Removal of Pb²⁺ and Fe²⁺ from Aqueous Solutions by Adsorption on “Kosovo” Clay

Teuta Selimi¹, Makfıre Sadiku¹*¹, Naim Hasani², Melek Behluli³, Avni Berisha¹
¹Department of Chemistry, Faculty of Natural Sciences, University of Prishtina, Str. "Nëna Terezë" n.n., Prishtinë, Kosovo.
²Department of Hydrotechnics, Faculty of Engineering and Architecture, University of Prishtina, Bregu i Dëllit, n.n., Prishtinë, Kosovo.
³Faculty of Economics, University of Prishtina, Str. ”Agim Ramadani”, Prishtinë, Kosovo.
*Corresponding author’s E-mail: makfire.sadiku@uni-pr.edu

Accepted on: 10-09-2016; Finalized on: 30-09-2016.

ABSTRACT

The use of clay in its natural and treated form obtained from Kamenica, state Kosovo, as adsorbent to remove Pb²⁺ and Fe²⁺ from aqueous solution was investigated using batch experiments. Adsorption experiments were carried out for various initial concentrations of ions and contact times while the amount of adsorbent was kept unchanged. From the results obtained, it was found that the removal of ions depends on initial concentrations and contact times, the amount of metal ions adsorbed was increased with increasing of initial concentration and contact time. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherms. The Freundlich isotherm model gave a better fit to the adsorption data than the Langmuir isotherm. Therefore, this study demonstrates that our clay could be used to adsorb heavy metals from aqua solutions.

Keywords: Adsorption, clay, isotherm, metal ion.

INTRODUCTION

The pollution by heavy metals currently it is becoming a big challenge and a concern for the water quality and also for the environment in general³. Some metal ions are toxic even if their concentration is very low, and their toxicity increases with accumulation in water and soils³.

Metals found to be of great environmental concern by the World Health Organization (WHO) are lead, mercury, chromium, zinc and iron.

Lead is one of the most toxic among these metals, is widely distributed in water and soil with recognized accumulative and persistent characteristics¹.

When accumulated in the human body, Pb(II) causes damage to organs and other systems (especially in young children)⁴. The assimilation of relatively small amount of lead over a long period of time in humans can cause malfunctioning of the organs and central nervous system, high concentration of lead can damage the brain, liver and kidney⁷.

Several treatment methods have been suggested for heavy metals mitigation, nevertheless, the search for cost effective, alternative technologies or sorbents for metals treatment from contaminated wastewater streams is needed. Natural materials that are available in large quantities or even certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents⁸.

Physiochemical methods such as coagulation, flocculation, ion exchange, membrane separation, photodegradation, and electrochemical oxidation have been used for the treatment of contaminated water.

Among them, adsorption is the most efficient, promising, and widely used in wastewater treatment because of its simplicity, economic viability, technical feasibility, and social acceptability⁹.

Clay has typical properties (large surface area, high cation exchange capacity chemical and mechanical stability and a layered structure) that predispose them to be good adsorbents. Bentonite belongs to the group of clay minerals. A number of studies have shown their effectiveness for the removal of metal ions¹⁰.

Keeping this in mind, the main purpose of the present work was to evaluate the feasibility of Kamenica’s clay to operate as sorbents to capture heavy metals from wastewater in order to propose other roles for these materials than its use as soil amendment.

MATERIALS AND METHODS

Reagents and Solutions

All the reagents used were of analytical grade and distilled de-ionized water was used in preparation of all solutions.

Solution of heavy metals, with different concentration was prepared by dissolving required quantity of their salts (PbCl₂ and FeCl₃) in water. Freshly prepared solution was used for each experiment.

Preparation of Acid-Ativated Bentonite

Kamenica’s (Kosovo) clay was obtained from Kamenica, Kosovo. The clay was dried and after that the clay was treated with 1M sulphuric acid in water bath in relation 1g bentonite with 5ml acid. The composition was shaken for 1h. The acid treated clay was centrifuged, air dried and ground to fine powder (< 0.12 mesh).
Adsorption Experiments

Adsorption tests were performed by batch experiments, under stirring at room temperature (20 °C). Each adsorption study was performed by adding 1g of the adsorbent to 5 ml of a given concentration of the adsorbate.

