Removal of arsenic from groundwater using low cost ferruginous manganese ore

S. Chakravarty, V. Dureja, G. Bhattacharyya, S. Maity, S. Bhattacharjee*

Analytical Chemistry Division, National Metallurgical Laboratory, Jamshedpur-831007, India

Received 1 November 1999; received in revised form 1 March 2001; accepted 1 May 2001

Abstract

A low cost ferruginous manganese ore (FMO) has been studied for the removal of arsenic from groundwater. The major mineral phases present in the FMO are pyrolusite and goethite. The studied FMO can adsorb both AS(III) and As(V) without any pre-treatment, adsorption of As(III) being stronger than that of As(V). Both As(III) and As(V) are adsorbed by the FMO in the pH range of 2–8. Once adsorbed, arsenic does not get desorbed even on varying the pH in the range of 2–8. Presence of bivalent cations, namely, Ni^{2+}, Co^{2+}, Mg^{2+} enhances the adsorption capability of the FMO. The FMO has been successfully used for the removal of arsenic from six real groundwater samples containing arsenic in the range of 0.04–0.18 ppm. Arsenic removals are almost 100% in all the cases. The cost of the FMO is about 50–56 US$ per metric tonne. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ferruginous manganese ore; Arsenic removal; Groundwater

1. Introduction

Occurrence of arsenic in groundwater may be both anthropogenic and geogenic in nature. Anthropogenic activities include mining, release of industrial effluents, wanton disposal of chemical wastes, to name a few. Arsenic from these wastes is released due to natural weathering and eventually contaminates the groundwater aquifer. Under extreme conditions, anthropogenic activities may also lead to geogenic release of arsenic to groundwater in soluble form. A typical case in point is the state of West Bengal in India where groundwater of at least six districts have been found to be contaminated with arsenic [1–3]. More recently, a very large area of Bangladesh has been reported to be severely affected with the arsenic contamination of groundwater [4,5].

The chemistry of arsenic in aquatic system is quite complicated as the element may exist in any one of the four stable oxidation states (+5, +3, 0, −3). However, in groundwater the arsenate (H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻) and arsenite (H₃AsO₃, H₂AsO₃⁻, HAsO₃³⁻) species are more predominant. A number of methods have been tried for the removal of arsenic from groundwater of which precipitation coagulation technique using Fe(III) salts or alum as coagulant has been most popular [6–11]. However, coagulation precipitation technique has been found to be not as efficient for As(III) as for As(V). As groundwater usually contains an appreciable proportion of As(III), an efficient arsenic removal by coagulation precipitation technique necessitates conversion of the total arsenic to As(V). Use of external oxidising agents tends to bring down the drinking water quality. Activated carbon [12] and activated alumina [7] have been separately used for removing As(V) from groundwater by adsorption. Lime softening has been reported for removing both As(III) and As(V) [13]. Other removal techniques include ion exchange, reverse osmosis and adsorption on a solid heterogeneous surface [14]. Recently a number of chelating resins have been prepared by impregnation of a porous polymer resin with chelating reagents that can absorb As(III) in the pH range of 0–0.15 [15].

*Corresponding author. Fax: +91-657-270527.
E-mail address: santanu@csnml.ren.nic.in
(S. Bhattacharjee).

0043-1354/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0043-1354(01)00234-2
Use of naturally occurring ores and minerals as adsorbent for removing arsenic has been attempted by some workers though not as extensively as precipitation coagulation technique. These include bituminous coal, lignite, illite, kaolinite [16], Ganga sand [17], hematite and feldspar [18].

In the present work a low cost ferruginous manganese ore (FMO) has been studied in detail for the purpose of removing arsenic from groundwater. The adsorption parameters, namely, shaking time, fineness of the particles and adsorbent dose have been optimised with respect to arsenic spiked tap water for both As(III) and As(V). Attempts have been made to ascertain adsorption mechanisms for As(III) and As(V) from appropriate adsorption isotherms. Finally, the FMO has been used for the removal of arsenic from six real life arsenic contaminated groundwater samples. The overall objective of the present study was to ascertain the capability of the FMO for removing arsenic from groundwater in a single step operation and without any pretreatment.

2. Experimental

2.1. Adsorbent

FMO used in the present study was collected from the Mineral Processing Division of National Metallurgical Laboratory, Jamshedpur. This is a low cost material abundantly available in South Bihar and Orissa. The average cost of the material is about US$50–56 per metric tonne. The material was powdered and washed with deionised water to remove dust and fines. The dried material was sieved and 250, 150 and 75 \( \mu \)m fractions were separated for the adsorption studies.

