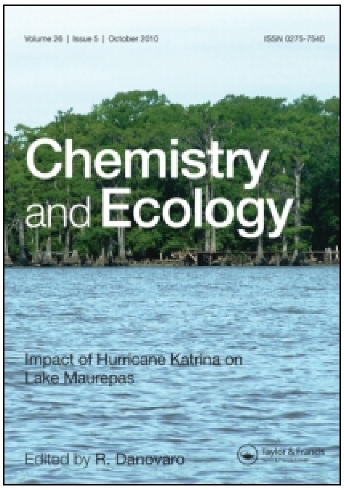

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Use of Manganic Ferrihydrite to treat As(V) contaminated water

S. S. Mohanty[a]; S. S. Baral[a]; D. Mohapatra[a]; G. Roy Chaudhury[a]
[a] Institute of Minerals and Materials Technology, Bhubaneswar, India

To cite this Article Mohanty, S. S. , Baral, S. S. , Mohapatra, D. and Chaudhury, G. Roy(2008) 'Use of Manganic Ferrihydrite to treat As(V) contaminated water', Chemistry and Ecology, 24: 1, 23 — 33

To link to this Article: DOI: 10.1080/02757540701814812

URL: http://dx.doi.org/10.1080/02757540701814812

Chemistry and Ecology
Vol. 24, No. 1, February 2008, 23–33

Use of Manganic Ferrihydrite to treat As(V) contaminated water

S.S. Mohanty, S.S. Baral, D. Mohapatra and G. Roy Chaudhury*

Institute of Minerals and Materials Technology, Bhubaneswar, India

(*Received 24 May 2007; final version received 08 November 2007*)

The As(V) removal efficiency of Manganic Ferrihydrite, having a different mole ratio to Fe-Mn, were evaluated. The As(V) removal efficiency of the adsorbent increased with the increase in Mn up to 40–60 mole% in the Ferrihydrite. Thereafter, further increase in the Mn concentration showed an opposite trend. The adsorption efficiency was constant at pH range of 6–7 whereas the efficiency slightly decreased at >pH 7. Adsorption studies were also carried out varying the adsorbent and the adsorbate concentrations, respectively. The adsorption process followed both Freundlich's and Langmuir's adsorption isotherm models. The maximum theoretical uptake was calculated using the two investigated models. Since adsorption efficiency showed better results when the Mn concentration was 40–60 mole%, Manganic Ferrihydrite compound (Fe:Mn ratio 1:1) was used to conclude the experiments. The adsorption kinetics followed dual rates, faster at the beginning and then slower. The adsorption kinetics followed 1st order kinetics. The IR and TGA analyses displayed that the compound was Manganic Ferrihydrite.

Keywords: Manganic Ferrihydrite; As(V) removal efficiency; adsorption isotherm models

1. Introduction

As(V) occurs in nature in the form of AsO_4^{-3}, $HAsO_4^{2-}$ and $H_2AsO_4^-$. Pentavalent species of As predominate and are stable in oxygen rich aerobic environments. It occurs naturally in a wide range of minerals, which together with widespread use of As(V) in pigments, insecticides and herbicides are the major source of As(V) in natural water [1]. As(V) is also found on the surface of food or fruits grown in As(V) affected areas and can affect the human body through ingestion, skin absorption or inhalation. Generally arsenic contamination of drinking water is a worldwide health concern. It is a protoplasmic poison due to its effect on a sulfydryl group of cells interfering with cell enzymes, cell respiration and mitosis. Large As(V) doses can cause chlorella-like symptoms (acute poisoning) and death. As(V) causes most prominent chronic manifestations which involve the skin, lungs, liver and blood system.

As(V) contaminated drinking water drawn from deep aquifers is a major problem in West Bengal, Bangladesh and some other parts of India [2]. The As(V)-contaminated drinking water has also been reported [3] for other countries like Taiwan, Chile, Argentina, China and Mexico. The world's four major countries whose ground water is As(V) contaminated are in Asia – Bangladesh,

---

*Corresponding author. Email: gr_chaudhury@yahoo.com

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540701814812
http://www.informaworld.com

India, China and Taiwan [4]. Due to the extreme toxicity of As(V) to human health, there is an urgent need to treat As(V)-contaminated drinking water to make it safe for consumption.

Among the abatement techniques, adsorption process was found to be more suitable due to less process control and ease of operation. For adsorption various adsorbents can be used which includes synthetic as well as naturally occurring materials. Among synthetic adsorbents, three different hydrites/oxides i.e. iron, aluminium and Mn hydrite are mainly used [5–8].

