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USE OF ZEOLITE OF THE SOKYRNYTSA DEPOSIT IN ENGINEERING OF ENVIRONMENT

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In the given article the theoretical bases of adsorption of typical contaminations of wastewaters are grounded. The review of literary data in relation to application of the klynoptylolite of Sokirnytsa deposit in engineering of environment is carried out. Experimental data of adsorption capacity of natural klynoptylolite are resulted. A mechanism and features of processes of adsorption in static terms is described. Conformities to the law of change of adsorption capacity in accordance to the parameters of molecules of adsorbate were observed.

Key words: zeolite, adsorptin, wastewater, external diffusion.

Обґрунтовано теоретичні основи адсорбції типових забруднень стічних вод. Проведено огляд літературних даних стосовно застосування клиноптилоліту Сокирницького родовища в інженерії довкілля. Наведено експериментальні дані сорбційної ємності природного клиноптилоліту. Описано механізм та особливості процесів адсорбції в статичних умовах. Встановлено закономірності зміни сорбційної ємності відповідно до параметрів молекул адсорбату.

Ключові слова: цеоліт, адсорбція, стічні води, зовнішня дифузія.

Formulation of the problem and its copulas with the important scientific or practical tasks

The change of composition of natural waters as a result of the tehnogenic influence needs the search of new safe methods of industrial wastewaters treatment. The existent methods of industrial wastewaters treatment, that consist in application of chemical reagents or physical influence on water, allow to withdraw from it contaminating the matters, changing physical and chemical properties of water and violating the natural balance of dissolved in it salts.

However in nature takes place the smoothing of salt balance of filtration waters and withdrawal from them of dangerous admixtures by passing of water through a geochemical barrier, that has an enormous adsorption capacity in relation to ksenobyotyks.

The protective function of geochemical barrier consists in presence in it clay minerals, carbonates, aluminosilicates, in particular zeolites, etc. Application of such natural minerals-adsorbents for treatment of wastewaters and natural muddy waters on the stage of defending will allow to withdraw by adsorption without application of chemical reagents not only the dangerous contaminating matters of antropogenic origin, but also to improve a structure and mineral composition of water.

In Ukrainian Carpathians are the famous mineral springs which have acquired their unique properties as a result of adsorption and ion exchange due to filtration of surface water through the layer of geological deposits, among of which clinoptilolite is distinguished by its special adsorption properties.

Adsorption properties of klynoptylolites are studied in a whole world. In particular application of the klynoptylolite of Sokirnytsa deposit in engineering of environment is actual.

Target of work. Generalization of experimental researches was the target of work in relation to application of natural klynoptylolite for the extracting from wastewaters the surfactants, organic and inorganic compounds, high molecular and low molecular substances.

Analysis of the last researches and publications. In literary sources is specified about the mechanism of ionic exchange with participation of zeolite according to the following scheme [1]:



In literature is specified about the row of adsorption selectivity of the zeolite towards to the following cations:



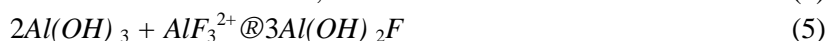
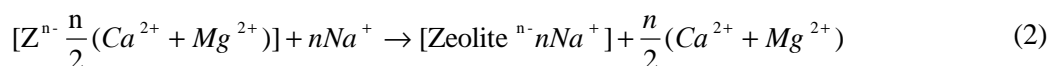
Authors consider that presence of potassium in a zeolite hinders the adsorption of NH_4^+ from the water [1]. On adsorption of cations the substantial influencing has also correlation the percentage of silicon to the aluminium. Exactly thanks to presence of aluminium in the zeolite framework appears ion exchange properties of sorbent [1,2]. In the previous publications the experimental data about of static capacity of zeolite of the Sokirnytsa deposit in relation to the row of cations, in particular to the ammonium and Cu^{2+} [1,3,4] surfactants, high molecular compounds[3], mineral oil [5] and organic acids [6] are represented. The mechanisms of takeover of anions are set, in particular fluorides [7] and phosphates[3,4].

Method of decision. For the investigation of adsorption capacity of zeolite in relation to test substances in glass retorts were placed 200 sm³ of solution prepared in the distilled water, at different initial concentrations ($C = 1 - 30 \text{ mg/dm}^3$), and added the identical hinge-plates of sorbent (~1 g). The range of concentrations of tested solutions was prepared corresponding to the concentrations of explored compounds in wastewaters of industrial enterprises. Flasks were hermetically closed and abandoned at periodic interfusion on the two days at a temperature +20°C. Sorbent was separated from solution which was analysed on the presence of the proper ions and the carbon radical. Concentration of copper ions was determined by a complexometric method, pH, concentrations of sodium, fluoride-ion – by use of ionometer IT-160, organic substances were analyzed by the method of permanganatometric titration of acid residual, concentration of albumin, phosphates and ammonium was analyzed by the photometric method accordingly to standard methods.

Experimental researches. Experimental research of adsorption was carried out in static terms. Experimental investigation of adsorptions of basic contaminations of wastewaters by the zeolite of the Sokirnytsa deposit it is represented on fig.1. and in table 1.

The results of experimental researches showed that the adsorption capacity of zeolite in relation to the adsorbed cations by an ion exchange process is proportional to quantity of exchangeable cations in zeolite framework. Except of cations, that are able to form insoluble compounds with the components of klynoptylolite. In particular adsorption of cuprum is accompanied by the process of chemisorption, therefore there was observed the increase of adsorption capacity of zeolite in relation to Cu^{2+} which is proportional with an adsorption capacity of zeolite to NH_4^+ and H^+ . [7]

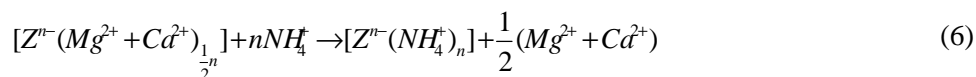
It is correlated to the adsorption ability of zeolite relatively to certain anions, in particular phosphate ion and F^- adsorbed by the formation of insoluble compounds and complexes.



