Use of Natural and Modified Clay for Zn2+ Removal

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The local natural clays from Chiuoarului Valley (kaolinite, illite, montmorillonite, nontronite, with small amounts of quartz) and Razoare areas (montmorillonite, kaolinite, illite, feldspar, clinoptilolite and quartz) were tested for the ability to adsorb Zn2+ ions from aqueous solutions. To increase the adsorption and cation-exchange capacity (CEC), the clays were treated with sodium chloride. The effect of initial concentration of Zn2+ ions on removal efficiency was studied. The equilibrium data were fitted with the Langmuir and Freundlich isotherm models. The Langmuir model described the experimental data better than the Freundlich model. The highest ion exchange capacity toward zinc ions was displayed by the Na-exchanged clays.

Keywords: ion exchange, clay, Zn2+ ions removal, wastewater

The presence of heavy metals in the waste streams of many industrial activities cause serious pollution problems in aquatic environment. These heavy metals are toxic and not biodegradable pollutants. They have the tendency to accumulate in living organisms, causing serious diseases and disorders, threatening the human and animal health [1-8].

The concentration of these Zn2+ ions in many natural and industrial waste streams must be controlled to be below the acceptable level, severity reduced every year according to the environmental regulation worldwide [7, 8].

In this work the sorption features of the native and sodium-exchanged form of clay samples from Valea Chioarului and Razoare areas towards Zn2+ ions from wastewaters were studied.

Experimental part

Materials

In this study, local natural clays from Chiuoarului Valley and Razoare areas have been investigated. Both samples were used in the raw form (polycationic form) as well as in the Na-exchanged form. The tested samples were denominated as: Ci - natural clay from Chioarului Valley, Cl1 - Na-clay from Chioarului Valley (64% smectite, SiO2/Al2O3 molar ratio = 8.95, SBET = 59 m2/g); Ri - raw clay from Razoare and R1 - Na-clay from Razoare (SiO2/Al2O3 molar ratio = 7.42, SBET = 39 m2/g, with significant amounts of clinoptilolite zeolite, illite clay and quartz) [2, 3, 9].

The Na-forms of the natural clays from Chioarului Valley and Razoare were prepared by treating the clay polycationic forms with NaCl 1M in a solid/liquid ratio of 1:10, at room temperature, under magnetic stirring for 12 h, followed by centrifugation, water washing and air drying at 80°C for 5 h. [10]

Clay Characterization

X-ray diffraction (XRD) powder patterns of natural clays were recorded with a Philips PW 1830 diffractometer (45 KV, 25 mA) using Ni-filtered CuKα radiation (0.154 nm).

Thermogravimetric analyses of the clays were carried out on a Mettler TG50 thermogravimetric analyzer. The samples were heated in O2 atmosphere at a rate of 5°C/ min from 25 to 990°C.

The mid-FTIR-PAS spectra were recorded on a Nicolet 20SX spectrometer equipped with a cell photoacoustics McCelland. For each sample were made approximately 500 scans with a resolution of 8 cm-1. PAS spectrometer was placed in a sealed chamber in which N2 gas was pumped completely dry in order to preserve evidence [11, 12].

Methods

To assess the performance overall in the trials of sorption of various of clay samples, they have contacted with solutions for various concentrations of Zn2+ ions and were determined levels for the detention of ions. Achieved studies from 20°C, while exchange ions for 24 h and report solid/liquid 8 g/L.

The sorption experiments were performed in batch technique, mixing in glass tubes placed in a thermostatic bath under occasional stirring. After a determined time for the equilibrium (24 h), the solid was filtrated and the solution was analyzed for their zinc content [13].

The amount of Zn2+ ions retained per gram of clay, q (mg/g), and the percentage of zinc removed, R (%), from the solution were calculated by the following equations:

\[ q = \frac{(c_0 - c) \cdot V}{m}, \text{mg/g} \]  
\[ R = \frac{(c_0 - c) \cdot 100}{c_0}, \% \]

where c0 and c are the initial and equilibrium zinc concentration in the solution (mg/L), m is the mass of clay (g), and V is the solution volume (L).

Results and discussions

Characterization of clays

The minerals identified by XRD in natural clay Ri are: clinoptilolite (zeolite), illite (2:1), quartz, kaolinite (1:1), montmorillonite (2:1) and feldspar, with a high degree of crystallinity (fig.1).

![Fig. 1. XRD powder pattern of natural clay Ri](image-url)

Cl: clinoptilolite, I: illite, Q: quartz, K: kaolinite, M: montmorillonite

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In the diffractogram of natural clay Ci (fig.2.) the peak of $2\theta = 6.92^\circ$, with basal interspaced $d_{001} = 12.69\text{Å}$ is specific to montmorillonite. It is also evident that the Ci clay contains: kaolinite, illite, montmorillonite, nontronite, with small amounts of feldspars and $\alpha$-quartz.

The DTG and TG curves for clays in Na$^+$ form (R1, C1) performed from 25 to 990°C under air atmosphere are given in figures 3 - 4.