2.2. Instrumental

A JEOL JSM 840 A Scanning Electron Microscope with CAVEX 8000 EDS was used for identifying the material constituents. Trace elemental analyses were carried out with GBC 908 AA atomic absorption spectrometer. Silica, manganese and iron were analysed by conventional wet chemical methods [19–21]. Arsenic was analysed by the silver diethyldithiocarbamate (SDDC) technique and occasionally cross-checked by graphite furnace atomic absorption spectrometry (GFAAS). Arsenic in natural water samples were all analysed by hydride generation atomic absorption spectrometry (HGAAS). Inorganic phases present in the adsorbent were ascertained using Siemens D-500 X-ray Diffractometer.

2.3. Reagents

All the reagents used, including acids, were of Analytical grade. Stock arsenic solutions (1000 mg/l) were prepared for As(III) and As(V) from sodium arsenite (NaAsO\(_2\)) and sodium arsenate (Na\(_2\)HASO\(_4\)-7H\(_2\)O), respectively, using 18 M\( \Omega \) ASTM Grade 1 water.

2.4. Batch adsorption experiments

Hundred millilitre of a synthetic arsenic solution of predetermined concentration (‘mother’ solution) was placed in a stoppered 250 ml conical flask. A quantity of adsorbent with a particular size was added to the mother solution and shaken in a wrist shaker for a definite period of time. For optimisation, adsorbent dose was varied between 0 and 0.8 g, particle size between 250 and 75 \( \mu \)m and shaking time between 0 and 30 min. The solution was allowed to settle for 1 h, filtered and analysed for arsenic. The arsenic content of the solution before and after adsorption represented the amount of arsenic adsorbed by the adsorbent. Adsorption experiments were carried out for both As(III) and As(V).

2.5. Optimisation of parameters

Adsorbent dose, adsorbent particle size and shaking time were optimised for maximum adsorption by the method of continuous variation following batch adsorption experiments mentioned above. Optimum adsorbent dose, shaking time and particle size was 0.2 g, 5 min and 75 \( \mu \)m for 100 ml of 0.12 ppm As(III) solution and 100 ml of 0.19 ppm As(V) solution. Subsequent adsorption experiments were carried out with only optimised parameters unless stated otherwise.

3. Results and discussion

3.1. Characterisation of ferruginous manganese ore (FMO)

Fig. 1 gives the EDX microanalysis of the FMO. It is apparent from Fig. 1 that the material is essentially a Mn, Fe and Si matrix with probable traces of K and Al. Fig. 1 is supported by the chemical analyses data given in Table 1 which shows that the material is indeed a ferruginous manganese ore with MnO\(_2\) content of about 76.9%. Si, Fe and K are the other major elements present in it with traces of Al and P. The material also contains an appreciable amount of volatile matter. Fig. 2 shows the X-ray diffractogram of the adsorbent in which the phases with \( d \)-values have been indicated. The only prominent phase observed in Fig. 2 is \( \beta \)-MnO\(_2\) (pyrolusite). However, there are some smaller, but well defined peaks which correspond to \( \alpha \)-FeO(OH) (goethite) and SiO\(_2\) (quartz). Presence of these phases are in accordance with chemical analyses. One may thus infer from the characterisation studies that the mineral...
presently being studied is a ferruginous manganese ore containing about 76.9% of MnO₂ and 8% of Fe₂O₃. The mineral phases present are primarily pyrolusite and goethite.

3.2. Adsorption isotherms

Figs. 3 and 4 show the adsorption of As(III) and As(V), respectively, with varying weights of the adsorbent. Adsorption profiles are similar for both As(III) and As(V). The adsorbent weighing 0.2 g could adsorb 72.58% of As(III) from 100 ml of 0.12 ppm of As(III) solution while the same amount of adsorbent could remove 72.16% of As(V) from 100 ml of 0.19 ppm of As(V) solution. It is inferred that beyond 0.2 g of the adsorbent there was practically no adsorption for As(III) while for As(V), addition of a further 0.2 g of the adsorbent could effect only 3% further adsorption.

Generally both Langmuir and Freundlich isotherms are used for explaining the adsorption of metal ions on naturally occurring minerals. Langmuir and Freundlich isotherm equations are given below.

3.3. Freundlich isotherm

\[
X = \frac{m}{C_e^{1/n}}
\]

where \(X\) is the amount of adsorbate absorbed, \(m\) the amount of adsorbent, \(C_e\) the equilibrium concentration of the adsorbate in the solution and \(k\) is constant.