At the end of the given contact time, the solid and liquid phases were separated by centrifugation. The initial (C₀) and equilibrium (Cₑ) concentrations of Pb²⁺ and Fe²⁺ in the solutions were determined by flame atomic absorption spectrometer (Parkin Elmer 370A). All measurements were carried out in air/acetylene flame. Each experiment was repeated and the mean value was calculated in order to minimize errors. The uptake capacity of the clay for Pb²⁺ and Fe²⁺ ions was calculated from the mass balance equation given in equation 1.

\[ qₑ = \frac{V * (C₀ - Cₑ)}{m} \quad (1) \]

Percent removal of Pb²⁺ and Fe²⁺ ions was calculated according to equation 2.

\[ R% = \frac{(C₀ - Cₑ)}{C₀} * 100 \quad (2) \]

Where \( qₑ \) is the uptake capacity (mg/g), \( C₀ \) is the initial ion concentration (mg/dm³), \( Cₑ \) is the concentration of ions remaining in solution at equilibrium (mg/dm³), \( V \) is the volume of ion solution used (dm³) and \( m \) is the mass of adsorbent.

RESULTS AND DISCUSSION

The chemical composition of Kamenica’s (Kosovo) clay is shown in Table 1.

### Table 1: Chemical Composition of Clay.

<table>
<thead>
<tr>
<th>Composition</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.75</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.61</td>
</tr>
<tr>
<td>K₂O</td>
<td>8.01</td>
</tr>
<tr>
<td>MgO</td>
<td>7.70</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.76</td>
</tr>
<tr>
<td>CaO</td>
<td>4.84</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.43</td>
</tr>
</tbody>
</table>

It is observed that silica and alumina are the major constituents.

In Table 2 and 3 heavy metal ion adsorption capacities of clay are presented as a function of the initial metal ions concentration. The initial metal ion concentration is an important factor to be considered in adsorption studies, since the rate of adsorption is dependent on the initial concentration of metal ion present in solution.

It is seen that the uptake capacity of the clay increased with increase in initial concentration of ions.

This increase is simply due to the presence of more metal ions in solution available for sorption and higher interaction between ions and adsorbent.

This is obvious also from the fact that this increase in the initial ions concentration provides an important driving force to overcome all of mass transfer resistance.

### Table 2: Adsorption Parameters for the Adsorption of Pb²⁺ on Clays at Different Initial Ions Concentration.

<table>
<thead>
<tr>
<th>Pb</th>
<th>( C₀ ) (mg/dm³)</th>
<th>( Cₑ ) (mg/dm³)</th>
<th>( qₑ ) (mg/g)</th>
<th>R %</th>
<th>( Cₑ / qₑ )</th>
<th>ln ( Cₑ )</th>
<th>ln ( qₑ )</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Clay</td>
<td>47.54</td>
<td>0.15</td>
<td>0.24</td>
<td>99.68</td>
<td>0.63</td>
<td>-1.90</td>
<td>-1.44</td>
<td>0.0141</td>
</tr>
<tr>
<td></td>
<td>93.84</td>
<td>2.50</td>
<td>0.46</td>
<td>97.34</td>
<td>5.47</td>
<td>0.92</td>
<td>-0.78</td>
<td>0.0072</td>
</tr>
<tr>
<td></td>
<td>137.63</td>
<td>9.15</td>
<td>0.64</td>
<td>93.35</td>
<td>14.24</td>
<td>2.21</td>
<td>-0.44</td>
<td>0.0049</td>
</tr>
<tr>
<td>Treated Clay</td>
<td>49.61</td>
<td>0.70</td>
<td>0.21</td>
<td>85.89</td>
<td>32.86</td>
<td>1.95</td>
<td>-1.55</td>
<td>0.0839</td>
</tr>
<tr>
<td></td>
<td>93.22</td>
<td>35.00</td>
<td>0.29</td>
<td>62.45</td>
<td>120.23</td>
<td>3.56</td>
<td>-1.23</td>
<td>0.0465</td>
</tr>
<tr>
<td></td>
<td>135.11</td>
<td>71.40</td>
<td>0.32</td>
<td>47.15</td>
<td>224.13</td>
<td>4.27</td>
<td>-1.14</td>
<td>0.0325</td>
</tr>
</tbody>
</table>