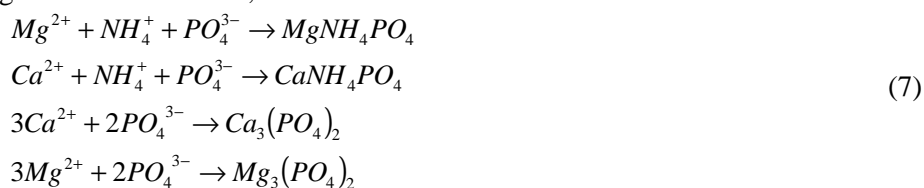
Existence of complex ions from $[AlF_2]^+$ to $[AlF_6]^{3-}$, and also the basic complexes of fluorides of the aluminium $[Al(OH)_2F_4]^{3-}$ was set. It is appropriate to assume that exactly the processes of complexation are dominating in the process of fluorides withdrawal from underground waters by filtration through the modified loads.

Adsorption of phosphates, including the compatible withdrawal of ammonium and phosphates, passes according to the following mechanisms:

1) Ionic exchange of ammonium on magnesium ions, calcium and other exchange cations in obedience to the reaction:



2) Formation of insoluble phosphates of calcium and magnesium, and also double salts ($MgNH_4PO_4$, $CaNH_4PO_4$) and others like that, at co-operation of phosphates with ammonium ions and exchangeable cations of magnesium and calcium, that are in solution.



Usually the reactions of precipitation pass at presence of centers of crystallization. However in this case we deal with the heterogenic system of adsorbent - adsorbate and formation of insoluble compounds passes on a surface of sorbent [3,4].

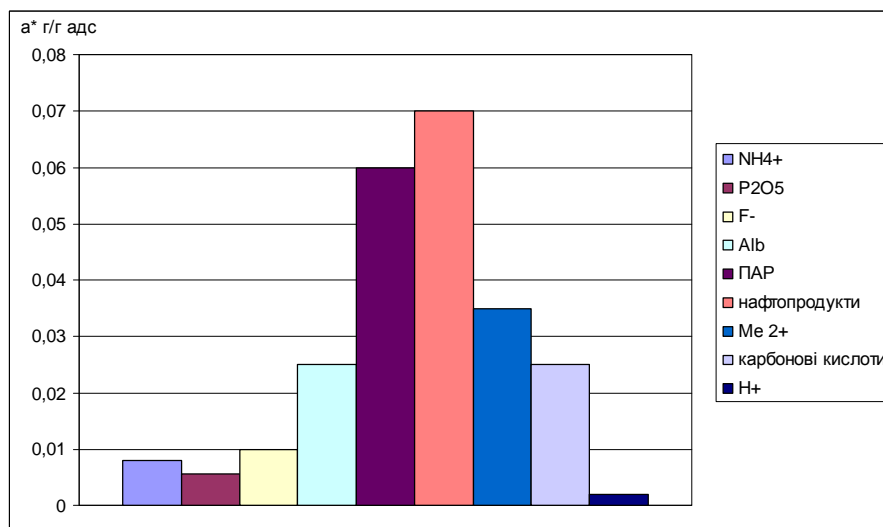


Fig. 1. Adsorption capacity of the klynoptylolite of Sokirnitsa deposit in relation to basic contaminations of industrial wastewaters

Examining the enough large molecules of adsorbed compounds it is possible to assert about influence of steric factor, that does not allow the molecule to get inside the pores of adsorbent. It can be an important moment and that, because of negative charge of zeolite framework, to it the exceptionally positively charged molecules can be attracted. As a result we observe, that quantity of oil, surfactants, carboxylic acids and proteins which are adsorbed by a zeolite and evaluated in gram-equivalent of adsorbed compound by one gram of zeolite is insignificant comparable with the amount of adsorbed H^+ . The capacity of zeolite in relation to an albumin amounts to $3,65 \cdot 10^{-7}$ g-ekv/kg. Obviously, an albumen is adsorbed only by the external surface of zeolite. Sodium dodetsilsulfat (surfactant) and oil, because of linear structure of molecules, can penetrate in pores of average size of klynoptylolite. Therefore for the

adsorption of high molecular compounds it is important to take into account the granulometrical composition of adsorbent.

Table 1

Dependence of static capacity of the klynoptylolite of Sokyrnytsa deposit according to the sizes of molecules of adsorbed compounds

Name	NH ₄ ⁺	P ₂ O ₅	F ⁻	Albumin	Surfactant	Mineral oil	Cu ²⁺	Carboxylic acids	H ⁺
a*, g/g	8,1·10 ⁻³	5,5·10 ⁻³	0,01	0,025	0,06	0,07	0,035	0,025	2,2·10 ⁻³
a*, g-ekv/g	4,4·10 ⁻⁴	1,3·10 ⁻⁵	5,26·10 ⁻⁴	3,65·10 ⁻⁷	2,08·10 ⁻⁴	4,12·10 ⁻⁴	2,78·10 ⁻⁴	2,78·10 ⁻⁴	2·10 ⁻³
M	18	142	19	68400	288,38	170	63	90,09	1

Conclusion

Comparison of adsorption properties of natural zeolite in relation to the row of typical contaminations of industrial wastewaters is done. The mechanisms of adsorption of the tested substances are resulted. Correlation of the relationship between the parameters of molecules of adsorbed substances and adsorption capacity of klynoptylolite was set. Investigated activity of zeolite indicate the prospects of zeolite materials application in environmental protection.

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