Taking the logarithm of Eq. (1)

\[
\log \left( \frac{X}{m} \right) = \log k + \frac{1}{n} \log C_e.
\]

If the adsorption data follow Freundlich pattern plot of \(\log (X/m)\) with \(\log C_e\) should yield a straight line and \(n\) and \(k\) may be calculated from the slope and intercept, respectively.

3.4. Langmuir isotherm

\[
\frac{C_e}{X/m} = \frac{1}{bV_m} + \frac{C_e}{V_m},
\]

where \(C_e\), \(X\) and \(m\) have the same meaning as described in Freundlich isotherm. \(b\) is a constant that represents adsorption bond energy and \(V_m\) a constant that represents maximum adsorption density corresponding to a monolayer covering the surface of the adsorbent.

Eq. (3) is also sometimes written as,

\[
\frac{1}{q_e} = \frac{1}{bV_m} \frac{1}{C_e} + \frac{1}{V_m},
\]
where $q_e$ is the equilibrium concentration of the adsorbate in the adsorbent (solid).

If the adsorption data follow Langmuir pattern, a plot of $C_e/(X/m)$ with $C_e$ (Eq. (3)) or a plot of $1/q_e$ with $1/C_e$ (Eq. (4)) should yield a straight line. Constants $b$ and $V_m$ may be calculated from the slope and intercept.

Attempts were made to fit the adsorption data for As(III) and As(V) in Freundlich (Eq. (2)) and Langmuir (Eq. (4)) isotherms separately upto 0.2 g of the adsorbent. The isotherms obtained are given below.

As(III)-Freundlich:

\[
\log \left( \frac{X}{m} \right) = 0.1281 \log C_e - 0.1662, \quad (R^2=0.8412); \text{ No. of observation } = 5.
\]

As(III)-Langmuir:

\[
\frac{1}{q_e} = 0.0134 \left( \frac{1}{C_e} \right) + 1.8631, \quad (R^2=0.7392); \text{ No. of observation } = 5.
\]

As(V)-Freundlich:

\[
\log \left( \frac{X}{m} \right) = 0.7836 \log C_e + 0.8962, \quad (R^2=0.7839); \text{ No. of observation } = 5.
\]

As(V)-Langmuir:

\[
\frac{1}{q_e} = 0.0683 \left( \frac{1}{C_e} \right) + 0.0650, \quad (R^2=0.8481); \text{ No. of observation } = 5.
\]

Freundlich and Langmuir constants ($k, n, b, V_m$) calculated from these isotherms are given in Table 2. In the case of As(III), the fit was better in the Freundlich
The value of $n$ usually lies between 1.4 and 5 for similar adsorption on soil [22]. However, in the case of As(III), a somewhat higher value of $n$ was observed. Interestingly, the Langmuir isotherm for As(III) was characterised by a very strong adsorption bond energy as indicated by the constant ‘$b$’, typical of monolayer adsorption which clearly indicated that the present FMO was an adsorbent for As(III). This was further supported by a low $V_m$ value which indicated a monolayer adsorption. In the case of As(V), the fit was slightly better in the Langmuir form. Relatively higher value of $V_m$ and lower value of ‘$b$’ pointed towards a probable multilayer adsorption. Comparison of ‘$b$’ values of As(III) and As(V) in the Langmuir isotherm clearly brings out the fact that the present FMO is an adsorbent for both As(III) and As(V) and between the two, it is a stronger adsorbent for As(III).

### 3.5. Adsorption and desorption at different pH

Adsorption studies presented so far were carried out at a pH of 6.3 for As(III) and a pH of 6.5 for As(V). It is apparent from Table 2 that the adsorption for both As(III) and As(V) are marked with strong adsorption bond energy as is evident from ‘$b$’ values. Also, it is clear from Table 2 that between themselves adsorption bond energy for As(III) is stronger than As(V). To establish this experimentally, adsorption and desorption studies were carried out with As(III) and As(V) using the FMO in the pH range of 2–8. For adsorption study, the procedure adopted so far was followed with 0.4 g of the adsorbent and 100 ml of 0.1 ppm of As(III)/As(V) at a desired pH. In the acidic range pH was adjusted with dilute HCl and in alkaline range pH was adjusted with dilute NaOH. For desorption study, initial adsorption was carried out with 0.4 g of the adsorbent and 100 ml of 0.1 ppm As(III)/As(V) at the pH of mother solution using the procedure adopted so far. Thereafter, the pH of the solution was adjusted to the desired pH by controlled addition of dilute HCl or dilute NaOH. The entire solution was shaken further for half an hour in a wrist shaker and allowed to settle for another hour before it was filtered and analysed for arsenic. The results are given in Table 3 where equilibrium arsenic concentration at every pH studied has been reported for adsorption and desorption experiments. It may be seen that 0.4 g of the FMO could adsorb the entire arsenic present in 100 ml of 0.1 ppm of As(III) solution in the whole pH range of 2–8. Equilibrium As concentration, $C_e$ was less than the As detection limit by the GFAA method [23]. Almost a similar situation was observed for As(V), though a minute trace of arsenic could be detected in the filtrate at a lower pH. These results are in accordance with our earlier observation where the adsorption bond energy constant ‘$b$’ for As(III) in the Langmuir isotherm was stronger than As(V). The desorption results also substantiated the same inference from a reverse direction. Once As(III)/As(V) became

