Arsenic removal from aqueous solutions by adsorption on red mud

H. Soner Altundoğan *, Sema Altundoğan, Fikret Tümen, Memnune Bildik
Fırat University, Department of Chemical Engineering, 23279 Elazığ, Turkey

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Abstract
Use of red mud, which is a waste product from bauxite processing, has been explored as an alternate adsorbent for arsenic in this study. The tests showed that the alkaline aqueous medium (pH 9.5) favored the removal of As(III), whereas the pH range from 1.1 to 3.2 was effective for As(V) removal. The process of arsenic adsorption follows a first-order rate expression and obeys the Langmuir’s model. It was found that the adsorption of As(III) was exothermic, whereas As(V) adsorption was endothermic. It would be advantageous to use this residue as an adsorbent replacing polyvalent metal salts. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Arsenic adsorption; Red mud; Langmuir isotherm

1. Introduction

Although environmental restrictions and regulations have limited the production and uses of arsenic and its compounds, they are still extensively used in metallurgy, agriculture, forestry, electronics, pharmaceuticals and glass and ceramic industry, etc. Arsenic, being one of the more toxic pollutants, is introduced into the environment through weathering of rocks and mine tailings, industrial wastes discharges, fertilizers, agricultural employments of pesticides, smelting of metals and burning of fossil fuels.

Arsenic occurs in $-3$, 0, $+3$ and $+5$ oxidation states in aquatic systems. The elemental state is extremely rare whereas $-3$ oxidation state is found only at extremely reducing conditions. Arsenate species (pentavalent state) are stable in oxygenated waters. Under mildly reducing conditions, arsenites (trivalent state) predominate [1]. Arsenic combines strongly with carbon in arsenical organic compounds which are used as pesticides, chemotherapeutic agents and chemical warfare agents.

The presence of arsenic in water causes toxic and carcinogenic effects on human beings. It has been reported that long-term uptake of arsenic contaminated drinking water has produced gastrointestinal, skin, liver and nerve tissue injuries. The toxicity of arsenic firmly depends on its oxidation state and trivalent arsenic has been reported to be more toxic than pentavalent and organic arsenicals [2].

The wastewaters from some industrial source such as gold, copper and zinc ore extraction, acid mine drainage and wood product preservation contain up to 130 mg l$^{-1}$ soluble arsenic [3,4]. Also, potable waters in some parts of the world have been found to contain 0.1–2 mg l$^{-1}$ arsenic [5,6]. The presence of arsenic in drinking water has been restricted to 0.05 mg l$^{-1}$ [2].

Arsenic is commonly removed from aqueous solutions by coprecipitation with polyvalent metal hydroxide flocs such as iron(III) [7] and aluminum hydroxides [8,9].

The use of solid adsorbents in removing such pollutants from wastewater compares favorably with conventional precipitation or flocculation methods. For example, in some flocculation treatments, a large amount of salt must be added which introduces pollutants such as sulfate ions into the water. Moreover, the cost of the chemical reagents used in such treatments can limit their commercial application. Activated carbon [10], activated bauxite [10], activated alumina [10,11], amorphous aluminum hydroxide [12], amorphous iron (III) hydroxide [13], iron(III) hydroxide loaded coral limestone [14] and hematite [15] can be mentioned among the adsorbents studied for arsenic removal from aqueous solution.

Red mud is formed during the digestion in the Bayer Process which is practised for alumina production from bauxite. Mineralogically, red mud consists mainly of...
different forms of iron and aluminum oxide minerals, calcium and sodium aluminum silicates, various titanium compounds, etc. Oxidic constituents are the undisolved part of bauxite whereas silicates are formed from dissolved silica and alumina during desilication of aluminate liquors [16,17].

The purpose of the present study was to test red mud waste from alumina production as an alternate arsenic adsorbent. In this paper, the results of an investigation on the arsenic removing characteristics of red mud are described.

2. Experimental

Red mud used in the present study was obtained from Etibank Seydişehir Aluminium Plant, Konya, Turkey. Red mud slurry was taken from the outlet of washing thickeners. Wet sieve analysis showed that more than 95% of the solid particles are less than 53 μm.

The suspension was wet sieved through a 200 mesh screen. A little amount remained on the sieve and was discarded. Suspension having —200 mesh particles was allowed to settle and decanted, the liquid fraction was discarded. The solid fraction was washed five times with distilled water by following the sequence of mixing, settling and decanting. The last suspension was filtered and the residual solid was then dried at 105°C, ground in a mortar and sieved through a 200 mesh sieve. The product was used in the study.