Although several studies have been carried out on the efficiency of removing As(V) from aqueous solution using ferrihydrite, alumina and Mn compounds, the literature is rather scant on modifying these compounds to improve their efficiency [9]. A previous study reported that goethite structure can be modified by incorporating ions like Mn, Si, Cu, and Al [10]. This incorporation modified the lattice structure and thereby the adsorptive behavior. The use of Mn substituted goethite to oxidise arsenite in aqueous solution was reported by Sun et al. [11]. Due to the importance of using different hydrite/oxides of Fe and Mn, the main aim of this work is to prepare different mixes of Manganic Ferrihydrite and to evaluate their efficiency in As(V) removal from water.

2. Material and methods

2.1. *Preparation of Manganic Ferrihydrite compounds*

The adsorbents were prepared by mixing 1M Mn solution with 1M ferric solution. The total volume of the mixture was kept constant at 500 ml. To prepare Manganic Ferrihydrite having 20 mole% of Mn, 400 ml of 1M Fe(III) solution was mixed with 100 ml of 1M Mn solution. The mixed solution was kept in a plastic container. The solution was stirred mechanically. The pH of the solution was kept constant between 11.8 and 12.0 by drop-wise addition of 10 M NaOH solution. The above experiments were conducted under constant bubbling of pure oxygen. The addition of alkali was continued till the solution pH showed no appreciable variation and the pH was maintained within the specified range. After stabilisation of pH the solution was diluted to 2.5 l adding distilled water. Then the total solution was kept in an oven at a constant temperature of 70°C. This ageing process continued for 24 h and the volume was kept constant by the addition of distilled water at regular intervals. After ageing, the solution was filtered and repeatedly washed with distilled water till it was free from alkali and nitrate ions. After washing, the sample was dried at 60°C for 48 h. Five different Fe-Mn compounds were prepared with Fe:Mn mole ratio varying from 0:5 to 5:0.

2.2. *Adsorption studies*

As(V) stock solution was prepared by dissolving requisite amounts of Na_3AsO_4(Analar grade) in double distilled water. The pH of the solution was adjusted by adding either dilute NaOH or H_2SO_4. Adsorption studies were carried out in stirred tank glass reactor. The agitation was done by a mechanical stirrer. At regular intervals, samples were collected to measure the pH and residual concentration of As(V). The As(V) concentration was measured by Perkin-Elmer make ICP-MS. All the experiments were performed in three replicates.

3. Results and discussion

3.1. *Adsorption studies using different Manganic Ferrihydrites*

Adsorption studies were carried out using the different Manganic Ferrihydrite compounds and the Mn concentration varied from 0–100 mole%. The initial pH, adsorbent and adsorbate

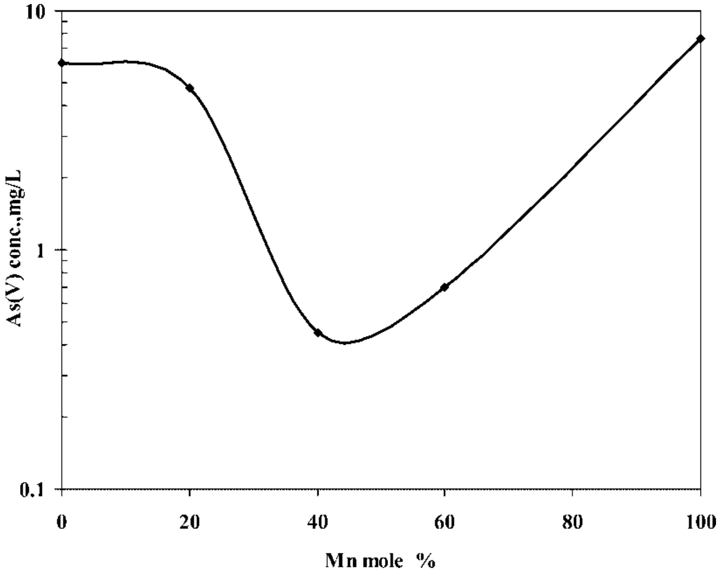

Figure 1. Development of Manganic Ferrihydrite contour (Condition: H(ini) = 6,4, As(V) = 10 mg/l, Adsorbent = 1 g/l).

