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ZINC SORPTION ON MONTMORILLONITE

Montmorillonite is a clay mineral from the group of phyllosilicates with laminated structure and permanent negative charge on the layers surface, which fact can be used for sorption of cations or ion exchange reactions. In this project, the exchange of zinc ions for sodium ions in interlayers is examined. For batch experiments the sodium form of montmorillonite was used. Different zinc salts were used: nitrate, sulphate and acetate. The results show that adsorption process can be described with Langmuir-Freundlich or Langmuir adsorption isotherm. Maxima of adsorbed amounts were 1,08 ± 0,07 $meq \cdot g^{-1}$; 1,25 ± 0,32 $meq \cdot g^{-1}$ and 0,86 ± 0,03 $meq \cdot g^{-1}$ in case of nitrate; sulphate and acetate respectively. The pH value of solutions increased during the adsorption except from acetate, where a small decrease can be observed.

Монтмориллонит является глинистым минералом группы слоистых силикатов и характеризуется полосчатой текстурой и постоянным отрицательным зарядом на поверхности слоев – особенность, которая может быть использована для сорбции катионов или ионообменных реакций. В рамках настоящего исследования было изучено замещение ионов натрия ионами цинка в структуре минерала. В серии экспериментов использована натриевая разновидность монтмориллонита. Применяли различные соли цинка: нитрат, сульфат и ацетат. Результаты эксперимента подтверждают, что процесс можно описать, используя изотерму адсорбции Ленгмюра – Фрейндлиха или Ленгмюра. Максимальный уровень адсорбции достигал 1,08 ± 0,07; 1,25 ± 0,32 и 0,86 ± 0,03 $мг\text{-}экв \cdot г^{-1}$ соответственно для нитратов, сульфатов и ацетатов. Показатели кислотности растворов увеличивались во время процесса адсорбции, за исключением ацетатов, где наблюдалось незначительное уменьшение кислотности.

1. Introduction

Clay minerals are basicaly natural porous materials with the ability to bind cations, which could be used for ion-exchange reactions. In this work, the ability of montmorillonite to bind Zn cations in its structure is examinated.

Na-montmorillonite (Na-MMT) and $Zn(NO_3)_2$, $ZnSO_4$ and $Zn(CH_3COO)_2$ are used for the experiment. The exchange of Zn ions for Na ions is observed and the mechanism of this exchange as well pH and sturctural changes are determined.

2. Theory

Montmorillonite. Montmorillonite (MMT) is a type of phyllosillicate. Phyllosilicates are clay minerals which are usually the major part of clays. Its structure contains 2D layers of tetrahedrons and octahedrons. MMT ranks among smectites which are phyllosilicates with 2:1-type layers – 2 layers of tetrahedrons and 1 layer of octahedrons. The central ions in tetrahedrons are usually Si and Al, in octahedrons Al, Fe and Mg. Due to vacantions and substitutions of mono-, di-, and trivalent cations for Si^{4+} in central positions of tetrahedrons and octahedrons there is a permanent negative charge on surfaces of the layers. Hence there are cations with their water shells in the interlayer area.

In this work, MMT with Na cations in interlayers (known as Wyoming MMT) was used for experiments. This MMT has cation exchange capacity (CEC) of 1,2 meq/g.

Adsorption. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Different adsorption isotherms are often used to describe this process. Adsorption isotherm is the function which connects the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid).

In case of clay minerals, two main adsorption processes can be observed – ion exchange and surface complexation. The former mechanism represents the sorption to interlayers (exchange of cations limited by cation exchange capacity) whereas the latter

