Research Article

Removal of Antimony(III) from Aqueous Solution by Using Grey and Red Erzurum Clay and Application to the Gediz River Sample

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1. Introduction

Heavy metal ions such as Sb(III) are toxic and carcinogenic at relatively low concentrations. Antimony has been extensively used in lead alloys, battery grids, bearing metal, cable sheathing, plumber’s solder, pewter, ammunition, sheet, and pipe. Among the most important uses of antimony in nonmetal products are textiles, paints and lacquers, rubber compounds, ceramic enamels, glass and pottery abrasives phosphorus (a beryllium replacement), and certain types of matches (SbCl₃). US EPA and EU have established 6 and 10 µg L⁻¹, respectively, of maximum permissible Sb concentrations in drinking water [3, 4]. In natural water, Sb mainly exists in the inorganic forms of Sb(III) and Sb(V) [5]. Antimony(III) is reported to be 10 times more toxic than Sb(V) [6–9]. When redox speciation determinations are performed, most studies report the dominance of Sb(V) under oxic conditions. However, the presence of significant proportions of Sb(III) is sometimes detected [10]. The analytical techniques more commonly used for the characterisation of aqueous antimony species are hydride generation methods coupled with AAS, AES, and MS detection systems. A variety of electrochemical methods have also been used for determination of total antimony in natural water samples. Determination of total antimony by differential pulse anodic stripping voltammetry (DPCSV) has been described by a few authors [11–14]. Niedzierski and Siepak presents a comparative description of different methods of determination of arsenic, antimony, and selenium: spectrophotometric, electroanalytical (voltammetry), activation analysis, atomic fluorescence, and the methods of inductive or microwave-induced plasma in combination with different detection methods (emission or mass spectrometry) [15]. A number of methods have been used for the removal of antimony. These include reduction and precipitation [16], solvent extraction [17], ion exchange [18], reverse osmosis [19], membrane filtration [20], sorption in fixed-bed column [21], and biosorption [22, 23]. On the other hand, adsorption method is more effective in reducing toxic metal concentration [24, 25]. The adsorption systems have many advantages of simplicity, fastness, and suitability for water and wastewater containing moderate and low concentrations of metals. Moreover, adsorbents must have a large surface area; a chemical nature and polarity of the adsorbent surface influence the attractive forces between the adsorbent and...
adsorbate [26–28]. Clay materials possess a layered structure and are considered as host materials [29]. Natural clay minerals are well-known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high adsorption properties, and potential for ion-exchange, clay materials are strong candidates as adsorbents. Abollino et al. have observed that Na-montmorillonite adsorbs Cd, Cr, Cu, Mn, Ni, Pb, or Zn even when organic substances (bonds) are present [30]. Cd, Cr, Cu, Ni, Pb, and Zn were adsorbed on mineral clays from solutions with several concentrations by Covelo et al. [31].

In this study, we characterized grey and red Erzurum clay and used it to remove the toxic metal ions such as Sb(III) from aqueous solution in batch adsorption system. The Sb(III) adsorption of the grey and red Erzurum clay was examined in an aqueous solution. The effects of contact time, pH, and temperature on the adsorption capacity were carried out. This method was applied on the real sample.

2. Experimental

2.1. Reagent. All reagents were of analytical grade. SbCl$_3$ was supplied from Merck (Darmstadt, Germany). The following buffer solutions were used at a concentration of 0.1 mol L$^{-1}$ to adjust the pH: citric acid/sodium citrate buffer (pH 3.0), acetic acid/sodium acetate (pH 4.0–6.0). Grey and red Erzurum clay was obtained from Erzurum (Oltu) in Turkey.

2.2. Instruments. Antimony (III) concentration measurements were carried out using Metrohm 746 VA Trace Analyzer differential pulse anodic stripping voltammetry. A conventional three-electrode system, comprising a medium-sized hanging mercuric drop electrode, with a surface area of 1.8 mm$^2$, a platinum wire counter electrode, and an Ag/AgCl (in saturated KCl) reference electrode was used in all experiments. The reported potentials were referred to the Ag/AgCl electrode. Solutions were deoxygenated with high purity nitrogen for 220 s prior to each experiment, and it was performed under a nitrogen atmosphere. The pH of solution was measured with a Hanna P211 microprocessor pH meter using a combined glass-calomel electrode. The shaking was carried out in a termostated electronic shaker Labart SH-5. X-ray analyses were carried out using JSDX 100 S 4 Jeol X-Ray diffractometer.

