Sorption of lead by natural and its iron (III) - modified zeolite

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Abstract

In this paper, results of lead sorption by the natural and its iron (III)-modified zeolite are presented. It was determined that, for both zeolites lead sorption increased with increasing the initial concentration of lead in solution. Much higher sorption of lead was achieved with the iron (III)-modified zeolite. The results were fitted to the Langmuir and Freundlich sorption isotherm. The best fit of experimental data was achieved with the Freundlich sorption isotherm (correlation coefficient >0.93). From Langmuir isotherm, maximally sorbed amount of lead was 0.318 and 0.642 mmol/g for the natural and iron (III)-modified zeolite, respectively.

Introduction

The presence of lead in the environment is detrimental to a variety of living spaces. The major sources containing lead are the wastewaters from process industries engaged in lead (acid batteries, paint, electronic, automobile emissions, etc). Presence of lead in live organisms can cause anemia, chills, diarrhea, and dysfunction of kidneys, reproductive system, liver, brain and central nervous system, etc [1]. Conventional methods for lead removal include ion exchange, precipitation and co-precipitation, surface complexation, reduction, etc [2]. Among all the methods ion exchange/sorption on zeolites (tectoaluminosilicates) and smectites (phylosilicates) is highly effective and economical. Lead can be immobilized on zeolites by two mechanisms: ion exchange and chemisorption [3]. The ion exchange usually takes considerable part in the sorption process. To establish better sorption of lead, surface of zeolite is often modified with iron (III) oxyhydroxides. Such iron (III) modified zeolites can be several times better sorbents then natural zeolites. In the present work, sorption of lead on the natural and its iron (III)-modified zeolite is investigated.

Experimental

The starting material was the natural zeolitic tuff from the Zlatokop deposit, Vranjska Banja, Serbia. After crushing and grinding the zeolite was sieved to the particle size below 0.043 mm. The mineralogical composition of the starting sample was primarily clinoptilolite (~80%) with small amounts of feldspar, quartz
and pyrite as determined by qualitative X-ray powder diffraction analysis (XRPD). Analysis was performed on diffractometer PHILIPS, Model PW-1710.

The iron (III)-zeolite was synthesized combining the method for pure goethite preparation [4] and method for preparation of iron-coated zeolite [5]. Thus, 50 g of zeolite was mixed with 25 ml of 10% FeCl₃ · 6H₂O solution and 700 ml of 0.1 M KOH (pH = 10) in 2 l container. The container was capped and the suspension was aged for 20 days at room temperature. After the reaction period the suspension was filtered and washed until Cl ions were no longer detected and dried. Chemical composition of the natural zeolitic tuff and its iron (III)–modified zeolite was done by the classical chemical analysis.

The examinations of lead sorption were carried out by shaking 1g of the natural and iron (III)-zeolite with 50 ml of aqueous solutions, containing various initial concentrations of PbNO₃ (1.7 – 34.8 mmol Pb²⁺/l) at 25°C. The initial and non sorbed concentrations of lead in supernatants were determined by atomic absorption spectrophotometry using the Analytic Jena Spekol 1300.

Results and discussion

Chemical composition of the natural zeolitic tuff (NZ) and its iron (III)-modified zeolite (INZ) are listed in Table 1.

Table 1. Chemical composition of NZ and INZ.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>I.L.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ</td>
<td>66.57</td>
<td>13.13</td>
<td>2.30</td>
<td>3.85</td>
<td>0.56</td>
<td>1.17</td>
<td>1.27</td>
<td>11.05</td>
</tr>
<tr>
<td>INZ</td>
<td>63.44</td>
<td>12.71</td>
<td>3.97</td>
<td>3.85</td>
<td>1.06</td>
<td>4.36</td>
<td>0.80</td>
<td>9.43</td>
</tr>
</tbody>
</table>

*ignition loss

The isotherms for lead sorption on natural zeolitic tuff and iron (III)-modified zeolite are given at Figure 1a [6], while Figure 1b presents the percentage of sorbed lead by both zeolites. From Figure 1a, it is observed that much higher sorption of lead was achieved with the iron (III)-modified zeolite. The results of sorption of lead on natural and iron (III)-modified zeolite were fitted to the Langmuir and Freundlich sorption model and the best fits of the data were obtained using the Freundlich model (R² >0.93). From Langmuir isotherm, the calculated maximum amount of lead sorbed by natural zeolite and iron (III)-modified zeolite are 0.318 mmol/g (64 meq/100g) and 0.642 mmol/g (128 meq/100g), respectively. The content of inorganic cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) released from the natural zeolite during lead sorption at the plateau of the isotherms was as follows: Ca²⁺ - 23 meq/100g, Na⁺ - 21 meq/100g, Mg²⁺ - 6 meq/100g and K⁺ - 2 meq/100g. The amounts of Ca²⁺, Mg²⁺, Na⁺ and K⁺ released from iron (III) modified zeolite were 35, 12, 2 and 44 meq/100g, respectively. Since in zeolites, for divalent cations the share of ion exchange is comparable to chemisorption [3], obtained results suggested that both processes are involved in lead sorption by both zeolites.
As can be seen from Figure 1b, for both sorbents, lead sorption indexes (calculated by dividing the sorbed amount of lead by the initial lead concentration) decreases with increasing the initial concentrations of pollutant. For lower initial concentration of lead, sorption index for both sorbents are close to each other and they are almost 100%, while for the higher initial lead concentration, difference in percentage is much visible; for example: for the initial lead concentration of 35 mmol/l, its sorption was 18% for the natural zeolite and 35% for iron (III)-modified zeolite.

![Figure 1](image)

**Figure 1.** a) Sorption of lead on natural (NZ) and iron (III)-modified zeolite (INZ); b) Percentage of sorption of lead as a function of its initial concentration.

**Conclusion**

In this paper, results of sorption of lead by the natural zeolite and its iron (III)-modified zeolite showed that significantly higher lead sorption has been achieved on iron (III)-modified zeolite. The experimental results were fitted to the Langmuir and Freundlich sorption isotherms. The best fit of experimental data was achieved with the Freundlich sorption isotherm ($R^2 > 0.93$). The results suggest that ion exchange is not the only mechanism responsible for lead sorption by both zeolites. That means that especially for iron (III)-modified zeolite chemisorption of lead plays a role in its sorption. Results indicated that iron (III) present in modified zeolite has influence on sorption of lead.

**Reference**