#### Table 2
Freundlich and Langmuir isotherm constants for As(III) and As(V)

<table>
<thead>
<tr>
<th>Species</th>
<th>Freundlich (Eq. (1))</th>
<th>Langmuir (Eq. (4))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$</td>
<td>$n$</td>
</tr>
<tr>
<td>As(III)</td>
<td>0.68</td>
<td>7.81</td>
</tr>
<tr>
<td>As(V)</td>
<td>7.87</td>
<td>1.28</td>
</tr>
</tbody>
</table>

#### Table 3
Adsorption and desorption study for As(III) and As(V) at different pH

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Desorption</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>$C_e$ (ppm)</td>
<td>pH</td>
<td>$C_e$ (ppm)</td>
</tr>
<tr>
<td>2.1</td>
<td>&lt;0.0002</td>
<td>2.0</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td>3.3</td>
<td>&lt;0.0002</td>
<td>2.6</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td>4.0</td>
<td>&lt;0.0002</td>
<td>3.6</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td>4.8</td>
<td>&lt;0.0002</td>
<td>4.6</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td>7.0</td>
<td>&lt;0.0002</td>
<td>6.8</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td>8.1</td>
<td>&lt;0.0002</td>
<td>7.9</td>
<td>&lt;0.0002</td>
</tr>
</tbody>
</table>

adsorbed onto the FMO, for both As(III) and As(V) the adsorption bond energy was strong enough to hold the adsorbate ions, even when there was a wide pH variation in the range of 2–8. However, between themselves, As(III)–FMO bond was stronger than As(V)–FMO bond.

The results of adsorption and desorption study are also important from another viewpoint. It is evident from Table 3 that the FMO used in the present study has a wide working pH range within which it could adsorb As(III) and As(V), thereby making it a versatile medium for the purpose of arsenic removal. The desorption study, on the other hand, shows that once the mineral adsorbs arsenic, it firmly holds it. Variation of pH due to natural weathering is unlikely to release the arsenic from the filter sludge easily. This should make the sludge disposal relatively less cumbersome.

3.6. Disposal of arsenic sludge

Arsenic filter sludge is generally disposed either by converting the entrapped arsenic in the sludge into insoluble inorganic compounds or by bio-transformation of arsenic in the sludge. Arsenic forms an insoluble mineral scorodite in the presence of iron having chemical formula, FeAsO₄·2H₂O. Arsenic trioxide in aqueous medium is converted into scorodite using acidic nitrate solution at temperatures ranging from 140°C to 160°C [24]. Bio-transformation of arsenic is essentially carried out through microorganisms which form mostly volatile methylated arsenic compounds [25]. A novel arsenic sludge management is being worked out at NML in which native earthworm species are being used for converting arsenic from plant available to plant unavailable form. Arsenic filter sludge is intimately mixed with soil and farmyard manure and a local earthworm species Perionyx excavatus is cultured in that medium. It has been observed that plant availability of arsenic goes down in the earthworm cast.

3.7. Adsorption mechanism

The adsorbent FMO used in the present study was characterised to be having primarily pyrolusite and goethite mineral phases, other than silica as quartz. There are reports in the literature on the adsorption of arsenic on hydrous manganese and iron oxides [26]. Adsorption sites of hydrous manganese and iron oxides are, however, different in nature. Hydrous iron oxides have a pHZpc of about 8.6 and arsenite and arsenate anions may be directly adsorbed onto it [26]. Hydrous manganese oxides on the contrary have a pHZpc of about 2.3 and arsenite and arsenate anions may not be directly adsorbed onto it. However, the pHZpc of hydrous manganese oxides may be modified to a positive surface charge by the adsorption of other bivalent cations, and then it may be used to adsorb As(III) and/or As(V) [26].

