The Survey of Sorption Ion-Exchange Properties of Paleozoic Natural Minerals in the Static Conditions

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Abstract. An experimental and exploring process’ results of iron’s ion, manganese and ammonium sodium extraction from aqueous solution by some Ural’s natural minerals in a static regime at certain physicochemical conditions: by the zeolite, montmorillonite and vermiculite in the static conditions. Values of maximum sorption capacity are estimated on a gram of natural sorbents for the present conditions. Comparison of the survey’s results shows that effective sorptions from exploring natural minerals can be used as a clinoptilolite and zeolite-mineral montmorillonite type.

1. Introduction
The research of the zeolite’s ion exchange properties is necessary for possible application the natural minerals in the field of environmental protection.

Surface waters and underground horizons in the Western Siberian region are characterized as an increased pollution by different substances of natural and technogenic origin, which include heavy metal cations, iron, ammonia nitrogen and others. Consequently, it is essential to make a reliable barrier from a wide range of pollution in the process of cleaning natural and waste water. Filtration is traditionally one of the latest technological parts for the cleaning natural and waste waters. For this purpose it widely used in filter layers of granular natural materials Nowadays zeolite breeds from different deposits are investigated as a download filter \cite{1, 2}. In the subpolar and polar Ural are opened deposits of zeolite breeds, it has an industrial sense.

2. Equipment and devices used in studies
2.1 Sorption and ion-exchange properties of natural minerals
The work’s purpose is to explore the sorption activity of natural Paleozoic minerals in Ural: zeolite-montmorillonite breeds, clinoptilolite, habasit and vermiculite concerning the ions of external solutions. The researchers noted that the exchanging complex’s nature of a given material’s sorption ability influences on it \cite{8, 9}. One of the most important aims in the kinetics of ion exchange is to find out the mechanism of the sorption process and the ability to rule its speed. During the survey of the new natural material in order to the comparing mark with known natural sorbents, a method is brought as the foundation which is used by explorers of the University of mineralogy, geochemistry and crystal chemistry of rare elements \cite{3, 5}.
This work is performed within the scientific-applied themes to the investigation of physicochemical properties of Paleozoic zeolites in Ural. The survey is leaded in the laboratories of the Industrial University of Tyumen on the basis of the Central laboratory of Tyumen [1, 2].

3. Results and discussion
For the evaluation of ion-exchange and sorption properties of zeolite-montmorillonite rocks, clinoptilolite, habazite, vermiculite, experiments were conducted on the sorption at static conditions, ions of iron, manganese and ammonium nitrogen. The solutions were prepared with the following parameters (mg/dm3): Ca\(^{2+}\)=40.0; Mg\(^{2+}\)=13.4; K\(^+\)=1.5 (approximate average composition of the surface waters of the West Siberian artesian basin). Then in the prepared solution was injected salt of the studied pollutants, the list of which was chosen taking into account the specifics of natural water pollutants and existing research findings in the literature [1-5]. In a flask were poured 10 g of sorbent and poured the prepared solution containing a salt of the investigated metal. The weight ratio of sorbent/solution 1:20. The contact time of sorbent with solution averaged about 14 hours to determine the stable adsorption. In the waste liquid were determined the contents of the investigated metal. Then the solution was replaced and the experiments were continued until complete saturation of the sorbent.

As the granular filters used powders fractions of 0.07-0.3 mm zeolite-montmorillonite rocks, clinoptilolite, chabazite, vermiculite, and to map the investigated organic sorbent-carbon (AG-3). The results are shown in the graphs (Fig. 1-3).

**Figure 1** – Sorption of ammonium nitrogen (NH\(_{4}^{+}\)) inorganic and organic sorbents in static conditions (initial content of the element in a solution of 5 mg/dm\(^{3}\), T= 200°C, the fraction 0.07-0.3 mm): 1 – zeolite-montmorillonite sorbent; 2 – clinoptilolite; 3 – habazite; 4 – vermiculite; 5 – carbon (AG-3); C\(_{0}\) NH\(_{4}^{+}\) – content of ions of ammonium in the solution after contact with the adsorbent (contact time 14 hours); Q – volume of preconditioning solution with the sorbent, dm\(^{3}\). A competitive movement of ions to mineral occurs in a complicated system of the mineral and the sorbing ions. All happened processes make essential influence on a character of diffusion transfer and common speed of exchange.
Figure 2 - Sorption of iron ions (Fe\(^{2+}\)) under static conditions (the content of Fe\(^{2+}\) ions of 20 mg/dm\(^3\), T = 200\(^\circ\)C, the fraction 0.07-0.3 mm): 1 – zeolite-montmorillonite sorbent; 2 – clinoptilolite; 3 – habazite; 4 – vermiculite; 5 – carbon (AG-3); \(C_{0Fe^{2+}}\) - the content of iron ions (Pb\(^{2+}\)) in solution after contact with the adsorbent (contact time 14 hours); Q – volume of preconditioning solution with the sorbent, dm\(^3\).