concentrations were 6.4, 1 g/l and 10 mg/l respectively (Figure 1). The As(V) adsorption was high when the Mn mole percentage increased from 0–40% whereas at 60%, a slight decrease in the adsorption efficiency was observed. The As(V) adsorption was low for pure Manganic and Ferrihydrite suggesting that Mn mole percentage may be varied between 40 and 60% for the efficient As(V) adsorption from aqueous solution. Further adsorption studies were carried out using only these two compounds, Mn concentration of 40 mole% (A) and Mn concentration of 60 mole% (B). The equilibrium pH result was higher than the initial values. Edwards [12] reported that the adsorption of strongly binding anions like arsenate and arsenite on oxide surfaces took place by a ligand exchange mechanism. This mechanism involved the exchange of an aqueous ligand with a surface hydroxyl group, resulting in the formation of an inner sphere complex. The formation of an inner sphere complex involves columbic interaction and is referred to as surface coordination [13]. The reaction can be shown as:

$$\underline{=}\mathrm{SOH} + \mathrm{H_2AsO_4^-} + \mathrm{H^+} \longrightarrow \mathrm{S - H_2AsO_4} + \mathrm{H_2O} \tag{1}$$

Arsenate sorption

$$\underline{=}\mathrm{SOH} + \mathrm{H_2AsO_3^-} + \mathrm{H^+} \longrightarrow \mathrm{S - H_2AsO_3} + \mathrm{H_2O} \tag{2}$$

Arsenite sorption

where $\underline{=}$SOH is a surface hydroxyl group. Thus according to the anion adsorption reaction given above, the equilibrium pH should be more than initial pH as it was observed in the experiments.

3.2. *Effect of pH*

The initial pH of the solution varied from 6 to 8 and was comparable to values reported in the As(V) contaminated drinking water of India/Bangladesh [2]. In this study the initial adsorbate and adsorbent concentration were kept constant at 10 mg/l and 1 g/l respectively (Figure 2).

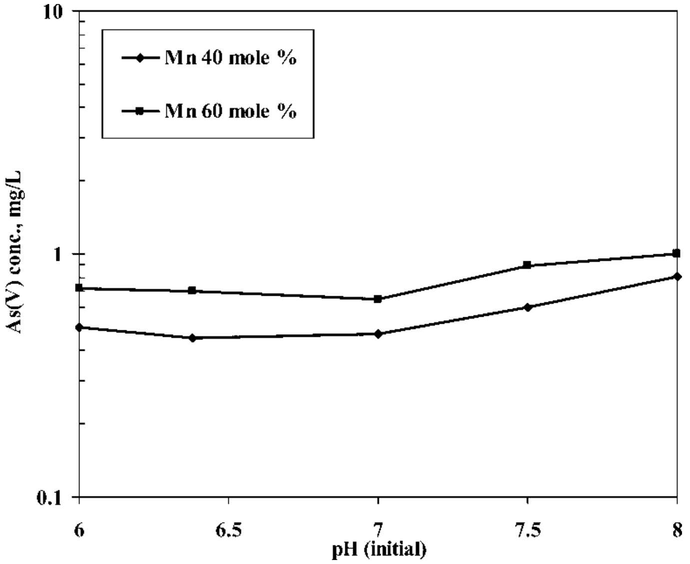

Figure 2. Effect of initial pH (Condition: As(V) = 10 mg/l, Adsorbent = 1 g/l).

Both compounds showed similar trends in terms of As(V) adsorption: the As(V) adsorption was independent at initial pH range 6–7 whereas >7 the adsorption efficiency slightly decreased.

The effect of pH on the adsorption process depends on several factors such as the nature of the adsorbent surface, speciation of As(V) species, the acid and base used to adjust pH of the solution. In order to explain the pH effect it is necessary to examine various mechanisms such as electrostatic attraction/repulsion, chemical interaction and ion exchange which are responsible for adsorption on adsorbent surfaces. Taking into account the stability diagram [14], the most abundant species are H_3AsO_4, $H_2AsO_4^-$,$HAsO_4^{2-}$, and AsO_4^{3-}. The pK values are 2.25, 6.67 and 11.53 for pK_1, pK_2, pK_3 respectively. Thus the most abundant species in our experimental pH range is expected to be $H_2AsO_4^-$or $HAsO_4^{2-}$. At higher pH, (>7.0), the decrease of adsorption efficiency may be due to competition between As(V) species and hydroxide ions, which are dominant at higher pH.

3.3. *Effect of initial As(V) concentration*

Adsorption studies were carried out varying the initial As(V) concentration from 1–10 mg/l to find out its effect on adsorption efficiency. The residual As(V) concentrations increased with the increase of initial As(V) concentrations (Figure 3). At the initial As(V) concentration of 1 mg/l, the residual As(V) concentration for compounds A and B were 0.02 and 0.05 mg/l, respectively which are within the acceptable limit for drinking water.