2.3. Method. Stock solutions (1000 mg L$^{-1}$) of Sb(III) were prepared by dissolving 0.9336 g SbCl$_3$ diluted to 500 mL with 5.0 M HCl. Standard solutions of antimony at required concentrations were prepared by appropriate dilution. The pH of the solutions was adjusted by using citric acid/sodium citrate, acetic acid/sodium acetate. The sample solution (5.0 mL) containing 10 mL 0.6 M HCl supporting electrolyte media and 10 mg L$^{-1}$ of Sb(III) was transferred into the voltammetric cell, and 10 s after addition of Sb(III), the stirrer was switched on and the solution was purged with nitrogen gas for 220 s. The accumulation potential (−190 mV) was applied to a fresh HMDE for 60 s whilst stirring the solution. Following the accumulation period, the stirrer was stopped, and after 5 s the voltammogram was recorded by applying a negative-going linear sweep scan from −300 to +50 mV the Ag/AgCl reference electrode under the scan rate of 10 mV s$^{-1}$ (Figure 1). The peak current for Sb(III) was measured at about −190 mV at 5 and 14 min after addition of antimony. A blank solution without antimony was used to obtain the blank peak current. The detection limits for determination of Sb(III) were 7.0 ng/mL.

2.4. Characterization of Grey and Red Erzurum Clay. FTIR analyses were carried out on the grey and red Erzurum Clay using Perkin Elmer FTIR System Spectrum BX spectrophotometer. Samples for FTIR determination were dried and ground with spectral grade KBr in an agate mortar. A fixed amount of sample (1% w:w) in KBr was used to prepare the pellet. All FTIR measurements were carried out at room temperature.

2.5. Batch Adsorption Experiments. Adsorption experiments were carried out in batch technique. 0.50 ± 0.02 g of each adsorbent (grey and red Erzurum clay) was put into beaker containing 50 mL of 200 mg L$^{-1}$ Sb(III) solution (in 5.0 M HCl), and the suspension was stirred. After decantation, the concentration of Sb(III) was analyzed by differential pulse anodic stripping voltammetry method. The amount of Sb(III) retained by the solid sorbent was measured by difference. The effect of contact time was studied 15–300 min. The effect of pH on Sb(III) adsorption was studied by using pH 3.0 (0.1 M citric acid–0.1 M sodium citrate) and pH 4.0–6.0 (0.1 M CH$_3$COOH–0.1 M NaCH$_3$COO) buffer systems. Isotherm studies were conducted with a constant grey and red Erzurum clay weight (0.50 ± 0.02 g) and varying initial concentrations of Sb(III) in the range of 10–50 mg L$^{-1}$. All the experiments were carried out twice. The percentage adsorption of antimony on adsorbate from aqueous solution was computed as follows:

\[
\text{Adsorption} (\%) = \frac{C_{\text{in}} - C_{\text{fin}}}{C_{\text{int}}} \times 100. \tag{1}
\]
3. Results and Discussion

3.1. X-Ray Analysis. The X-ray analysis for the grey and red Erzurum clay is shown in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grey clay (%)</th>
<th>Red clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.36</td>
<td>58.17</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.06</td>
<td>13.22</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.85</td>
<td>10.06</td>
</tr>
<tr>
<td>CaO</td>
<td>8.6</td>
<td>5.39</td>
</tr>
<tr>
<td>MgO</td>
<td>3.0</td>
<td>1.52</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.49</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.7</td>
<td>1.74</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.41</td>
<td>0.23</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.16</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) Grey Erzurum clay
(b) Red Erzurum clay with Sb³⁺

The amount of metal ion adsorbed was calculated according to the following equation:

\[ q_e = \frac{C_{\text{in}} - C_{\text{fin}}}{W} \times V, \]

where \( C_{\text{in}} \) is the initial Sb(III) concentration (mg L⁻¹), \( C_{\text{fin}} \) is the final Sb(III) concentration (mg L⁻¹), \( V \) is the volume of the Sb(III) solution (L), and \( W \) is the weight of the grey and red Erzurum clay (g).

