Arsenic adsorption from aqueous solutions by activated 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

Heat treatment and acid treatment methods have been tested on red mud to increase its arsenic adsorption capability. The results indicate that the adsorptive capacity of red mud can be increased by acid treatment. This treatment causes sodalite compounds to leach out. As(III) and As(V) adsorption characteristics of activated red mud have similar tendencies with raw red mud. Batch adsorption studies have shown that activated red mud in dosages ranging from 20 to 100 g 1⁻¹ can be used effectively to remove arsenic from aqueous solutions. The process is pH dependent, the optimum range being 5.8–7.5 for As(III) and 1.8–3.5 for As(V). The maximum removals are 96.52% for As(V) and 87.54% for As(III) for solutions with a final pH of 7.25 and 3.50, respectively, for the initial arsenic concentration of 133.5 µmol l⁻¹ (10 mg l⁻¹), activated red mud dosage of 20 g 1⁻¹, contact time of 60 min and temperature of 25 °C. The adsorption data obtained follow a first-order rate expression and fit the Langmuir isotherm well. Isotherms have been used to obtain the thermodynamic parameters. It was found that the adsorption of As(III) was exothermic, whereas As(V) adsorption was endothermic. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Arsenic adsorption; Activation of red mud; Langmuir isotherm

1. Introduction

Arsenic is one of the priority pollutants in waste discharges. It is introduced in the aqueous system through geochemical reactions, industrial waste discharges, or agricultural use of arsenical pesticides. The toxic and carcinogenic effects of arsenic on living beings are well documented [1,2]. In most countries, the arsenic level of water is limited with the value of 0.05 mg/l [3]. Therefore, a water treatment process is necessary to remove arsenic from industrial wastes in order to reduce its concentration.

The most common method used for the removal of arsenic is coagulation [4,5]. On the other hand, recent interest associated with the removal of arsenic in wastewater has prompted the possible utilization of solid adsorbents instead of coagulants such as ferric salts and alum. Of these, activated carbon [6], amorphous aluminum hydroxide [7], activated alumina [6,8], activated bauxite [6], amorphous iron hydroxide [9] and haematite [10] are most often mentioned.

Red mud is a bauxite processing residue discarded in alumina production. Oxide and silicate compounds are differentiated in the composition of red mud. The oxides mostly originate from bauxite ore used in the Bayer Process, whereas silicate compounds are formed in the desilication step [11,12]. It has been reported that the red mud exhibits an adsorption towards anionic pollutants such as phosphate [13] and chromate [14]. In both investigations, it has been shown that an acid treatment step increased the adsorption capacity of red mud.

In a previous work [15], we studied the adsorption of arsenite and arsenate on red mud. It was found that the Langmuir Isotherm was obeyed. The aim of this study was to activate the red mud in order to increase its adsorption capacity. Also, arsenic adsorption characteristics of activated red mud were explored.

2. Experimental

2.1. Preparation of raw red mud

The red mud suspension provided by the Seydişehir Aluminium Plant, Konya, Turkey, was wet-sieved through a 200 mesh screen. The little amount of red
mud remaining on the sieve was discarded. The suspension having -200 mesh particles was allowed to settle and was then 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. This product was used in the study. It was subjected to wet chemical analysis [16]. The X-ray diffraction technique was used for mineralogical analysis. The chemical and mineralogical compositions of raw red mud are shown in Table 1.

### 2.2. Activation of red mud

Two methods were used to activate the red mud. In the first method, 50-g batches of dry red mud placed in porcelain dishes were heat-treated at various temperatures (200, 400, 600 and 800 °C) for 4 h. The powder was mixed at 30 min intervals during the heat-treatment. At the end of the treatment, weight loss was determined. The powder was then ground in a mortar and sieved through a 200 mesh sieve. In the second method, red mud was activated through acid treatment. For this purpose, 50-g batches of dry red mud were suspended in 1 l of 0.25–2.0 M HCl solutions and the suspensions were stirred for 2 h. The treated red mud was separated from the acid solution by filtration and the cake was washed once with 1 l of distilled water to remove the residual acid and soluble compounds. It was then dried at 105 °C for 4 h and used in the experiments.

In order to follow the amount of solubilized fraction, iron, aluminium and sodium were determined in the waste solutions discarded from acid treatments. Also, activated products obtained through both methods were subjected to XRD analysis.

