Adsorption of Cu^{2+} and Cr^{3+} cations by modified sorbents

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Abstract – the present article substantiates the theoretical bases of adsorption of heavy metals on modified adsorbents. The aim of this work was to study the simultaneous adsorption of copper and chromium cations on the surface and in the zeolite volume under static conditions. The regularity of the change in the amount of absorbed copper and chromium cations by a zeolite in the initial solution was established. It was settled the chromium ions were better adsorbed on zeolite modified by phosphoric acid. It was established that adsorbents modified in acid conditions were more selective to heavy metals then zeolites modified by NaOH .

Keywords – adsorption, modified sorbents, heavy metals, waste waters, external diffusion.

I. Introduction

Heavy metals are considered as hazardous pollutants due to their toxicity, even at low concentrations and inability to biodegradation. Increasing the level of heavy metals in natural reservoirses poses a serious threat to all living organisms, including humans [1,2]. It is important that the concentration of heavy metals in waste waters waters before dumping in the reservoir does not exceed the MPC. The most common methods available for reducing the concentration of heavy metals are chemical deposition, ion exchange, adsorption and reverse osmosis. Taking into account the characteristics of the crystalline structure of zeolites this adsorbents are capable to absorb only metal cations, and the chemical modification of the internal surface of the natural sorbent expands the range of sorption capacity of zeolites in relation to anions and nonpolar organic compounds.

The modification process consists in the reaction of ion exchange of the exchangeable cation of surface with exchangeable cations of the inner surface of the zeolite, for example, by aliphatic quaternary amines, acid activation of the natural sorbent, and the like. Previous studies have shown that with a two-component system containing both ions of copper and chromium at the same time, it is possible to remove mostly only copper, which is significantly less toxic than chromium cations. In Ukraine, the MPC for copper according to the sanitary limit value of harm is 1.0 mg / g, for chromium trivalent 0.5 mg / g, for chromium hexavalent 0.1 mg / g. The purpose of this work was to create an effective sorbent for the removal of heavy metal ions and to study the process of simultaneous adsorption of cuprous and chromium cations on the surface and in the volume of modified zeolite under static conditions.

II. Experimental

Modification of natural clinoptilolite was carried out by acid method, consisting in processing samples with solutions of sulfuric, hydrochloric, phosphoric and acetic acids in a certain period of time during heating and stirring. This method of influence on natural mineral sorbents actually accelerates the processes occurring in the natural environment under the influence of air, water containing carbon dioxide, pressure for a long time (the process of chemical weathering in the zone of hypergenesis) [3, 4]. And also a solution of sodium hydroxide. The test material of a homogeneous fractional composition was obtained by sieving the natural clinoptilolite through a sieve with a cell size of 2-3 mm. For the acid modification of the sorbent, a solution of phosphatic acid (20%) was added in a volumetric ratio of 1: 2 (solid phase: solution), thoroughly mixed, and kept the suspension formed under normal conditions for 24 hours.

For alkaline modification of the sorbent, a solution of sodium hydroxide (20%) was added in a volumetric ratio of 1: 2 (solid phase: solution), thoroughly mixed, and kept the suspension formed under normal conditions for 24 hours. Solid phase was washed with distilled water in a volume ratio of 1:10 (suspension: distillate). After precipitating, the resulting precipitate was collected and dried at 105 ° C

For the study of the change in the chemical composition of zeolite after the adsorption of heavy metals from the liquid phase, natural zeolite – klinoptilolit Sokirnitsky deposit was used modified with 20% solutions of H_3PO_4 and NaOH. The model solution contained a mass of ions of cuprum and chromium in a ratio of 1: 1. The concentration of each ion in the investigated solutions was 0.01, 0.2, 0.4, 0.6 and 1 g / dm^3.

To the contents of each sample, weight of mofied zeolite was added, stirred and sealed. The adsorption process was carried out for 48 hours in a thermostat at a temperature of 20 ± 0, 5°C. After completion of the process, the solution was filtered, and the zeolite was dried to constant weight. The amount of absorbed ions of cuprum and chromium was determined by photometric method.

III. Results and interpretation

We carried out studies on adsorption of a mixture of copper or chromium ions on a modified sorbent. The following types of sorbents were used: clinoptilolite modified with sodium hydroxide and clinoptilolite modified with phosphate acid. We stadied that in spite of the fact that copper in the initial solution is bivalent and chromium is trivalent, selective removal of copper from a two-component solution takes place. We have established the possibility of the following chemical reactions in the adsorbent-adsorbate system at the same time: precipitation – dissolution of contaminants in the form of sparingly soluble precipitates (hydroxides, salts, complex compounds), ion-exchange and non- ion-exchange sorption and desorption on the active surface of the sorbent.