A sample was subjected to wet chemical analyses [18]. Mineralogical analyses was done by a Siemens D-5000 XRD equipment. The chemical and mineralogical compositions are given in Table 1.

Stock solutions containing 1 g As(III) l$^{-1}$ were prepared by dissolving 1.320 g As$_2$O$_3$ (Merck 123) in 10 ml of 5 M NaOH and making up to 1 l with distilled water. Na$_2$HAsO$_4$.7H$_2$O salt (Merck 6284) was dissolved in water for 1 g l$^{-1}$ As(V) stock solution. These stock solutions were used to prepare experimental solutions of specified concentrations.

One gram of red mud powder was placed in a conical flask. Solutions containing 125 to 1500 μg arsenic and 5 ml of 0.1 M NaCl solution were made up to 50 ml using distilled water. Thus, solutions representing wastewaters in the concentration range 2.5–30 mg l$^{-1}$ were obtained. The solution was added to the powder in a flask. The initial pH value of the solutions was adjusted with either HCl or NaOH solutions the concentration of which are 0.01, 0.1 and 1.0 M. The flasks containing mixtures were capped tightly and immersed into the temperature controlled water bath and then shaken at the rate of 800±50 cycle/min with a mechanical shaker. At the end of the contact period, the mixture was then centrifuged for 10 min at 10 000 rpm and the final pH of the supernatants was measured. The solutions were analyzed spectrophotometrically, using silver diethyldithiocarbamate method [19] which is used to determine both arsenic species.

All chemicals used were of analytical reagent grade. All labware used in the experiments was soaked in diluted HCl solution for 12 h, washed and then rinsed four times with distilled water.

The experiments were performed in duplicate and the mean values were considered. In order to ascertain the reproducibility of results, a group of experiments were repeated a number of times and the results were found to vary within ±5%. The blank experiments showed no detectable As(III) and As(V) adsorbed on the walls of the flask.

3. Results and discussion

3.1. Effect of pH

Preliminary studies carried out at the original pH of mixtures (without acid or base addition) showed that the

<table>
<thead>
<tr>
<th>Constituent</th>
<th>% (w/w)</th>
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<tr>
<td>Al$_2$O$_3$</td>
<td>20.39</td>
</tr>
<tr>
<td>CaO</td>
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<tr>
<td>Fe$_2$O$_3$</td>
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<tr>
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<td>CO$_2$</td>
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</tr>
<tr>
<td>S</td>
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<tr>
<td>L.O.I. (900°C)</td>
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Table 1
Chemical and mineralogical compositions of the red mud

<table>
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<th>Chemical composition</th>
<th>Mineralogical composition</th>
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<tbody>
<tr>
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</tr>
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<td>Sodalite</td>
</tr>
<tr>
<td>CaO</td>
<td>Cancrinite</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Hematite</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>Diaspore</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Rutile</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Calcite</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>Minor minerals: Bayerite: Al(OH)$_3$; Boehmite: AlOOH; Quartz: α-SiO$_2$; Anatase: TiO$_2$; Kaolinite: Al$_2$Si$_2$O$_5$(OH)$_4$</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>L.O.I. (900°C)</td>
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</table>
removal of As(III) attained equilibrium in 45 min whereas equilibration time of As(V) was 90 min, for 133.5 μmol l⁻¹ initial concentration, at 20 g l⁻¹ adsorbent dosage and 25°C temperature. At these conditions, maximum adsorption of As(III) and As(V) were about 48 and 26%, respectively. Since the initial pH values of solutions were different for As(III) and As(V) and the nature of red mud is basic, the final pH values were also found different and measured as 10.5 and 9.9, respectively.

The effect of pH on As(III) and As(V) adsorption by red mud was studied in the initial pH range between 1 and 13 at the contact time of 60 min for As(III) and 120 min for As(V). Fig. 1 shows the effect of pH on adsorption density ($q$, μmol g⁻¹) which is a measure of the degree of adsorption. As(III) is effectively adsorbed at about pH 9.5. Adsorption decreases at both lower and higher pH values. Variations in As(V) adsorption on red mud at the pH range 1.1–3.2 were found to be slight. As(V) adsorption decreased sharply above pH 3.2. The adsorbed amount of arsenic species are 4.31 μmol g⁻¹ at the pH of 9.5 for As(III) and 5.07 μmol g⁻¹ at the pH of 3.2 for As(V). These results clearly show that red mud absorbs As(III) better in basic medium while As(V) is favourably adsorbed in an acidic pH range.