Figure 3 - Sorption of manganese ions (Mn\(^{2+}\)) in static conditions (initial content of the element in a solution of 5 mg/dm\(^3\), T = 200\(^\circ\)C, the fraction 0.07-0.3 mm): 1 – zeolite-montmorillonite sorbent; 2 – clinoptilolite; 3 – habazite; 4 – vermiculite; 5 – carbon (AG-3); \(C_{0Mn^{2+}}\) - the content of manganese ions (Mn\(^{2+}\)) in solution after contact with the adsorbent (contact time 14 hours); Q – volume of preconditioning solution with the sorbent, dm\(^3\).

Analysis of the own and previous results of exchange of the one-bivalent natural zeolites [1-3] cations shows that the speed of the ion processes increases with the concentration of the solution, also by temperature and decrease of the counter-ion size.

The main parameters of ion-exchange capacity are the sorption and technological properties. The exchange capacity is necessary at study of kinetic and equilibrium values of ion-exchange [8]. Distinguish the maximum exchange capacity, which is corresponded to the full substitution of one ion to another and the exchange capacity which is realized at the certain physicochemical conditions. The last one is especially important by the choice and calculation of resource technological equipment.
Calculated at the certain specific physical and chemical conditions of the exchange capacity indicates the sorption capacity of the zeolite-montmorillonite mineral, clinoptilolite, chabazite and vermiculite. Zeolite-montmorillonite and clinoptilolite species are highly sorbent for extraction of iron from liquids to 9.2 mg per 1 gram of sorbent (on this indicator has no competitors among the studied sorbates); extracts from the solution (1 gram of sorbent) of 1.5 mg of manganese; 4.0 mg ammonium nitrogen [6].

Vermiculite absorbs from the solution effective only to the manganese exchange capacity (by 1 gram of sorbent) of 1.13 mg of manganese. Thus, the investigated minerals - zeolites of the Paleozoic Urals characteristics are known (younger) zeolites of the Far East, Carpathians, Caucasus [7].

4. Conclusions
Presented dependencies experimentally demonstrate the existence of the optimum time’s contact, quantity of the sorbent and the initial concentration of the removed substance, for the maximum sorption’s attainment. High effectiveness was being achieved at the removing iron from water and the ammonium nitrogen, manganese zeolite-montmorillonit and clinoptilolit. It testifies to these natural materials can be used at water processing, purification of the turnaround and waste waters.

References
[1] Germanova T.V., Valieva I.R. Application of zeolites and zeolite-montmorillonitovyh of breeds of Ural Mountains for effective sewage treatment from ammonium nitrogen and accompanying катионов//News of the Samara centre of science of the Russian Academy of Sciences. 2014. Т. 16. N 1-7. P. 1828-1.
[2] Valieva I.R., Germanova T.V. Ionic an exchange of natural Paleozoic zeolites under various physical and chemical conditions. Natural and engineering science. 2015. N 6 (84). P. 114-119.
[3] Edy Wibowo, Mamat Rokhmat, Sutisnaa, Khairurrijalа, Mikrajuddin Abdullah. Reducing the salinity of sea water using natural zeolite (Clinoptilolite): adsorption isotherms, thermodynamics and kinetics. Desalination Volume 409, May 1, 2017, p. 146-156.
[4] H. Y. GU, J. W. K. Wong, R. D. Tyagi. Bioleaching of heavy metals from sewage sludge for land use. Modern developments in biotechnology and Bioengineering, Solid Waste Management 2017, p. 241-265.
[5] Kun-Yi Andrew Lin, Ah, Zhang-Xuan business woman, Andrew P. Jochems. Adsorption behavior methylimidazolium ionic liquids with Y-type zeolite in water: kinetics, isotherms, thermodynamics and interference. Journal of molecular liquids. Volume 232, April 2017, p. 269-276.
[6] Tinpan Man, Hong Chen, Junzhong Lin, Zhang Lin, Junliang Sun. Zeolite synthesized from alkaline helped pre-activated halloysite for effective removal of heavy metals in polluted river water and industrial wastewater. Journal of the science of the environment.
[7] Watts, H. Zhou, H. Liu, P. W. Chay, T. Kuznicki, S. M. Kuznicki. Natural zeolite clinoptilolite-phosphate composite membranes for desalination by pervaporation. Journal of membrane science, Volume 470, 15 November 2014, p. 431-438.
[8] Ayten Ates, Christopher Hardacre. The effect of various treatment conditions on natural zeolites: ion exchange, acidic, thermal and steam treatment Article Journal of Colloid and Interface Science, Volume 372 , Issue 1, 15 April 2012, Pages 130-140.
[9] Carlo Perego, Roberto Bagatin, Marco Taliabu, Rodolfo Vignola. Zeolites and related mesoporous materials for multi-purpose environmental solutions. Microporous and mesoporous materials, volume 166, January 15, 2013, p. 37-49.