To determine the rate of activation, the samples of treated red mud were subjected to standardized adsorption tests with As(III) solutions of 10 mg/l prepared in 0.01 M NaCl. Standard adsorption experiments were performed at the conditions of a solid dosage of 20 g l⁻¹, a temperature of 25 °C, a contact time of 60 min and a shaking frequency of 800±50 cycle min⁻¹. At the end of the contact period, the mixture was centrifuged for 10 min at 10000 rpm and arsenic was determined in the supernatants.

### 2.3. Preparation of solutions

All experiments were run at a constant ionic strength provided by 0.01 M NaCl. Solutions were prepared from As₂O₃ and NaOH for As(III) and from Na₂HAsO₄•7H₂O for As(V). 5 ml of 0.1M NaCl solution were added to the solutions containing 125–1500 μg As and final volumes were made up to 50 ml using distilled water. The initial pH of the solutions was adjusted with either an acid (HCl) or a base (NaOH) solution.

### 2.4. Adsorption experiments

In the adsorption study, As(III) and As(V) adsorption characteristics of activated red mud were investigated. The arsenic solutions were added to the weighed activated red mud powder placed in a conical flask. The flasks were immersed into the temperature controlled water bath and then shaken at the rate of 800±50 cycle min⁻¹ with a mechanical shaker. At the end of the predetermined contact periods, the mixtures were centrifuged for 10 min at 10000 rpm, pH and arsenic concentration of the supernatants were determined.

### 2.5. Methods of analysis

The solutions were spectrophotometrically analyzed for arsenic by the silver diethyldithiocarbamate method by which both As species could be determined [17].

In the waste solutions obtained in acid treatment, iron and aluminium were determined by atomic absorption

### Table 1

Chemical and mineralogical compositions of the red mud

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>% (w/w)</th>
<th>Mineralogical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constituent</strong></td>
<td><strong>% (w/w)</strong></td>
<td><strong>Minerals</strong></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.39</td>
<td>Sodalite</td>
</tr>
<tr>
<td>CaO</td>
<td>2.23</td>
<td>Cancrinite</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>36.94</td>
<td>Hematite</td>
</tr>
<tr>
<td>Na₂O</td>
<td>10.10</td>
<td>Diaspore</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15.74</td>
<td>Rutile</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.98</td>
<td>Calcite</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.50</td>
<td>Minor minerals: Bayerite: Al(OH)₃; Boehmite: AlOOH</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.05</td>
<td>Quartz: α-SiO₂; Anatase: TiO₂</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.04</td>
<td>Stilbite: Al₂Si₂O₅(OH)₄</td>
</tr>
<tr>
<td>S</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>L.O.I.(900 °C)</td>
<td>8.19</td>
<td></td>
</tr>
</tbody>
</table>

* Constituents are given in the bases of oxides.
spectrophotometry, whereas sodium was determined by flame photometry.

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.

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

3. Results and discussion

3.1. Activation studies

As seen from Table 1, raw red mud contains hematite and other oxides. Adsorption capability may be attributed to these constituents. However, sodium aluminium silicates (sodalite and cancrinite) formed from aluminate and solubilized silica during the alkaline digestion of bauxite in Bayer Process constitutes a substantial part of red mud. Results of standard As(III) adsorption tests carried out using red mud activated by heat treatment are shown in Figs. 1 and 2. These figures show the relationship between initial and final pH of suspensions and the effect of final pH on adsorption density (q, μmol g⁻¹) which is a measure of the degree of adsorption. As seen in Fig. 2, As(III) adsorption yields obtained by red mud activated at 400 °C are slightly higher compared to those of raw red mud. The little increase may be attributed to the dehydration of red mud. Maximum As(III) adsorption of red mud heated at 400 °C took place around pH 9.5. Heating the red mud at temperatures higher than 400 °C caused a decrease in As(III) adsorption. This decrease may be due to clogging the pores by partly melted silicates.

XRD analyses of heat-treated red mud showed that the cancrinite phase disappeared above 200 °C, whereas the sodalite peaks reduced above 400 °C probably due to phase changes. However, it was observed that peaks of rutile and some minor constituents such as quartz, boehmite and bayerite were reduced in the samples heated at higher temperatures.