The removal of such anionic pollutants from aqueous solutions by adsorption is highly dependent on pH of the media which affects the surface charge of the solid particles and degree of ionization and speciation of adsorbate. Earlier investigators propose the mechanism below for surface behaviour of the solid–solution interface [20]:

$$\text{M}^{\text{III}}\text{O}^\text{2+} + \text{H}^+ \rightarrow \text{M}^{\text{III}}\text{O}_2\text{H}^\text{+}$$

where M stands for metallic component of the oxidic adsorbent. Hence, the hydroxylated surface of the adsorbent develops charge in aqueous solution through amphoteric dissociation. On the other hand, arsenicous and arsenic acids constitute different anionic species depending on pH. Dissociation constants have been calculated by using the Güntelberg approximation [21] for 0.01 M ionic strength as 9.14 (pK₁) and 13.39 (pK₂) for arsenic acid (fraction of AsO₃³⁻ species can be neglected) and as 2.21 (pK₁), 6.63 (pK₂) and 11.29 (pK₃) for arsenic acid. To interpret the experimental data by using amphoteric dissociation theory, the value of pH_{spc} is needed where the surface charge is zero. Surface is positively charged below the pH_{spc} while it will have negative charge above this pH. It can be determined by potentiometric titration route for oxidic adsorbents. But, in the present work, the pH_{spc} value of red mud could not be determined since some red mud components (e.g. sodalites) were dissolved during the potentiometric titration.

In the pH range 4.0–9.5, predominant species are H₃AsO₃ and H₂AsO₄⁻. As pH increases, the amount of negative arsenic species rises while the positively charged surface sites decrease up to the pH_{spc}. For example, at pH 7.5, the predominant arsenic species is H₃AsO₃ corresponding to 98% of total amount. However, at pH 9.5, the amount of H₂AsO₃ is decreased to 30% and the amount of other species (H₂AsO₄⁻ and only a little amount HAsO₃³⁻) is increased. In this connection, it can be stated that the arsenic can be adsorbed through an attraction of the neutral species to positively charged surface sites at lower pHs. But the adsorption mechanism at higher pHs may be expressed by binding the negative species to partially positive surface. The decrease in the adsorption yield above pH 9.5 may be attributed to an increase of negative surface sites and amount of negative arsenic species.

In a study carried out at comparable conditions with present study, it has been reported that As(III) adsorption by hematite is maximum at pH 7.0 [15]. Although, the red mud mainly consists of hematite (~35%), it does not exhibit similar surface properties with hematite since its surface is covered by sodium-aluminum silicate compounds (sodalites) which are precipitated during desilication of aluminate liquor in Bayer Process. Thus, different favourable pH values can be attributed to the complicated composition of red mud.

3.2. Effect of contact time

It was felt to be necessary to check the equilibration times for both arsenic types at the optimum pH values. The effect of contact time on adsorption at optimum final pH values of 9.5 for As(III) and 3.2 for As(V) is shown in Fig. 2. As can be seen, the removal of As(III) and As(V) increase with time and attains equilibrium
within 45 and 90 min, respectively. Data obtained in this study were fitted in the following first order rate expression of Lagergren (Fig. 3):

$$\log q_e - q = \log q_e - \left( \frac{K_{ad}}{2.303} \right) t$$

(2)

where $q_e$ and $q$ are the amounts of arsenic adsorbed at the equilibrium and at any time $t$ and $k_{ad}$ is adsorption rate constant. Linear plots of $\log(q_e - q)$ vs $t$ indicate the applicability of Eq. (2).

The $k_{ad}$ values, calculated from the slopes of the lines in Fig. 3, are 0.109 and 0.049 min$^{-1}$ for As(III) and As(V), respectively.

### 3.3. Adsorption isotherms and thermodynamic parameters

The adsorptions of As(III) and As(V) were found to be concentration dependent. It can be calculated from isotherm data that the amount adsorbed increased from 1.35 to 7.46 mmol g$^{-1}$ for As(III) and from 1.54 to 6.41 mmol g$^{-1}$ for As(V) in the initial concentration range of 33.4–400.4 mmol l$^{-1}$ at 25°C. The removal percentages calculated were 80.6–37.3 and 92.2–32.0 for As(III) and As(V), respectively. The experimental data obtained under these conditions were applied to linearized forms of Langmuir, Freundlich, Frumkin and Temkin isotherms [Eqs. (3)–(6), respectively] which are suitable for evaluation of adsorption.

$$C_e/q_e = 1/(bQ^o) + C_e/Q^o$$

(3)

$$\ln q_e = \ln b + n \ln C_e$$

(4)

$$q_e = (Q^o/2D) \ln[b(Q^o - 1)] + (Q^o/2D) \ln(C_e/q_e)$$

(5)

where $C_e$ is equilibrium concentration (mmol l$^{-1}$), $q_e$ is amount adsorbed at equilibrium (mmol g$^{-1}$), $Q^o$, $b$, $n$ and $D$ are isotherm constants. The values of $Q^o$, which is adsorption maxima or adsorption capacity (mmol g$^{-1}$) in Eqs. (3) and (5), can be compared with each other, whereas the definitions of $b$, $n$ and $D$ are different for the various models.