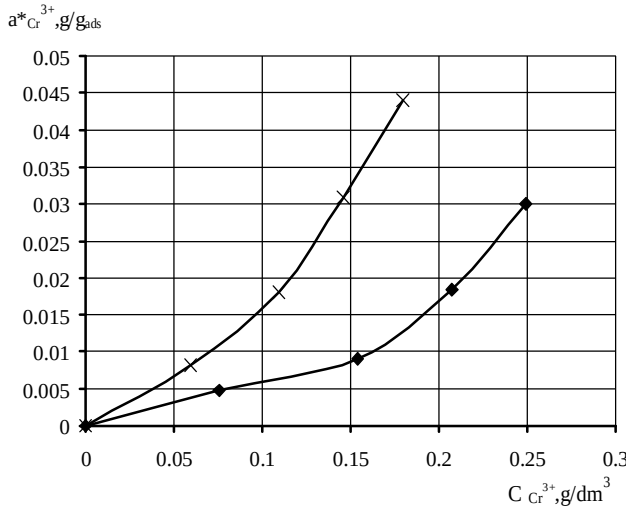

Fig.1 Isotherm of compatible adsorption of Cr (III) on modified sorbents: X – zeolite modified by H_3PO_4; ♦ – zeolite modified with NaOH

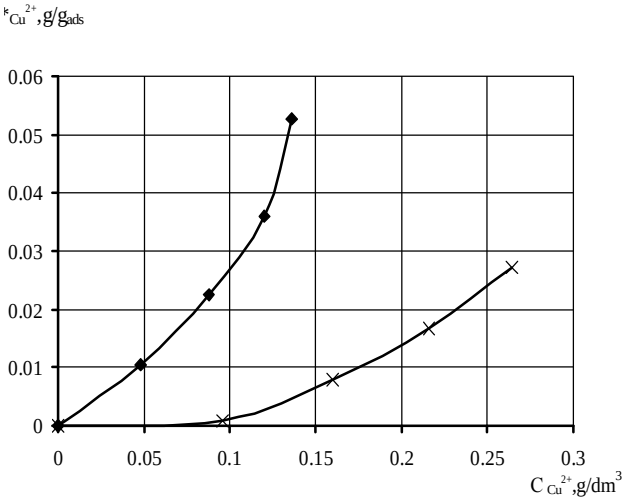

Fig.2 Isotherm of compatible adsorption ofCu (II)) on modified sorbents: X – zeolite modified by H_3PO_4; ♦ – zeolite modified with NaOH

The adsorption of ion-exchangeable ions on zeolite modified in alkali conditions was more intensive compared to phosphoric acid-modified sorbent.

Adsorption of chromium chromium ions passes intensively on the surface of the sorbent modified with phosphate acid. The comparison of the sorption isotherms presented in Figs 1 and 2 with the preliminary data [5, 6, 7] indicates an increase in the sorption capacity of the modified zeolite almost twice as compared with the naturally occurring sorbent.

The reason for this is the formation of wider pores as a result of the dissolution of the zeolite rock. This trend is confirmed by many researchers working in the field of modifying sorbents with mineral acids. It is indicated by the formation of a large number of mesos and macropores that allow absorbing large-sized molecules.

Conclusion

The expediency of using natural and modified sorbents due to high adsorption, ion exchange and filtration properties, as well as their prevalence on the territory of Ukraine and relatively low cost is substantiated.

On the basis of the analysis of experimental studies, the efficiency of the use of clinoptilolite, modified by acid activation as a sorbent of Cu (II) and Cr (III) ions from waste waters, was confirmed.

The sorption properties of modified zeolite against Cu2 + +Cr3 + ions have been checked. It has been established that the modification of zeolite with phosphate acid increases the capacity of zeolite in relation to heavy metal cations compared with natural clinoptilolite and zeolites modified by alkali. On the basis of the analysis of experimental studies, the efficiency of the use of clinoptilolite of the Sokirnitsky deposit, modified by the method of phosphate acid activation of natural zeolite as a sorbents of Cr (III) and Cu (II) ions from waste waters, was confirmed.

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