As (III) on multimedia of IOCS-I & AOCS

Group II Test

Fluoride removal by multimedia with IOCS-I & AOCS with fluoride concentration 3.5 mg/L and flow rate 15 ml/minute ($2.36 \text{ m}^3/\text{m}^2/\text{hr}$). Media arrangements 20 cm top AOCS & 20 cm bottom IOCS. As Figure 2 depicts, breakthrough was observed two hours.

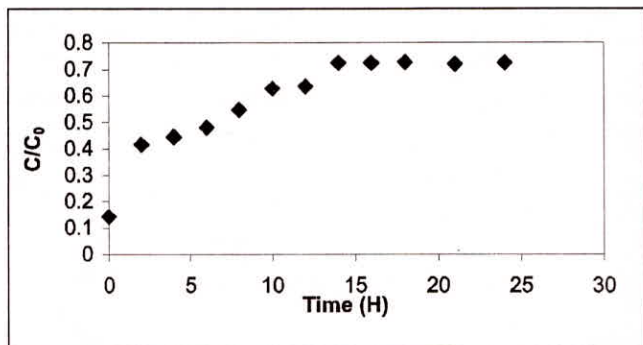


Fig. 2: Breakthrough curve for adsorption of F⁻ on multimedia of IOCS-I & AOCS

Group III Test

Microbes removal by multimedia with IOCS & AOCS with microbes concentration 600 MPN/ 100 ml and flow rate 2.36 m³/m²/h. Arrangement of adsorbents in the following manner, in bottom 20 cm placed IOCS and just above 20 cm of AOCS. As Figure 3 depicts, breakthrough was observed as 28 hours.

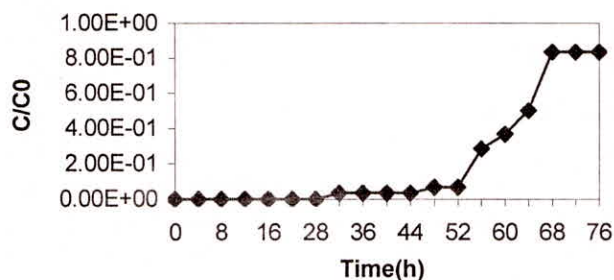


Fig. 3: Breakthrough curve for adsorption of MPN on Multimedia of IOCS-I & AOCS

Group IV Tests

The influent concentration was 1 mg/L for As (III) and 2.5 mg/L for F⁻ and discharge was 2.36 m³/m²/h. Multimedia arrangements 20 cm top AOCS & 20 cm bottom IOCS.

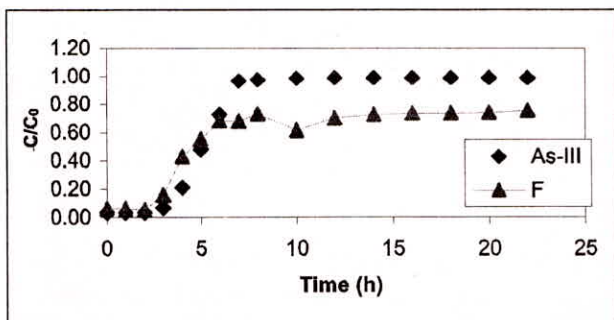


Fig. 4: Breakthrough curves of different elements by multimedia of IOCS-I & AOCS

As shown in Figure 4 the breakthrough curve among all the adsorbents As (III) and F removal were achieved 5, and 5 hours respectively.

Group V Tests

The influent concentration were kept as As-III 1 mg/L, F 2.5 mg/L and microbes 500–600 MPN/100 ml with discharge 2.36 m³/m²/h. Multimedia arrangements 20 cm top AOCS & 20 cm bottom IOCS. As shown in Figure 5 the breakthrough curve among all the adsorbents As (III), F and microbes removal were achieved 2, 4 and 20 hours respectively.

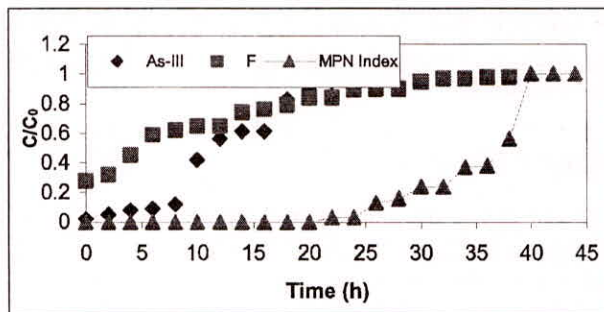


Fig. 5: Breakthrough Curve for adsorption of As(III), F & MPN on multimedia of quartz IOCS-I & AOCS with Fe conc 4 mg/L

CONCLUSIONS

1. Batch study results with IOCS and AOCS showed that the arsenic and fluoride adsorption can be best describe by the Langmuir isotherm based on the correlation co-efficient.
2. The present experimental equilibrium relationship could also be described quite well by the langmuir isotherm model (R₂>0.95) (Matis, K.A. *et al.*, 1999).
3. According to the Freundlich model, the trends in sorption capacity are largely captured in the parameter KF.
4. According to Treybal (1968), the value of N>1, represent favorable sorption capacity.
5. Apparently, the value of 'n' is greater than 1 in all the cases.
6. Column study results showed that multimedia adsorbent removal capacity was higher in case of individual contaminants applied.
7. In case of combined contaminants application, removal capacity of multimedia adsorbent was slightly reduced, because of all contaminants having negative charge.
8. The coated sand could be an alternative emerging technology for water treatment without any side effect or treatment process alteration.

9. Better applicability of this technique requires further studies to enhance the adsorption capacity.

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