For both clays, the weight loss is due to removal of water physisorbed, with a maximum speed at 78.7°C for R1 and 71.3°C for C1, zeolitic water between 200 to 320°C for R1, assigned to clinoptilolite, and water by dehydroxilation of OH structural groups associated to internal structure of layers, between 600-700°C for sample C1 [14, 15].

**Zn$^{2+}$ ions removal study**

In order to evaluate the sorption performances, the natural (Ri, Ci) and Na-exchanged clays (R1, C1) were contacted with solutions of different initial concentrations in Zn$^{2+}$ ions at 20°C for 24 h of contact at a solid/liquid ratio of 8 g/L. The retention degrees, $R$ (%) were determined and the results are presented in figure 5.

The degree of Zn$^{2+}$ ions removal from aqueous solution decreases with the increase of the initial concentration. Clays are efficient as sorbent for Zn$^{2+}$ ions only from diluted aqueous solutions. At low zinc concentrations, the clays in the Na-form exhibit a good affinity for zinc ions. At both low and medium zinc ions concentration, the clay R1 show better sorption than C1 sample. The sodium form of the clays behaves better than the native one, probably due to structure ordering associated to the sodium exchange step [16-18]. The decrease of the retention degree with the concentration of the zinc ions can be related either to the low exchangeable ions concentration in the clay, either to the quite limited void volume in the structure where the ions can accommodate in adsorption sites. Contribution of adsorption is higher than that of ionic exchange on the overall ion uptake.

Influence of temperature on the sorption of ions Zn$^{2+}$ on clays exchanged with native and sodium is shown in figure 6. Temperature rise is beneficial on the amount of retained metal ions from solutions, as is expected, since diffusion of ions is favored by higher temperatures.

Distribution in the amount of zinc ions retained on the unit mass of adsorbent at equilibrium concentration in solution is shown in figure 7. The exchange was conducted at 293 K, the native and modified clays.

The affinity of the clays for ammonium ions decreases in the following order: R1 > R > C1 > C. The zinc sorption depends on the interlayer space of the clays, because of the ion exchange between Zn$^{2+}$ ions in the solution and Na$^+$ ions inside the space of the clay layers. It is worthy to note that the sodium initial exchange is crucial for the improvement of the sorption capacity of the clay of Razoare.
To explain the experimental data, the Langmuir and Freundlich models in the linear forms were applied [19, 20].

The mathematical form of Langmuir model is given by the following equation:

$$
\frac{c}{q} = \frac{1}{q_0 K_L} + \frac{c}{q_0}
$$

where $q_0$ is the maximal monolayer adsorption capacity (mg/g) and $K_L$ is the equilibrium binding constant, a measure of energy of sorption.

The Freundlich model is described by the linearized equation:

$$
\log q = \log K_F + \frac{1}{n} \log C
$$

where $K_F$ and $n$ are the coefficients of Freundlich isotherm indicating the capacity of the sorbent and favourableness.

The coefficients of both isotherm models were calculated by the slopes and intercepts of presented straight lines (figs. 8 and 9).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_0$ (mg/g)</td>
<td>$K_L$ (L/g)</td>
</tr>
<tr>
<td>Cl</td>
<td>8.196</td>
<td>41.4157</td>
</tr>
<tr>
<td>Ri</td>
<td>21.739</td>
<td>10.7647</td>
</tr>
<tr>
<td>C1</td>
<td>12.820</td>
<td>9.0613</td>
</tr>
<tr>
<td>R1</td>
<td>25.641</td>
<td>6.4049</td>
</tr>
</tbody>
</table>

The sorption isotherm constants for zinc retention by natural and modified clays, and their correlation coefficients $(R^2)$ are summarized in Table 1.

The values of $R^2$ from Table 1 show that the sorption isotherms data for Zn$^{2+}$ ions can be better described by the Langmuir.

For ionic adsorbed species, the increase in the retention capacity of the solid is more significant only up to 0.2 mg/mL, showing that the sorption is effective only for low toxic ions concentration values.
Another parameter that indicates the effectiveness of an adsorbent to remove ions Zn$^{2+}$ is the time to reach equilibrium adsorption.

Data presented in figure 10 show that the equilibrium is reached after 10-15 min. This suggests that the limiting factor is the process of diffusion of ions inside the solid particles.

The kinetic sorption data fitted well to the second-order kinetic model, indicating an intraparticle diffusion mechanism.

Conclusions

Natural clays and modified clays in Na-form are good adsorbents for Zn$^{2+}$ removal from aqueous solutions. The enrichment of the natural multicationic clays with Na$^+$ ions leads to increase in adsorption capacity towards Zn$^{2+}$ ions.

The constants in equilibrium isotherms of Langmuir and Freundlich models for the studied systems are determined. It was found that Langmuir model describe better the experimental data.

The retention of Zn$^{2+}$ ions onto clays takes place by adsorption on active sites of surface hydroxyl groups and by ion exchange on ion exchange sites inside the alumino-silicate framework.

The sorption of Zn$^{2+}$ from aqueous solutions on original and modified clays depends on the initial ion metal concentration, temperature and contact time. The equilibrium sorption data fitted well to the Langmuir model.

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