3.2. FTIR Spectroscopy. The FTIR spectra were shown of the grey and red Erzurum clay in Figures 2 and 3. The IR spectrum of grey and red Erzurum clay exhibits an adsorption band from 3600 to 3200 cm⁻¹ due to stretching vibration of the Si–OH, Al–OH and other metal hydroxide groups. In the spectrum of grey and red Erzurum clay, the definition of a peak near 1600 cm⁻¹ is attributed to the vibration of water molecules retained in the silica or alumina matrix. The peaks at 469 cm⁻¹ may be defined as asymmetric stretching modes of Si–O–Si bond.

3.3. Effect of the Adsorbent Dose and Particle Size on Sorption of Antimony(III). The effect of the adsorbent dose on the capacity of the antimony ions Sb(III) was shown in Figure 4. The amount of the adsorbent was varied in the range 0.1–1.0 g. 50% and 81% adsorption capacity was observed for 0.5 g of the red and grey clay, respectively. 99% adsorption was observed for 1 g of red and grey Erzurum clay. Adsorbent dose was chosen as 0.5 g based on these results. The adsorbent particle size was varied in the range of 100–500 mesh. 97% adsorption capacity was found for 100 mesh of adsorbent dose. Adsorption capacity was increased to 99% for 500 mesh size. Adsorbent particle size was chosen to be 500 mesh.

3.4. Effect of Contact Time on Sorption of Antimony(III). The effect of the contact time on the capacity of the antimony ions Sb(III) was shown in Figure 5. The contact time was varied in the range 15–300 minute, and the initial metal concentration was fixed at 200 mg L⁻¹. As shown in Figure 5, it was remarkable that an increase in the contact time for Sb(III) ions led to an increase in the adsorption capacity of grey and red Erzurum clay. After 45 minutes adsorption was observed in
Figure 5: Effect of the adsorption time on the adsorption capacities of grey and red Erzurum clay for Sb(III) ions (○: grey clay, ■: red clay).

Figure 6: Effect of the pH on the adsorption capacities of grey and red Erzurum clay for Sb(III) ions (○: grey Erzurum clay, ■: red Erzurum clay) (50 mL, 200 mg L\(^{-1}\), 0.5 g adsorbent, and 45 min. contact time).

Figure 7: The graph obtained by using the visual Minteq programme for Sb(III) species in the presence of 0.1 M HCl and 0.1 M KCl in the pH range 2–12.

3.5. Effect of pH on Sorption of Antimony(III). The pH of the aqueous solution is an important parameter in adsorption processes. To prevent precipitation, experiments were carried out at pH < 6.0 to ensure solubility of metal ions [33–35]. At higher pH values decrease in adsorption efficiency is due to the formation of soluble hydroxylated complexes of the antimony and their competition with the active sites, and as a consequence, adsorption would decrease [1]. The adsorption of Sb(III) ions was highly dependent on the pH of the metal solution because pH can affect the solubility of the metal ions and at the same time influence the ionization state of the functional groups existing on the adsorbent [36]. The effect of pH on the adsorption of antimony (III) ions was studied at different pH values (1.0–6.0) using grey and red Erzurum clay (500 mg) at constant metal ion concentration (200 mg L\(^{-1}\)).

pH selection in the range of 1.0–6.0 was rationalized by the fact that while pH > 2.0 could result in the formation of metal hydroxide precipitates, the results indicate that the maximum uptake of Sb(III) ions takes place at pH 1.5. Similar results have also been reported for the sorption of antimony [37–39]. Effect of pH on sorption of Sb(III) ions was shown in Figure 6. The results were shown, which indicated that sorption of Sb(III) on grey and red Erzurum clay decreased above pH 2. It was observed from the graph of the variation of the concentrations of the antimony(III) species with pH obtained using the visual Minteq program [40] (Figure 7) that after pH 2 species SbO\(^{+}\) and Sb(OH) decreases while Sb(OH)\(_3\) increases, which explains the weak sorption after pH 2.

Although high adsorption was observed at low pH, we carried out all studies at natural water’s pH without using any buffer solution.