All these isotherms were fitted to the adsorption data obtained. Calculated correlation coefficients for these isotherms by using linear regression procedure for As(III) and As(V) adsorption at different temperature are shown in Table 2. As seen, The Langmuir isotherm yielded best fits to the experimental data. Langmuir plots for the adsorption of As(III) and As(V) on red mud are shown in Fig. 4. The values of the Langmuir constants were calculated from slopes and intercepts of plots (Table 3).

It has been reported that the adsorption of As(III) by hematite [15], As(III) and As(V) by activated carbon, activated bauxite, activated alumina [10] and amorphous iron hydroxide [9], As(V) by amorphous aluminum hydroxide [12] follows Langmuir isotherm. Langmuir isotherm which leads the adsorption process indicates that the reaction is a reversible phenomenon [10] and the coverage is monolayer [10,15].

The remarkable removal of arsenic could not be achieved by red mud when compared with other separation techniques such as coprecipitation with aluminum and iron salts and adsorption by preformed aluminum and iron hydroxides. On the other hand, it can compete against the adsorbents such as hematite, activated bauxite, activated alumina and iron(III) hydroxide loaded coral lime stone (Fe-coral) which have limited effecitivity. It has been reported that the maximum As(III) adsorp-
tion capacity of these adsorbents are 2.63, 16, 14 and 0.17 μmol g⁻¹, respectively. For As(V) adsorption by activated bauxite, activated alumina, activated carbon and the Fe-coral, the calculated corresponding values are 52, 67, 10 and 0.2 μmol g⁻¹ [10,14,15]. In the present study, As(III) and As(V) adsorption capacities of red mud at 25°C, estimated from Langmuir isotherm, are 8.86 and 6.86 μmol g⁻¹, respectively. It is evident that red mud is more effective than hematite and Fe-coral. However, Fe-coral has an advantage compared to other adsorbents because it is effective in a wide pH range. In this connection, activated bauxite and activated alumina seem to be more advantageous adsorbents but the red mud is an attractive material in view of being inexpensive and a very fine material.

To determine if the arsenic adsorption process by red mud is favourable or unfavourable, for the Langmuir type adsorption process, the isotherm shape can be classified by a term “r”, a dimensionless constant separation factor, which is defined as below [22–24].

\[
r = 1/(1 + bC_0)
\]

where \( r \) is a dimensionless separation factor, \( C_0 \) is initial concentration (μmol l⁻¹) and \( b \) is Langmuir constant (l μmol⁻¹). The parameter \( r \) indicates the shape of the isotherm accordingly:

- \( r > 1 \): Unfavorable
- \( r = 1 \): Linear
- \( 0 < r < 1 \): Favorable
- \( r = 0 \): Irreversible

The \( r \) values for As(III) and As(V) adsorption can be calculated from Langmuir constants which are given in Table 3. For example, at 25°C and an initial concentration of 133.5 μmol l⁻¹, \( r \) values were calculated as 0.232 and 0.057 for As(III) and As(V), respectively. All calculated \( r \) values indicate that adsorption of As(III) and As(V) on red mud are favorable at all concentrations and temperatures studied. Also, it can be stated that the reversibility of As(V) adsorption is lower than that of As(III). The lower reversibility of As(V) adsorption by red mud suggests that the mechanism governing the process may be chemical adsorption.

Standard Gibbs free energy (\( \Delta G^0 \)), standard enthalpy (\( \Delta H^0 \)) and standard entropy changes (\( \Delta S^0 \)) for the adsorption process have been calculated from the Eqs. (8)–(10), respectively.

\[
\ln(1/b) = \Delta G^0 / RT
\]

\[
\ln b = \ln b_0 - \Delta H^0 / RT
\]

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

where \( b \) is Langmuir constant which is related to the energy of adsorption, \( b_0 \) is a constant, \( R \) is an ideal gas constant (4.187 J mol⁻¹ K⁻¹) and \( T \) is temperature (K).