The results of As(III) adsorption tests of red mud activated by acid treatment are given in Figs. 3 and 4. An increase in concentration of acid used in acid treatment up to 1.0 M causes an increase in adsorption efficiency of red mud, thereafter a decrease is observed. For example, raw red mud adsorbs about 65% As(III) from a 133.5 μmol l⁻¹ As(III) solution, whereas adsorption efficiencies were about 70; 88; 77 and 75 under the same conditions for red mud activated by 0.75; 1.0; 1.5 and
2.0 M HCl solutions, respectively. An increase in adsorption efficiency may be due to the leaching out of sodalite compounds which may block the active sites of the adsorbent. XRD analyses of acid treated red mud confirm the removal of sodalites. Accordingly, solubilization rates of sodium and aluminium calculated from the concentration of waste solutions of acid treatment prove these findings (Table 2). A decrease in adsorption efficiency of red mud treated by acid solutions having concentrations of more than 1.0 M, may be attributed to the dissolution of some small particles that causes a decrease in surface area. On the other hand, it was observed that mixtures of red mud-acid solution of 0.25 and 0.50 M exhibited colloidal properties during treatment. Red mud treated by these acid solutions exhibited low adsorptivity due to covering the silicic acid of the active oxidative sites.

In addition, maximum As(III) adsorption declines towards pH 7 due to an increase in the concentration of acid used in treatment. This may be another indication of the generation of oxide compounds in adsorption. It has been reported that the pH_{zpc} value of hematite, which is main component in red mud, is 7 [10]. Thus, it can be said that the physicochemical properties of hematite plays an important role in the adsorption of arsenic.

As a result, it can be stated that the adsorption ability of red mud can be increased by acid treatment. Therefore, the following study was carried out with red mud activated with a 1 M HCl solution. This product was named activated red mud (ARM).

### 3.2. Adsorption studies

Fig. 5 shows the relationship between the arsenic adsorbed on ARM and the final pH of the solution. Favourable adsorption takes place at pH 7.25 for As(III), whereas As(V) is removed most effectively in the pH range of 2–3.50. It can be noted that favourable As(III) adsorption declines to a pH of 7.25 when it is compared with a corresponding pH value of 9.50 for
raw red mud (RRM). However, RRM and ARM exhibited similar pH values for favourable As(V) adsorption.

The removal of As(III) and As(V) increases with time and attains equilibrium in 45 and 60 min, respectively, for the initial arsenic concentration of 133.5 μmol l⁻¹ (Fig. 6). The same observations were noted for raw red mud in the previous study [15], however, removal efficiencies are higher for activated red mud. It is further noted from Fig. 6 that the adsorption yield of As(V) is slightly higher than that of As(III). It is evident from Fig. 7 that the linear plot of log(qₑ/qₐ) vs. t shows the applicability of the Lagergren equation which is a first order rate expression. The values of k_ads obtained from the slopes of lines in the previous study [15] for raw red mud and in the present study for activated red mud are listed together in Table 3.

\[
\log(q_e - q) = \log q_e - (k_{ads} \times t)/2.303
\]  

(1)

Where qₑ and q (μmol g⁻¹) are the amounts of arsenic adsorbed at equilibrium and at any time t (min), and k_ads (min⁻¹) is the adsorption rate constant.

As a result, it can be stated that the maximum removals are 96.52% for As(V) and 87.54% for As(III) in solutions with final pH values of 7.25 and 3.50, respectively, and an initial arsenic concentration of 133.5 μmol l⁻¹.

The linear plot of \( C_e/q_e \) vs \( C_e \) shows the applicability of Langmuir isotherm for various temperatures [Eq. (2), Fig. 8a and b]. Langmuir constants b and \( Q^o \) were found from the slope and intercept of lines obtained from plotting \( C_e/q_e \) vs \( C_e \), respectively. In addition, \( \Delta H^o \) was found from the slope of the line obtained plotting 1/\( T \) and ln b [Eq. (4)].

\[
C_e/q_e = 1/(bQ^o) + C_e/Q^o
\]

(2)

\[
\ln(1/b) = \frac{\Delta G^o}{RT}
\]

(3)

\[
\ln b = \ln b_0 - \frac{\Delta H^o}{RT}
\]

(4)

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

(5)

where \( C_e \) is the equilibrium concentration (μmol l⁻¹), \( Q^o \) (μmol g⁻¹) and b (l μmol⁻¹) are Langmuir isotherm constants, \( b_0 \) is a constant, \( R \) is an ideal gas constant (4.187 J mol⁻¹ K⁻¹), \( T \) is temperature (K), \( \Delta G^o \) (J mol⁻¹), \( \Delta H^o \) (J mol⁻¹) and \( \Delta S^o \) (J mol⁻¹ K⁻¹) are free energy, enthalpy and entropy changes, respectively.