The adsorption data were fitted to linearly transformed Freundlich and Langmuir adsorption isotherms. The linearised Freundlich equation can be shown as:

$$\ln(X/M) = \ln K + 1/n \log C_e \tag{3}$$

where X/M is the amount of As(V) species adsorbed per unit mass of the adsorbent (mmole/g), C_e is the residual As(V) concentration at equilibrium (mmole), K is a measure of adsorption capacity and 1/n is a measure of adsorption intensity. The data obtained from the experiment using Manganic Ferrihydrite as adsorbent are fitted to equation-3 and a linear plot being obtained for lnX/M versus $\ln C_e$ for two different adsorbents. Substituting the values obtained from the

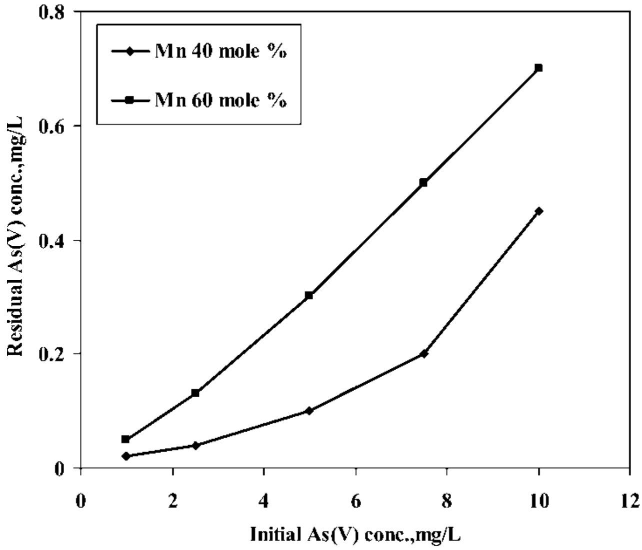

Figure 3. Effect of initial As(V) concentration (Condition: pH(ini) = 6, Adsorbent = 1g/l).

graph (slope and intercept values calculated by regression method), the Freundlich equation takes the form:

For compound-A (Mn 40 mole%)

$$X/M = 6.23\,C_e^{(0.7187)}. \tag{4}$$

For compound-B (Mn 60 mole%)

$$X/M = 6.95\,C_e^{(0.8571)}. \tag{5}$$

The linear form of the Langmuir adsorption isotherm is represented as:

$$C_e/X/M = (1/b)Q + C_e/Q \tag{6}$$

where C_e is the equilibrium concentration of adsorbate in solution, Q is the number of moles of solute adsorbed per unit weight of adsorbent in forming monolayer on the adsorbent surface and b is the Langmuir constant related to binding energy. A graph was plotted between $C_e/X/M$ versus C_e for the two Manganic Ferrihydrite adsorbents under different initial As(V) concentration. The linearity confirms the formation of monolayer on the adsorbent surface. The values Q and b are calculated from the slope and intercept respectively (Table 1). The theoretical C_e values were calculated using Langmuir's and Freundlich's isotherm equations and are reported in Table 1. From the values of C_e, it can be concluded that the adsorption process follows both the isotherm models.

3.4. *Effect of adsorbent concentration*

The adsorbent concentration varied from 0.2–1 g/l to evaluate its effect on As(V) adsorption efficiency. The initial pH and As(V) concentration was 6 and 10 mg/l respectively. The uptake of As(V) per gram of adsorbent decreased with the increase of adsorbent dose whereas the percentage of As(V) adsorption increased with the increase of adsorbent dose. For 1 g/l adsorbent concentration, the uptake was 9.55 and 9.3 mg/g of adsorbent for the compounds A and B, respectively. Higher percentage of adsorption with the increase of adsorbent concentration may be due to

Table 1. Freundlich's and Langmuir's constants along with theoretical and actual equilibrium As(V) concentration.

		Freundlich's constant		Langmuir's constant		Ce(Th) mg/l		
As(V) conc., mg/l	Mn mole %	k	n	Q	b	Freund.	Langm.	C_e(Exp) mg/l
1	40	6.23	1.39	0.194	12.17	0.015	0.07	0.02
2.5						0.05	0.017	0.04
5						0.13	0.07	0.1
7.5						0.21	0.17	0.2
10						0.31	0.45	0.45
1	60	6.95	1.17	0.363	7.076	0.047	0.046	0.05
2.5						0.14	0.1	0.13
5						0.3	0.34	0.3
7.5						0.48	0.54	0.5
10						0.68	0.65	0.7
1	50	5.54	1.24	0.295	6.65	0.04	0.04	0.04
2.5						0.12	0.16	0.12
5						0.28	0.41	0.3
7.5						0.47	0.5	0.48
10						0.67	0.53	0.65

the availability of more surface area. The decrease in As(V) uptake at higher adsorbent dose may be due to competition of the As(V) ions for the available adsorption sites. Further agglomeration of the adsorbent particle may be another possible reason of the decrease in uptake.