### Table 3: Adsorption Parameters for the Adsorption of Fe²⁺ on Clays at Different Initial Ions Concentration.

<table>
<thead>
<tr>
<th>Fe</th>
<th>( C₀ ) (mg/dm³)</th>
<th>( Cₑ ) (mg/dm³)</th>
<th>( qₑ ) (mg/g)</th>
<th>R %</th>
<th>( Cₑ / qₑ )</th>
<th>ln ( Cₑ )</th>
<th>ln ( qₑ )</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Clay</td>
<td>34.97</td>
<td>0.50</td>
<td>0.17</td>
<td>98.57</td>
<td>2.90</td>
<td>-0.69</td>
<td>-1.76</td>
<td>0.0387</td>
</tr>
<tr>
<td></td>
<td>69.94</td>
<td>6.08</td>
<td>0.32</td>
<td>91.31</td>
<td>19.04</td>
<td>1.81</td>
<td>-1.14</td>
<td>0.0197</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>16.84</td>
<td>0.42</td>
<td>83.16</td>
<td>40.50</td>
<td>2.82</td>
<td>-0.88</td>
<td>0.0138</td>
</tr>
<tr>
<td>Treated Clay</td>
<td>33.41</td>
<td>0.80</td>
<td>0.16</td>
<td>97.61</td>
<td>4.91</td>
<td>-0.22</td>
<td>-1.81</td>
<td>0.0748</td>
</tr>
<tr>
<td></td>
<td>64.85</td>
<td>3.50</td>
<td>0.31</td>
<td>94.60</td>
<td>11.41</td>
<td>1.25</td>
<td>-1.18</td>
<td>0.0400</td>
</tr>
<tr>
<td></td>
<td>99.17</td>
<td>7.00</td>
<td>0.46</td>
<td>92.94</td>
<td>15.19</td>
<td>1.95</td>
<td>-0.77</td>
<td>0.0265</td>
</tr>
</tbody>
</table>
The Langmuir and Freundlich adsorption isotherms were applied to the data obtained on the effect of initial metal ion concentration.

Each isotherm was assessed based on the closeness of the value of the regression coefficient ($R^2$) to 1.

The linearized form of the Langmuir and Freundlich isotherms are given in equations 3 and 4 and in Figures 1, 2, 3 and 4, respectively.

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{qmb} \quad (3)$$

$Ce$ (mg/dm$^3$) is the concentration of heavy metal ions in equilibrium, $qe$ (mg/g) is the equilibrium uptake capacity, $qm$ (mg/g) is the maximum adsorption capacity corresponding to a complete monolayer coverage and $b$ (dm$^3$/mg) is the Langmuir isotherm constant which quantitatively reflects the affinity between the adsorbent and the adsorbate.

$$lnq_e = lnKf + \frac{1}{n}lnCe \quad (4)$$

$n$ is a dimensionless constant describing the adsorption intensity and $Kf$ (dm$^3$/g) is the Freundlich isotherm constant describing the adsorption capacity of the adsorbent.

The experimental adsorption isotherms were fitted to Langmuir and Freundlich models to describe the adsorption characteristics of natural and treated clay with a correlation coefficient of 0.9947-0.9999 (Tables 4).

A linear plot of $Ce/qe$ against $Ce$ confirms the Langmuir isotherms and are shown in Figure 1 and 2. $qm$ and $b$ were calculated from the slope and intercept respectively.

The Langmuir isotherm parameters are given in Table 4. The value of $b$ (Langmuir constant) obtained is low which implies that the sorption of Pb$^{2+}$ and Fe$^{2+}$ ions onto our clay is a favorable one.

The Langmuir constant ranged between 1.47 and 0.71 for natural clay and 0.22 and 0.37 for treated clay shows that the adsorption was more favorable for the treated clay.

The dimensionless separation factor ($R_L$), as a measure of the adsorption favorability, was calculated ($0 < R_L < 1$, the smaller is the more favorable) by using the following equation:

$$R_L = \frac{1}{1+bCo}$$

The Freundlich isotherms were confirmed by the plot of In$qe$ against In$Ce$ shown in Figure 3 and 4.