Calculated values of Langmuir parameters \( b \) and \( Q^0 \) and the energy parameters \( \Delta G^0 \), \( \Delta H^0 \) and \( \Delta S^0 \) are given

![Fig. 4. Langmuir plots for As(III) and As(V) adsorption by red mud (initial concn.: varied from 33.4 to 400.4 μmol l⁻¹; contact time: 60 min for As(III) and 120 min for As(V); pH: 9.5 for As(III) and 3.2 for As(V); red mud dosage: 20 g l⁻¹).](image-url)
in Table 3. The estimated value of $Q^o$ for As(III) adsorption decreases with rise in temperature while it increases for As(V) adsorption. The other Langmuir parameter $b$ exhibits similar trends. It can be stated that As(III) adsorption is exothermic whereas the adsorption of As(V) is endothermic. These results can also be seen from calculated $H$ values (Table 3). Hence, it can be concluded that the nature of As(III) adsorption is physical and that of As(V) is chemical. The negative Gibbs’ free energy values indicate the adsorption of both arsenic types are spontaneous. The decrease in free energy change with the rise in temperature shows an increase in feasibility of adsorption at higher temperatures [25]. The positive values of entropy change suggest some structural changes in adsorbate and adsorbent.

3.4. Effect of adsorbent dosage

Fig. 5 shows the effect of red mud dosage on the removal of arsenic. The arsenic removal efficiency is increased with the amount of red mud. Final arsenic concentrations and removal efficiencies were also calculated from the isotherms in Fig. 4. In Fig. 5, results from dosage study and values extracted from isotherms are given with solid and dashed lines, respectively. It can be stated that there is an acceptable fit between the results of isotherm and dosage studies.

Final arsenic concentration can be reduced below the regulation limits by increasing the adsorbent dosage. In general, the red mud adsorbed As(V) effectively more than the As(III). About a 100 g l$^{-1}$ red mud dosage is sufficient for a final arsenic concentration below the regulation values of potable waters for As(V) while more is needed to adequately remove As(III).

4. Conclusion

The solid fraction of red mud was tested to find out its As(III) and As(V) adsorption characteristics. Batch experiments show that red mud is capable of removing arsenic from aqueous solutions.

As(III) and As(V) adsorptions are equilibrated within 45 and 90 min respectively, at 25°C, 133.5 μmol l$^{-1}$ (10 mg l$^{-1}$) concentration and 20 g l$^{-1}$ red mud dosage. For As(III) and As(V), favorable adsorptions take places at pH 9.5 and 3.2, respectively. It should be noted that the adsorption densities at these conditions are 4.31 and 5.07 μmol g$^{-1}$ for As(III) and As(V), respectively. Data obtained from equilibration time study fit Lagergren

<table>
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<tr>
<th>Arsenic species</th>
<th>Temperature (°C)</th>
<th>Langmuir constants</th>
<th>Thermodynamic parameters</th>
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<tr>
<td></td>
<td>$b$ (l μmol$^{-1}$)</td>
<td>$Q^o$ (μmol g$^{-1}$)</td>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
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<tr>
<td>As(III)</td>
<td>25</td>
<td>0.025</td>
<td>8.86</td>
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Fig. 5. Effect of red mud dosage on the As(III) and As(V) adsorption (initial concn.: 133.5 μmol l$^{-1}$; contact time: 60 min for As(III) and 120 min for As(V); pH: 9.5 for As(III) and 3.2 for As(V); temperature: 25°C).
equation for both arsenic species. Isotherm studies show that the Langmuir equation fits the experimental data reasonably well. Thermodynamic calculations based on the data from the study on temperature indicate that As(III) adsorption reaction is exothermic and that of As(V) is endothermic.

A practically usable adsorbent should be readily separated from the liquid, effective in a wide range of pH, inexpensive and able to be reutilized. The difficulties in solid-liquid separation and its being effective in a narrow pH range decrease the usability of red mud as an adsorbent. However, red mud is a very economical material since it is a waste product and is very fine grained. In addition, arsenic adsorbed red mud may be reused in some red mud usable metallurgical processes which are recommended to utilize red mud as an iron source [16].

In conclusion, since red mud is a waste, is fine grained and inexpensive it can be economically used for the removal of arsenic from wastewaters. Its adsorption capacity may be increased by activation. On the other hand, liquid phase of red mud constituting a weak alkaline aluminate solution may be utilized for arsenic removal by coagulation. Forthcoming studies based on developing the arsenic adsorption capacity of red mud by activation and utilizing the liquid phase of red mud in the removal of arsenic by coagulation are in progress.

Acknowledgements

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References