3.5. *As(V) adsorption using Manganic Ferrihydrite where Mn mole ratio (50%)*

Our results suggest that Manganic Ferrihydrites, containing 40–60% mole Mn, display good As(V) adsorption property and for this reason, the further experiments were carried out using Manganic Ferrihydrite containing 50 mole% of Mn.

3.6. *Effect of contact time*

To evaluate the kinetics of As(V) adsorption the contact time varied up to 8 h. The pH, initial As(V) and adsorbent concentrations were 6.8, 10 mg/l and 1 g/l respectively (Figure 4). At the beginning, the kinetics were fast and then decreased. The faster initial kinetics accounted for more than 80% of total adsorption and it occurred during the initial 1st hour. This may be due to easy availability of large number of adsorbent surface to the adsorbent. As the surface was slowly covered by the adsorbent, the kinetics of adsorption decreased in the later stages. Similar dual adsorption rate have been reported in previous studies [15]. All subsequent adsorption studies were carried out for 6 h, as beyond that period the adsorption rate was almost negligible.

3.7. *Effect of initial pH*

Adsorption experiments were carried out varying the initial pH of the As(V) solution from 6 to 8. During these experiments the adsorbate and adsorbent concentration were kept at 10 mg/l and 1 g/l respectively. The As(V) adsorption was independent at pH 6–7 and >7 there was a decrease in the adsorption efficiency by the adsorbent (Figure 2).

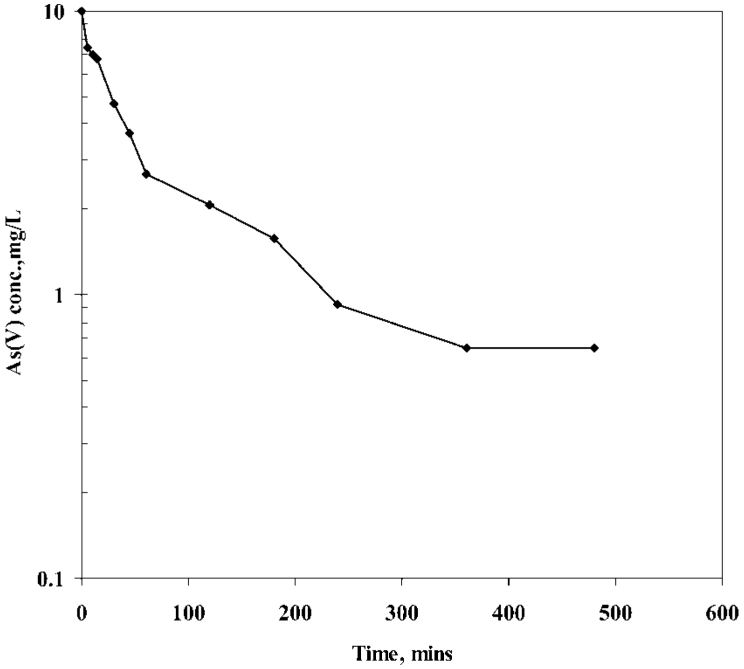

Figure 4. Effect of contact time (Condition: pH(ini) = 6.8, As(V) =10 mg/l, Adsorbent = 1 g/l).

3.8. *Effect of initial As(V) concentration*

The initial As(V) concentration varied from 1–10 mg/l to evaluate the effect on the adsorption kinetics (Figure 5). It was observed that in all cases the adsorption kinetics followed dual rates, i.e. initial faster followed by slower kinetics and the adsorption rates, are shown in Table 2. The initial faster and final slower rates depend on the initial As(V) concentration.