### Table 4: Langmuir and Freundlich Constants for the Adsorption of Pb$^{2+}$ and Fe$^{2+}$ Ions on Clay.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Metal Ion</th>
<th>$q_m$</th>
<th>$B$</th>
<th>$R^2$</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>Pb$^{2+}$</td>
<td>0.68</td>
<td>1.47</td>
<td>0.9892</td>
<td>$0 &lt; R_L &lt; 1$</td>
</tr>
<tr>
<td>Treated</td>
<td>Pb$^{2+}$</td>
<td>0.34</td>
<td>0.22</td>
<td>0.9994</td>
<td>$0 &lt; R_L &lt; 1$</td>
</tr>
<tr>
<td>Natural</td>
<td>Fe$^{2+}$</td>
<td>0.44</td>
<td>0.71</td>
<td>0.9901</td>
<td>$0 &lt; R_L &lt; 1$</td>
</tr>
<tr>
<td>Treated</td>
<td>Fe$^{2+}$</td>
<td>0.61</td>
<td>0.37</td>
<td>0.9497</td>
<td>$0 &lt; R_L &lt; 1$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clay</th>
<th>Metal Ion</th>
<th>$N$</th>
<th>$K_f$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>Pb$^{2+}$</td>
<td>4.15</td>
<td>0.37</td>
<td>0.9991</td>
</tr>
<tr>
<td>Treated</td>
<td>Pb$^{2+}$</td>
<td>5.66</td>
<td>0.15</td>
<td>0.9921</td>
</tr>
<tr>
<td>Natural</td>
<td>Fe$^{2+}$</td>
<td>4.00</td>
<td>0.21</td>
<td>0.9999</td>
</tr>
<tr>
<td>Treated</td>
<td>Fe$^{2+}$</td>
<td>2.12</td>
<td>0.18</td>
<td>0.9934</td>
</tr>
</tbody>
</table>

The Langmuir and Freundlich adsorption isotherms were applied to the data obtained on the effect of initial metal ion concentration.

Each isotherm was assessed based on the closeness of the value of the regression coefficient ($R^2$) to 1.

The linearized form of the Langmuir and Freundlich isotherms are given in equations 3 and 4 and in Figures 1, 2, 3 and 4, respectively.

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{qmb} \quad (3)$$

$Ce$ (mg/dm$^3$) is the concentration of heavy metal ions in equilibrium, $qe$ (mg/g) is the equilibrium uptake capacity, $qm$ (mg/g) is the maximum adsorption capacity corresponding to a complete monolayer coverage and $b$ (dm$^3$/mg) is the Langmuir isotherm constant which quantitatively reflects the affinity between the adsorbent and the adsorbate.

$$lnq_e = lnKf + \frac{1}{n}lnCe \quad (4)$$

$n$ is a dimensionless constant describing the adsorption intensity and $Kf$ (dm$^3$/g) is the Freundlich isotherm constant describing the adsorption capacity of the adsorbent.

The experimental adsorption isotherms were fitted to Langmuir and Freundlich models to describe the adsorption characteristics of natural and treated clay with a correlation coefficient of 0.9947-0.9999 (Tables 4).

A linear plot of $Ce/qe$ against $Ce$ confirms the Langmuir isotherms and are shown in Figure 1 and 2. $qm$ and $b$ were calculated from the slope and intercept respectively.

The Langmuir isotherm parameters are given in Table 4. The value of $b$ (Langmuir constant) obtained is low which implies that the sorption of Pb$^{2+}$ and Fe$^{2+}$ ions onto our clay is a favorable one.

The Langmuir constant ranged between 1.47 and 0.71 for natural clay and 0.22 and 0.37 for treated clay shows that the adsorption was more favorable for the treated clay.

The dimensionless separation factor ($R_L$), as a measure of the adsorption favorability, was calculated ($0 < R_L < 1$, the smaller is the more favorable) by using the following equation:

$$R_L = \frac{1}{1+bCo}$$

The Freundlich isotherms were confirmed by the plot of In$qe$ against In$Ce$ shown in Figure 3 and 4.
The Freundlich isotherm is a common model for adsorption processes, characterized by the Freundlich isotherm constant \( K_F \) and the exponent \( 1/n \). These parameters are determined from the slope and intercept of the linearized Freundlich isotherm equation, respectively.

In this study, the Freundlich isotherm was found to be a more suitable model for the adsorption of Pb\(^{2+}\) and Fe\(^{3+}\) ions from aqueous solutions on Kosovo clay. The Freundlich isotherm parameters were determined to be \( K_F \) = 12.97 and \( 1/n \) = 0.125, indicating a favorable adsorption process.

The percentage of adsorption of Pb\(^{2+}\) and Fe\(^{3+}\) from aqueous solution onto Kosovo clay was up to 99.68%. This result suggests that Kosovo clay is an effective adsorbent for removal of Pb\(^{2+}\) and Fe\(^{3+}\) from aqueous solutions.

**REFERENCES**

14. Selimi T, Sadiku M, Behluli M, Hasani N, Berisha A. Batch...


Source of Support: Nil, Conflict of Interest: None.