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WATER SORPTION PURIFICATION FROM AMMONIUM POLLUTION

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Abstract. Water sorption purification from ammonium pollution has been investigated. The sorption ability of natural clay sorbents has been characterized. The isotherms of ammonium ions adsorption by natural zeolites, palyhorskyties and glauconites were plotted. It was established that water purification from ammonium ions mainly corresponds to the model of surface diffusion at non-linear isotherm.

Keywords: ammonium pollution, clay sorbents, adsorption.

1. Introduction

One of the main and important tasks of ecological and epidemiological safety is providing population with high-quality water. However, the modern state of water basin and growing demand for drink water which satisfies all sanitary regulations need the extensive operations aimed at the search of new water treating technologies.

Recently the physico-chemical analysis of groundwater has shown the abnormal content of many pollutants, ammonia nitrogen in particular, that threatens mass poisoning of the population. The modern state of water basin in many countries is an evidence of the sanitary norms regarding NH_4^+ exceeding and impossibility of water supply from underground sources directly to the users without water primary purification. It means that enterprises have to apply the additional measures connected with expensive and power-consuming technologies. Ammonium ions rank one of the most dominating places among drinking water pollutants. The reason is a wide expansion of pollutions sources: excessive introduction of inorganic and organic fertilizers; sewage of cattle-breeding complexes, domestic and industrial waters, mainly of chemical and food industries; landfill wastes containing nitrogen compounds.

The analysis and comparison of different methods of ammonia nitrogen removal from aqueous solutions allow to assert that the ion-exchange method using natural dispersed sorbents is one of the most effective from the techno-economic point of view [1, 2]. Now the natural sorbents are widely used for environmental protection in the following directions:

- fine cleaning and drying of waste gases;
- selective purification of surface and underground water from heavy metal ions, radioactive elements, ammonium ions, oil and petroleum products, dies, *etc*.;
- using together with fertilizers to increase the crops;
- purification of petroleum products, water, transformer oil, ethanol, bromine, crude alcohol.

The purification of aqueous solutions using dispersed sorbents meet most demands of ecologically friendly and energy-saving production based on wasteless technology. Considerable geological reserves, cheap mining operations, simple preparation for transportation and usage, possibility to use waste sorbents in other technologies due to which there is no necessity of expensive regeneration are the main advantages of minerals usage. Natural sorbents, in particular zeolites, palyhorskyties and glauconites have good ion-exchange selectivity of heavy metals cations. Moreover they are available and do not need the complicated primary treatment.

Zeolite is the insignificantly dispersed aluminum silicate $Me_{2/n}O{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}yH_2O$. This mineral is widely distributed in the depths of Ukraine. Sokyrnytske basin of natural zeolites (Western Ukraine) is one of the greatest in the world. The mineral composition of zeolite deposits consists of clinoptilolite (60–90 %), quarts and feldspar (6–7 %), clay minerals (2–6 %) and plagioclase (till 2 %).

Palyhorskite $Mg_{2\text{-}5}[(H_2O)_2|OH|Si_4O_{10}]2H_2O$ is a mineral consisting of dual chains of silica-oxygen tetrahedrons elongated in parallel to the symmetry axis. It belongs to the group of minerals that naturally have high adsorption properties, caused by a peculiar composition of the mineral crystalline structure formed from rocks – palyhorskite. Unique deposits of palyhorskite clays are in Dashukivske basin. Palyhorskite clay index of plasticity varies from 10.54 to 30.2; the average moisture content is 67.9 %.

Glauconite is $K,Na,Ca\ (Fe^{3+},Fe^{2+},Al,Mg)_2([Al_xSi_{4\text{-}x}O_{10}](OH){\cdot}nH_2O$. The minerals of Adam group of the Khmelnitskyi region deposits contain 50–70 % of glauconite. Glauconite microconcretions have high effective specific surface, high capacity of cation exchange and high capacity of monolayer.

The promising methods of drinking water purification from ammonium ions are adsorption methods using natural dispersed minerals as the adsorbents. The advantage of natural dispersal sorbents are low cost, so there is no need of their expensive regeneration. Used sorbents can be employed to improve soil structure with the simultaneous introduction of ammonium ions, which are the essential nutrients, or for the production of mineral fertilizers.

On the basis of all above-mentioned the research aimed at the study of ammonium ions sorption from drinking water using natural sorbents is actual and important for assurance society vital activities.

The analysis of the latest publications shows that investigations using natural sorbents are concentrated on the determination of ion-exchange capacity [3, 4] or regeneration conditions [5, 6]. Unfortunately there is no unique approach to the mechanism of occurred processes. It is well-known that the analysis of isolated processes, such as sorption over natural sorbents, may be carried out using the mathematical stimulation method. For this purpose it is necessary to conduct a series of experiments. On provided condition that experiments are carried out, the mathematical model is developed for the process analysis, computer program for the calculations is developed and approved, the constants necessary for the process calculations will be determined.