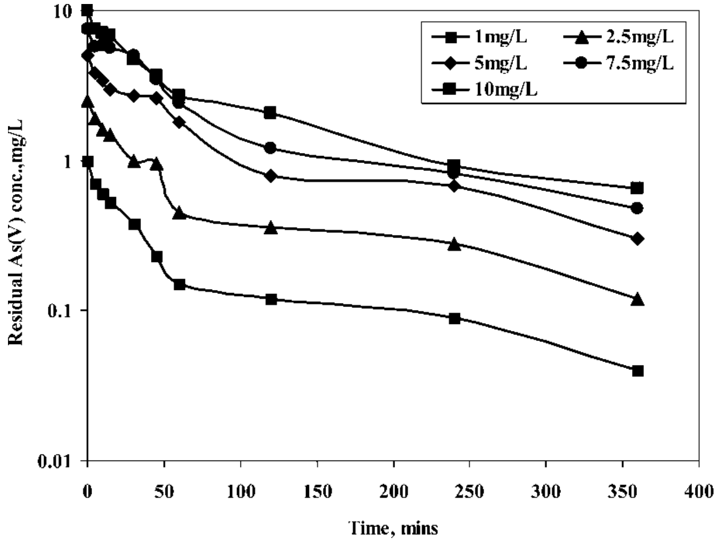

Figure 5. Effect of initial As(V) concentration (Condition: pH(ini) = 6.8, Adsorbent = 1 g/l).

Table 2. Initial faster and final slower adsorption rate for different initial As(V) concentrations.

Initial As(V) concentration (mg/l)	Initial faster adsorption rate (mg/l/min)	Final slower adsorption rate (mg/l/min)
1	0.012	0.0004
2.5	0.0287	0.0009
5	0.0407	0.004
7.5	0.0719	0.0058
10	0.1072	0.0071

If the adsorption reaction is 1st order then the rate of adsorption can be written as:

$$-\mathrm{dc}/\mathrm{dt} = \mathrm{k}(\mathrm{C}) \tag{7}$$

where C is the As(V) concentration.

On integrating and rearranging:

$$\ln \mathrm{C}_t / C_0 = -\mathrm{kt} \tag{8}$$

where k = specific reaction rate

C_t = Concentration of As(V) at time t

C_0 = Initial As(V) concentration.

So if the adsorption process follows 1st order kinetics then by plotting ln $\mathrm{C}_t/\mathrm{C}_0$ should give a straight line and the slope would be k. Figure 6 shows the plot of ln $\mathrm{C}_t/\mathrm{C}_0$ versus time for different initial As(V) concentrations and all the lines show good linearity as the coefficient of determinant of each one was more than 0.9. The specific reaction rate for each initial As(V) concentration was calculated and shown in Table 3. To find out the dependence factor, lnk needs to be plotted against ln(initial As(V) concentration) (Figure 7). The dependence factor was calculated from the slope and found to be 0.3.

The equilibrium adsorption isotherms for different initial As(V) concentrations were tested for two classical adsorption isotherms models as discussed previously (Table 1).

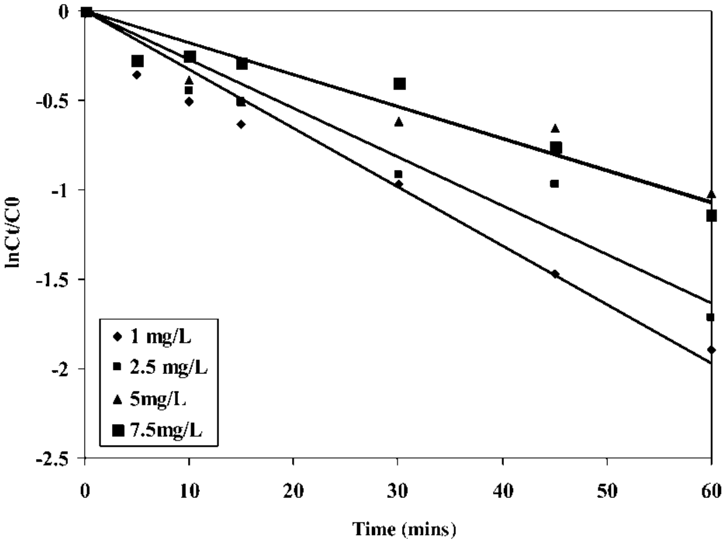

Figure 6. 1st order plot for various initial As(V) concentrations.

Table 3. Specific reaction rate for different initial As(V) concentrations.