3.6. Effect of Temperature on Sorption of Sb(III) Ions. In this study, the adsorption process was assessed at different temperatures between 10 and 40°C. Figure 8 shows that the temperature had no important effect on the adsorption of Sb(III). Maximum adsorption was observed at 25°C. It can be seen in Figure 8 that over 25°C adsorption was decreased a little. As seen in Figure 8, adsorption capacity was decreased a little with an increase in temperature. With increasing temperature, the attractive forces between the grey and red Erzurum clay surface and metal ion are weakened, and then sorption decreases. Adsorption temperature was chosen at 25°C.

3.7. Adsorption Isotherm Models. Adsorption isotherms are used to express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption...
Table 2: Langmuir and Freundlich isotherm constants for adsorption of Sb(III) ions on grey and red Erzurum clay.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Langmuir isotherm constants</th>
<th>Freundlich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q$ (mg g$^{-1}$)</td>
<td>$b$</td>
</tr>
<tr>
<td>25°C</td>
<td>9.15</td>
<td>71.4</td>
</tr>
<tr>
<td>40°C</td>
<td>8.58</td>
<td>33.3</td>
</tr>
</tbody>
</table>

Table 3: Thermodynamic parameters for Sb(III) ions.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey Erzurum clay</td>
<td>$-202.439$</td>
<td>$23.744$</td>
<td>$0.796$</td>
</tr>
<tr>
<td>Red Erzurum clay</td>
<td>$-200.258$</td>
<td>$55.403$</td>
<td>$0.903$</td>
</tr>
</tbody>
</table>

Figure 8: Effect of the temperature on the adsorption capacities of grey and red Erzurum clay Sb(III) ions (● grey Erzurum clay, ■ red Erzurum clay) (50 mL, 0.5 g adsorbent, and 45 min. for Sb(III)).

Figure 9: Langmuir plot for Sb(III) adsorption on red Erzurum clay at equilibrium (10°C).

3.8. Adsorption Thermodynamics. To investigate the controlling mechanism of the adsorption processes, temperature-dependent distribution coefficient was computed as follows:

$$K_d = \frac{C_{ad}}{C_e},$$  \hspace{1cm} (4)

where $K_d$ is the equilibrium constant, $C_{ad}$ and $C_e$ are equilibrium concentrations (mg L$^{-1}$) of Sb(III) on the adsorbent and in the solution, respectively. The adsorption process was also assessed at different temperatures between 10 and 40°C. Temperature effects on adsorption were shown in Figure 8. Thermodynamic parameters including the change in free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) were calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_d,$$  \hspace{1cm} (5)

where $R$ is the universal gas constant (8.314 J/mol K), $T$ is the temperature (K), and $K_d$ ($q_e/C_e$) is the distribution coefficient. The enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) parameters were estimated from the following Van’t Hoff equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}.$$  \hspace{1cm} (6)

Values of the standard Gibbs free energy change for the adsorption process obtained from (6) were listed in Table 3.

capacities of the sorbents for pollutants in aqueous solutions. In this study, the two adsorption isotherm models, Langmuir and Freundlich isotherms, were selected to fit the equilibrium data. The Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between sorbed species [41]. In mathematical form, it is written as

$$\frac{C_e}{q_e} = \frac{1}{Q \cdot b} + \frac{C_e}{Q},$$ \hspace{1cm} (3)

where $C_e$ is equilibrium concentration of the metal (mg L$^{-1}$) and $q_e$ is the amount of the metal adsorbed (mg) per unit of the adsorbent. When $C_e/q_e$ is plotted against $C_e$, a straight line with a slope of $1/Q$ and intercept was obtained, which shows that the adsorption of Sb(III) follows Langmuir isotherm model. The Langmuir parameters $Q$ (mg g$^{-1}$) and $b$ (L mg$^{-1}$) were calculated from the slope and intercept and were given in Table 2. According to the results, Langmuir model was found to describe adsorption successfully than Freundlich model isotherm in respect to linearity coefficients obtained for both models ($R^2 = 0.9996$ and 0.9555) (Figure 9 and Table 2) for Sb(III) ions. The Langmuir model predicts the formation of a monolayer of the adsorbate on the adsorbent surface [42]. In this study the maximum adsorption capacity of grey and red Erzurum clay for Sb(III) was determined as 9.15 mg g$^{-1}$.
The positive value of $\Delta H$ (23.744 kJ mol$^{-1}$) and the positive value of $\Delta S$ (0.796 kJ K$^{-1}$ mol$^{-1}$) indicate that the adsorption processes are spontaneous at high temperatures for Sb(III) ions. The negative value of $\Delta G$ (−202.439 kJ mol$^{-1}$) shows an adsorption process proceeds spontaneously. $\Delta H^* = (55.403 \text{ kJ mol}^{-1})$, $\Delta S^* = (0.903 \text{ kJ K}^{-1} \text{ mol}^{-1})$, and $\Delta G^* = (−200.258 \text{ kJ mol}^{-1})$ were found for red Erzurum clay.