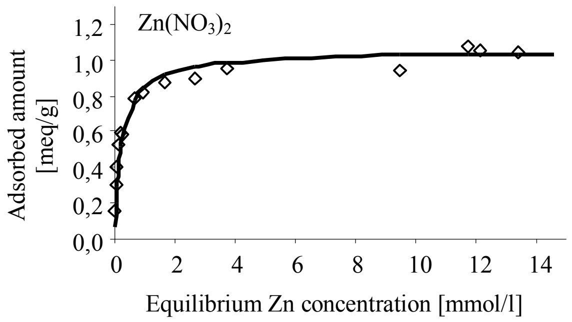

Fig.1. Langmuir AI – $Zn(NO_3)_2$

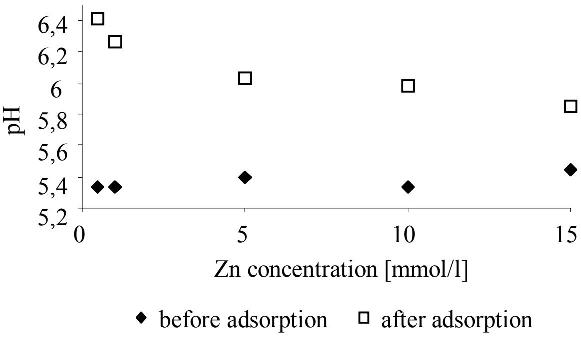

Fig.4. pH changes – $Zn(NO_3)_2$

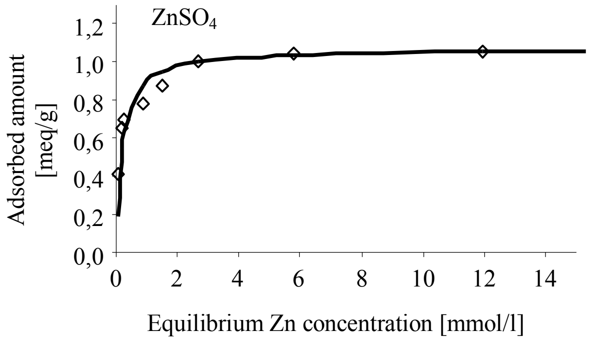

Fig.2. Langmuir AI – $ZnSO_4$

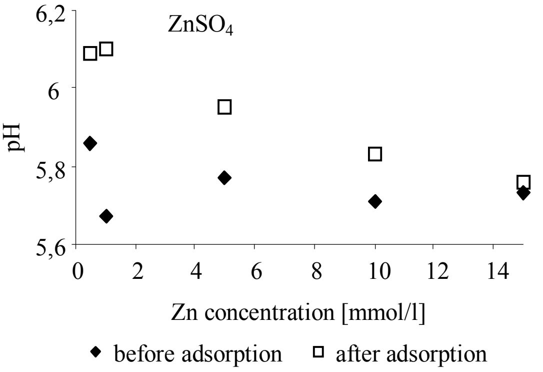

Fig.5. pH changes – $Zn(NO_3)_2$

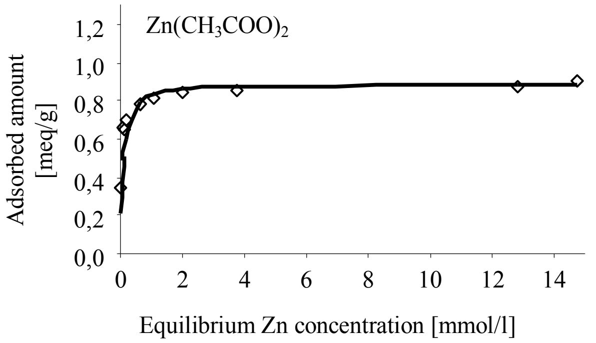

Fig.3. Langmuir AI – $Zn(CH_3COO)_2$

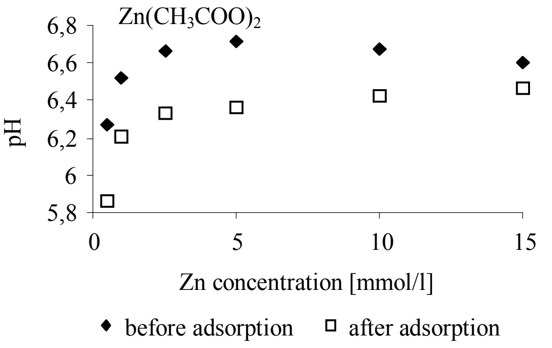

Fig.6. pH changes – $Zn(CH_3COO)_2$

process involves forming complexes between cations and hydroxyl groups on the surface of clay particles and becomes important when the interlayer area is fully saturated.

3. Experiment

Materials and methods. Adsorption of zinc ions from aqueous solutions on Na-MMT was studied. Different salts of zinc ($Zn(NO_3)_2$, $ZnSO_4$ and $Zn(CH_3COO)_2$) were used to compare adsorbed amounts.

Sets of solutions with different concentration of zinc were prepared and shaken with montmorillonite (100 ml of solution and 0,1 g Na-MMT) for 24 hours. Zinc concentration before and after the adsorption process as well as pH was measuered. Atomic absorption spectroscopy and pH meter were used for that. Simultaneously, solid samples of montmorillonite with adsorbed zinc (Zn-MMT) were prepared and measured by X-Ray diffraction to observe the structure changes during the adsorption.

4. Results and discussion

Adsorption isotherms (*AI*). Results show that from all types of adsorption isotherms, the

Langmuir AI fits the data best. Differences in adsorption from different zinc salts are shown in Fig.1 – Fig.3. It can be observed that adsorbed amount maxima are close to 1 meq/g for nitrate and sulphate and 0,9 meq/g for acetate. This shows that the cation exchange capacity is not reached due to forming the equilibrium between Na and Zn ions in the solution (close to concentration of zinc 4 mmol/l) and the dominant process is the cation exchange.

pH changes. During the process of adsorption, pH changes (Fig.4 – Fig.6). In case of nitrate and sulphate, there is a decrease of H^+ion concentration, which could be caused by the exchange of $H^+$to interlayers. In case of acetate, there is a decrease of pH, which is probably a consequence of forming surface complexes between zinc and hydroxyl groups and releasing H^+ion.

X-Ray powder diffraction (*XRD*). Solid samples of Zn-MMT (prepared from 0,4 mmol/l and 20 mmol/l zinc solutions) were studied by XRD. A shift of the intarlayer distence (0,1-0,22 nm) was observed. Since zinc ion is much bigger than sodium ion, this shift illustrates the exchange of Zn for Na in the MMT structure.

5. Conclusion

Zinc sorption on montmorillonite is a process of cation exchange (Zn for Na) and runs until the equilibrium between these two ions forms in the solution. The cation exchange capacity is not reached so the main sorption mechanism is the cation exchange. The process is affected by Zn concentration in the solution, by used zinc salt (anion) and pH and could be described with Langmuir adsorption isotherm satisfactorily. Differences between sorption from acetate and from nitrate and sulphate are probably caused by lower dissociation of $Zn(CH_3COO)_2$. X-Ray diffraction confirmed the shift of the interlayer distance during adsorption.

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