Initial As(V) concentration (mg/l)	Specific reaction rate (mg/l/min)	Coefficient of determinants
1	0.0328	0.96
2.5	0.0273	0.93
5	0.0173	0.91
7.5	0.0179	0.93

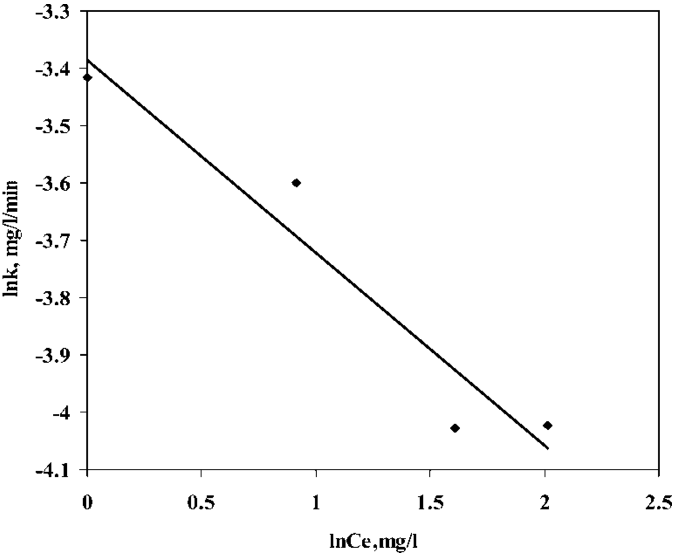

Figure 7. Evaluation of dependence factor with respect to initial As(V) concentrations.

3.9. *Effect of adsorbent concentration*

The adsorbent concentration varied from 0.2 to 1 g/l at the initial pH and As(V) concentration was 6.8 and 10 mg/l respectively. The adsorption rates for different initial adsorbent concentrations are shown in Table 4 and we observed that the initial and final adsorption rates varied with the initial adsorbent concentration.

The adsorption results for different time intervals were fitted to 1st order plot (Figure 8) and the specific reaction rate for different initial adsorbent concentrations were calculated according to the slope. To determine the dependence factor, ln(specific rate) was plotted against ln(adsorbent concentration). The dependence factor was calculated from the slope of the plot and was found to be 1.5.

Table 4. Initial faster and final slower adsorption rate for different initial adsorbent concentrations.

Initial adsorbent concentration (g/l)	Initial faster adsorption rate (mg/l/min)	Final slower adsorption rate (mg/l/min)
0.33	0.0372	0.0034
0.4	0.0413	0.0077
0.5	0.0611	0.0072
1	0.1072	0.0071

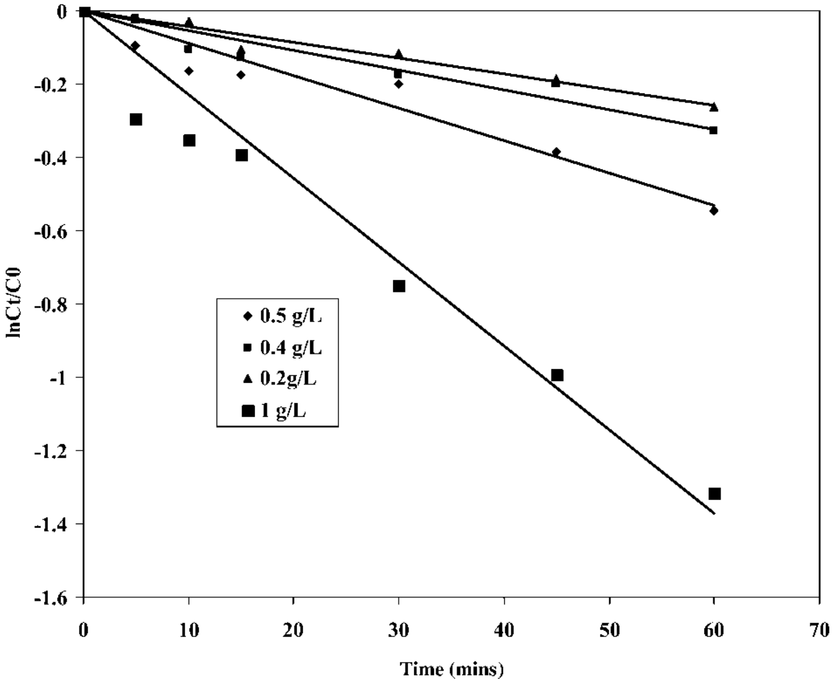

Figure 8. 1st order plot for different initial adsorbent concentrations.

So using the dependence factor the adsorption rate equation can be written as:

$$\text{Rate of adsorption} = \text{k(initial As(V) con.)}^{0.3}\text{(adsorbent con.)}^{1.5} \qquad (9)$$

where k = Pseudo 1st order reaction rate.

3.10. *Characterisation of the compound*

XRD analysis indicated the compound is amorphous in nature. The IR showed peaks at 3450 and 1648 cm^{-1} indicated the presence of water molecules. The TGA/DTA analysis showed an endothermic peak at 150°C, which indicated the compound ferrihydrite [10]. the TGA/DTA analysis displays that the compound is Manganic Ferrihydrite.