The FMO used in the present study comprises goethite, which has the molecular formula FeO(OH) and it can directly adsorb arsenite and arsenate anions. However, pyrolusite, which is the major mineral phase in the ore has the chemical formula MnO₂ and does not have any hydroxy group attached to it. Therefore, the analogy with MnOOH does not strictly apply to it. However, it is evident from the LOI value that the FMO contained an appreciable amount of chemically bound moisture. This might allow the major mineral phase β-MnO₂ present in the FMO behave in a similar manner as hydrous manganese oxide. To ascertain this, additional adsorption experiments were carried out with As(III) and the FMO in the presence of a number of individual bivalent cations, namely, Ni⁺², Co⁺² and Mg⁺², the results of which are given in Table 4. It may be observed that in all the three cases presence of 30 ppm of the cation had a remarkable effect on As(III) adsorption, which increased by 14%. It is also interesting to note that all the three cations behaved in a similar manner which indicated that pyrolusite (β-MnO₂) present in the FMO studied behaved in the same manner as MnOOH. This phenomenon is being looked into in more detail for other mono-, bi-, tri-, hexa-, and hepta-valent cations. It was also observed in our laboratory that heating the FMO at 900°C completely destroyed its arsenic adsorption capacity.

3.8. Application of the FMO to real life groundwater samples

The FMO studied was used for the removal of arsenic in six natural groundwater samples collected from North-24 Paraganas, one of the most severely arsenic affected districts of West Bengal. Seventy-five micron (0.2 g) FMO was mixed with 100 ml groundwater sample and shaken for 5–10 min and allowed to settle for 1 h. The water was filtered and the arsenic content was analysed before and after adsorption using HGAAS technique. The results are shown in Table 5 which also gives Fe, Mn, Cr, Ni, Co, Ca, Mg, Zn, P and pH values of the water samples before and after adsorption. It may

Table 4
Effect of bivalent cations on As(III) adsorption

<table>
<thead>
<tr>
<th>Bivalent cations</th>
<th>Ce (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No cations</td>
<td>0.084</td>
</tr>
<tr>
<td>30 ppm Co²⁺</td>
<td>0.064</td>
</tr>
<tr>
<td>30 ppm Ni²⁺</td>
<td>0.064</td>
</tr>
<tr>
<td>30 ppm Mg²⁺</td>
<td>0.062</td>
</tr>
</tbody>
</table>
be seen that the arsenic contents of the six groundwater samples varied from 0.04 to 0.18 mg/l, and in all the six water samples 0.2 g of the FMO could bring down the arsenic level well below the detection limit of As by HGAAS [23]. Per cent removals of arsenic in six water samples varied from 98.5% to 99.8%. It was also heartening to note that the FMO lowered the iron level of all the six water samples after adsorption below 0.1 mg/l, the highest desirable value for Fe in drinking water. Since the FMO was actually a lean manganese ore, it was essential to ascertain if there was any leaching of manganese from ore to water. Manganese could not be detected in any of the water samples after adsorption. There was also a lowering of the phosphate level (given as P) in all the six water samples after adsorption. A slight increase in the calcium content of the water samples after adsorption could be observed but it was still much less than the highest desirable value, 40 mg/l. There was no significant change in the magnesium contents after adsorption.

4. Conclusion

The conclusions of the present study may be listed as follows:

The ferruginous manganese ore (FMO) used in the present study comprises 76.9% MnO₂, 8.0% Fe₂O₃, 5.7% of SiO₂ and 4.2% of K₂O as major constituents.

Primary mineral phases present in the FMO are pyrolusite (β-MnO₂), goethite α-FeO(OH) and quartz (SiO₂).

The FMO used is an efficient adsorbent for both As(III) and As(V) in the pH range of 2–8. The adsorbed arsenic does not become desorbed from the filter sludge even at pH 2, under laboratory conditions.

Presence of bivalent cations, namely, Ni²⁺, Co²⁺ and Mg²⁺ up to a certain level enhances the adsorption capability of the FMO.

Pyrolusite (β-MnO₂), the major mineral phase of the FMO behaves in a similar manner as hydrous manganese oxide, MnO(OH), because of the presence of chemically bound moisture.

The FMO has been successfully used for the removal of arsenic in six real life arsenic contaminated water samples.

There is no leaching of Mn or any other elements from FMO to water after adsorption.

Acknowledgements

The authors wish to thank the Director of NML for his kind permission to publish this work. Encouragement from HOD, ANC is gratefully acknowledged. The authors
express their gratitude to K.K. Gupta, Scientist, ANC Division for critically examining the manuscript. Help received from S.K. Das for EDX analysis, Ravi Kumar for XRD and Engineering division for the tracings are sincerely appreciated. The authors also gratefully acknowledge the help received from the NGO, Jana Sanghati Kendra, Madhyamgram, West Bengal in collecting the real life arsenic contaminated groundwater samples.

References