3.9. Application of (III) Removal in Gediz River Samples. The physical and chemical parameters of water and the level of heavy metal concentration in water and sediment samples were analyzed in five different stations of Gediz River by Öner (2008) and Kayar (2003). The average level of some parameters is BOD: 67.7 mg/L, COD: 88.7 mg/L, pH: 7.6, and turbidity: 440 mg/L SiO$_2$. In water samples, the metals in high level are Pb: 27.0 ± 0.8% μg/L at Nif River, Cr: 48.9 ± 0.9% μg/L at Muradiye Bridge, Cd: 12.1 ± 0.6% μg/L at Istanbul Bridge, Cu: 90.2 ± 0.4% μg/L at Muradiye Bridge, and Ni: 309.8 ± 0.7% μg/L, Fe: 914.1 ± 0.3% μg/L, and Zn: 208.3 ± 0.5% μg/L in Karaçay [43]. According to the results obtained, the highest metal concentrations were found as 1.00 mg/L Pb (Karaçay); 0.09 mg/L Cr; 2.70 mg/L Ba; 3.9 mg/L Al (Muradiye Bridge); 0.04 mg/L Cd; 0.39 mg/L Cu (Istanbul Bridge); 0.90 mg/L Ni (Nif Çay); and an average value of 1.00 mg/L Fe and 3.15 mg/L Zn (all stations) [44]. The quality of water is at the level of four, according to Water Pollution Control Regulations. Therefore, Gediz River was chosen for this study. The river waters were taken from 3 stations in the vicinity of Manisa, Muradiye Gediz River Bridge, the Karaçay, and Nif Stream. The pH of the samples were measured, 7.8, 8.2, and 7.4, respectively. Sb(III) level was measured by DPP-ASV. Sb(III) removal from Gediz River samples using optimized experimental parameters (contact time: 45 min, temperature: 25°C) was studied. The results were given in Table 4.

4. Conclusions

In this study, the equilibrium, thermodynamics of the adsorption of Sb(III) from aqueous solution using low cost adsorbent (grey and red Erzurum clay) were investigated using a batch system. The maximum adsorption capacity of grey and red Erzurum clay for Sb(III) was found to be 9.15 mg/g 25°C. Based on a linearized correlation coefficient the Langmuir isotherm model gives better fit than the Freundlich isotherm model. Red Erzurum clay was used in real sample (Gediz River) for removal of Sb(III). In conclusion, grey and red Erzurum clay have been proven to be effective adsorbents for removal of toxic metal ion such as Sb(III).

### List of Symbols

- $\Delta G$: Energy change
- $\Delta H$: Enthalpy change
- $\Delta S$: Entropy change
- $C_e$: Equilibrium concentration
- $C_r$: Residual lead concentrations
- $C_{ini}$: Initial Pb(II) concentration
- $C_{fin}$: Final Pb(II) concentration
- $q$: The amount of the metal adsorbed
- $Q$: Capacity of the adsorbent calculated from the slope of Langmuir isotherm
- $b$: Capacity of the adsorbent calculated from the intercept of Langmuir isotherm
- $V$: Volume of the solution
- $m$: Amount of the adsorbent
- $R$: Universal gas constant
- $K$: Temperature
- $K_d$: Distribution coefficient
- $W$: Weight of the adsorbent

### References


[23] T. Pérez-Corona, Y. Madrid, and C. Câmara, “Evaluation of selective uptake of selenium (Se(IV) and Se(VI)) and antimony (Sh(III) and Sh(V)) species by baker’s yeast cells (Saccharomyces cerevisiae),” Analytica Chimica Acta, vol. 345, no. 1–3, pp. 249–255, 1997.