4. Conclusions

The As(V) adsorption capacity of the adsorbent increased with an increase in Mn concentration up to 40–60 mole% and the uptake capacity decreased in relation to the increase in Mn concentration. There was a slight decrease in As(V) adsorption when the Mn concentration increased from 40–60 mole%. The initial pH of the solution varied between 6 and 8. The As(V) adsorption was independent of initial pH between 6–7 and on further increase, the adsorption dropped. The initial As(V) concentration was varied from 1–10 mg/l to find out its effect on adsorption. The residual concentration decreased with the decrease of initial As(V) concentration. At an initial 1 mg/l As(V) concentration, the residual concentration was 0.02 and 0.05 mg/l for 40 and 60 mole% of Mn, respectively. The adsorption isotherm can be described using Langmuir's and

Freundlich's models. The initial adsorbent concentration varied and the As(V) uptake increased with decrease of adsorbent concentration. The optimum adsorption capacity was observed for the adsorbent having a Mn concentration of between 40 and 60 mole%. Therefore Manganic Ferrihydrite having a Mn concentration of 50 mole%, i.e. the average of 40 and 60 mole%, was prepared. The efficiency of As(V) adsorption was the same for Manganic Ferrihydrite (40 mole% of Mn). The adsorption kinetics could be divided into the initial faster rate followed by a final slower rate. The initial faster rate accounted for 80% of total adsorption and continued for 60 min. The adsorption reaction followed 1st order kinetics and the specific reaction rate for each initial As(V) concentration was worked out.

Acknowledgements

The authors are thankful to the Director of the Institute of Minerals and Materials Technology, Bhubaneswar for his kind permission to publish.

References

[1] M. Kumaresan and P. Riyazuddin, *Overview of speciation chemistry of arsenic*, Curr. Sci. 80 (2001), pp. 837–846.
[2] B.K. Mondal et al., *Arsenic in ground water in seven districts of West Bengal, India – The biggest arsenic calamity in the world*, Curr. Sci. 70 (1996), pp. 976–986.
[3] *Death and devil water*, New Scientist 14–15 September 1995.
[4] M.M. Rahman et al., *Magnitude of ground water arsenic contamination in Mursidabad, one of the nine arsenic affected districts in West Bengal*, Arsenic in Asia and Pacific Region (Adelaide) November, 2001, pp. 59–61.
[5] D. Mohan and C. Pittman, *Arsenic removal from water/wastewater using adsorbents – A critical review*, J. Hazardous Materials 142 (2007), pp. 1–53.
[6] B. Saha, R. Bains, and F. Greenwood, *Physicochemical characterization of granular ferrichydroxide for As(V) sorption from water*, Sepn. Sci. Technol. 40 (2005), pp. 2909–2932.
[7] Y. Masue, R.H. Loeppert, and T.A. Karmer, *Arsenate and arsenite adsorption behaviour on coprecipitated Al:Fe hydroxides*, Environ. Sci. Technol. 41 (2007), pp. 837–842.
[8] S. Maity, S. Chakravarty, S. Bhattacharya et al., *A study on arsenic adsorption on polymetallic sea nodules in aqueous medium*, Water Res. 39 (2005), pp. 2579–2590.
[9] R.G. Robins, T. Nishimura, and P. Singh, *Removal of arsenic from drinking water by precipitation, adsorption or cementation*, Technologies for arsenic removal from drinking water, BUET-UNU 31-42 (May 2001).
[10] J.L. Jambor and J.E. Dutrizac, *Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide*, Chem. Rev. 98 (1998), pp. 2549–2585.
[11] X. Sun, H.E. Doner, and M. Zavarin, *Spectroscopy study of arsenite (III) oxidation on manganese substituted goethite*, Clays Clay Minerals 47 (1999), pp. 474–480.
[12] M. Edwards, *Chemistry of arsenic removal during coagulation and Fe-Mn oxidation*, JAWWA (1994), pp. 64–78.
[13] J. Pradhan, J. Das, and S.N. Das, *Adsorption of phosphate from aqueous solution using activated red mud*, J. Colloid Interface Sci. 204 (1998), pp. 169–172.
[14] N.J. Welham, K.A. Malatt, and S. Vukcevic, *The effect of solution speciation on iron-sulfur-arsenic-chloride system at 298°K*, Hydromet. 57 (2000), pp. 209–223.
[15] S.P. Mishra and G. Roy Chaudhury, *Biosorption of copper by Penicillium sp.*, Min. Proc. Extrac. Met. Rev. 14 (1995), pp. 111–126.