The calculated Langmuir and energy parameters are given in Table 4. Enthalpy changes for As(III) and

Table 2

<table>
<thead>
<tr>
<th>HCl Conc., M used in acid treatment</th>
<th>Solubilized amount (%)</th>
<th>Na</th>
<th>Al</th>
<th>Fe</th>
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<tr>
<td>0.25</td>
<td></td>
<td>66.70</td>
<td>12.38</td>
<td>0.04</td>
</tr>
<tr>
<td>0.50</td>
<td></td>
<td>76.92</td>
<td>37.67</td>
<td>0.07</td>
</tr>
<tr>
<td>0.75</td>
<td></td>
<td>80.32</td>
<td>49.18</td>
<td>0.19</td>
</tr>
<tr>
<td>1.00</td>
<td></td>
<td>80.32</td>
<td>49.18</td>
<td>0.33</td>
</tr>
<tr>
<td>1.50</td>
<td></td>
<td>81.45</td>
<td>50.93</td>
<td>0.65</td>
</tr>
<tr>
<td>2.00</td>
<td></td>
<td>83.72</td>
<td>49.38</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Arsenic species</th>
<th>Adsorption rate constants (k_ads; min⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>0.109</td>
</tr>
<tr>
<td>As(V)</td>
<td>0.049</td>
</tr>
</tbody>
</table>

* Previous study [15].

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Fig. 8. Langmuir Plots for As(III) and As(V) adsorption by activated red mud (Initial conc.: varied from 33.37 to 400.4 μmol l⁻¹; Contact time: 60 min for As(III) and 90 min for As(V); pH: 7.25 for As(III) and 3.50 for As(V); Activated red mud dosage: 20 g l⁻¹).
As(V) adsorption processes were calculated as $-6.88$ and $7.08 \text{kJ mol}^{-1}$. These results are in agreement with those of the adsorption of both arsenic species by RRM [15]. However, the comparison of the values of $Q^*$, which is the measure of adsorption capacity, determined in this and previous studies confirms that the treatment process increases the adsorption ability of red mud. The magnitude of $\Delta G^*$ values of ARM are rather high compared to those of RRM. On the other hand, the negative values of $\Delta G^*$ are indicative of the spontaneous nature of the process. These findings also support the increase in adsorption efficiency by acid treatment.

The effect of the dosage of ARM on the removal of arsenic is given in Table 5. Removal efficiencies and final arsenic concentrations obtained with ARM and RRM are summarized in Table 5. As can be seen that the final concentrations of $0.077$ and $<0.02 \text{mg l}^{-1}$ for As(III) and As(V), respectively, can be achieved by contacting the arsenic solutions ($10 \text{mg l}^{-1}$ or $133.5 \text{mg l}^{-1}$) with the ARM in a dosage of $100 \text{g l}^{-1}$. It is clearly seen that final As(III) and As(V) concentrations can be reduced to values near the regulatory limits by using lesser amounts of ARM than of RRM. Furthermore, final As(V) concentration can be reduced below the regulatory limits.
4. Conclusion

Red mud, an abundant waste product of the aluminium industry, can be used as an adsorbent for arsenic in aqueous solutions. Based on the experimental results of this study, the following conclusions can be drawn.

The arsenic adsorptivity of red mud can be improved by acid treatment, which removes sodalite compounds. However, more advantageous results were obtained with activated red mud compared to the results obtained with raw red mud in the previous study. Since the red mud is a waste product and acid treatment can be achieved by simple stirring of the red mud in a 1M HCl solution at ambient conditions, the cost of this adsorbent may be lower than that of i.e. activated carbon and activated alumina, which are currently regarded as advantageous adsorbents. It seems that it may be worth studying that the waste solution discarded from the acid treatment to determine if it may be used as coagulant due to its high aluminium content. The use of this waste solution may further reduce the cost of the arsenic removal process.

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References