The aim of this work is to investigate the adsorption process of ammonium ions from drinking water over natural dispersive absorbents, to conduct theoretical analysis of the absorption process and to realize the identification of the experimental data using known methods.

Since different types of adsorbents may be used for drinking water purification, it is necessary to carry out experimental and theoretical researches with them. The final result is the development of suggestions concerning implementation of ammonium ions adsorption process using natural dispersed sorbents. The perspective way should be the addition of sorbent to drinking water with further adsorption of ammonium ions and separation of solid phase at the stage of water purification from mechanical impurities (such stage is obligatory for all water treatment technologies).

2. Experimental

The adsorption process of ammonium ions from drinking water by palyhorskite, glauconite and zeolite was investigated and obtained data were identified in accordance with the known theoretical models.

To estimate the amount of adsorbed substance and to establish the sorption mechanism of ammonium ions by different types of water-soluble salts the following procedure was used. The prepared solution of ammonium salt was loaded into a hermetic vessel together with investigated sorbent. For these investigations the initial concentration of ammonium ions in the solution was 70 mg/l. The mixture was mechanically agitated. The infusion time was sufficiently great to achieve the equilibrium state with the guarantee. Then the sample was withdrawn and analysis for anion and cation presence in ammonium salt was carried out. Ammonium carbonate and ammonium chloride were used. The salts initial concentrations are represented in Table 1. In every experiment the solution volume was 150 cm^3, temperature 293 K, adsorbent mass 30 g and sorbent fraction 1 mm. The infusion time of every model mixture was 8 days.

For the further investigations the model solutions were prepared by dilution of NH_4Cl in distilled water. The ammonium ions concentration was 14 mg/l in all experiments. It is approximately by 10 times higher than the permissible content of ammonium ions in drinking water that corresponds to the real level of pollution. The model solutions in the quantity of 200 ml were poured into hermetic vessels with previously weighted portions of investigated sorbents. In all experiments the portions were 2; 5; 10; 15; 20 and 30 g and sorbent fraction was 1 mm. The investigated mixture (polluted water + sorbent) was sustained in hermetic thermostated state for 8 days under periodical agitation. It was the guarantee of adsorption equilibrium achievement at the moment of sampling. At the same time during long settling the sorbent complete precipitation was achieved. Due to this fact the correct photometric analysis of the sample was ensured. The adsorption temperature in all cases was 293 and 308 K. The sample was analyzed for the content of corresponding ions.

3. Results and Discussion

The experimental results with different types of ammonium salts are represented in Table 1. One can see that using strong acids salts (NH_4Cl) the chlorine ions concentration is not changed in the solution. Obviously it is connected with salt complete dissociation in water. Hence the sorption proceeds *via* chemosorption mechanism (ionic exchange). Using salt solutions obtained from weak acids ($(NH_4)_2CO_3$) the decrease in CO_3^{2-} ions concentration is observed, testifying the partial physical sorption of non-dissociated molecules by sorbents.

Table 1

Sorption of ammonium salts by natural dispersed sorbents

System	Concentration, mg/dm^3			
	$(NH_4)_2CO_3$		NH_4Cl	
	NH_4^+	CO_3^{2-}	NH_4^+	Cl^-
Initial solution	70	115	70	138.7
Final solution + palyhorskite	1.15	102.6	1.15	139
Final solution + glauconite	36	96.3	4.6	138.9
Final solution + zeolite	0.54	103.4	absent	138.9

The experimental results of sorption activity of all three types of sorbents are represented in Fig. 1.

Zeolite has the best sorption ability. Its amount higher than 15 g allows to achieve the complete removal of pollutants from the system. Even the maximum amount of glauconite purifies water to only 70 %.

Within the investigated temperature range (293–308 K) the difference between the obtained results is negligible. Thus, in the investigated interval representing the real temperature of polluted water, it does not affect the mass-exchange process. Therefore the experimental data for these temperatures were described by the same dependence.

The data present in Fig. 1 are used for the adsorption isotherms plotting (Fig. 2). Using zeolite and glauconite, the experimental isotherms may be approximated by straight-line section of the isotherm (Henry isotherm). Tangent of the slope angle for these isotherms is equal to the rate coefficients of ion-exchange rate: $k = 1.227$ and 0.0227 m^3/kg for zeolite and glauconite, respectively.

One can see from Fig. 2 that the experimental isotherm of palyhorskyte deviates from linearity that causes the necessity of its analysis by means of identification known theoretical models. At the same time the experimental results show that the temperature within the chosen interval does not practically influence the adsorption capacity of ion-exchange. This fact gives the possibility to unite data bulk by the same isotherm.

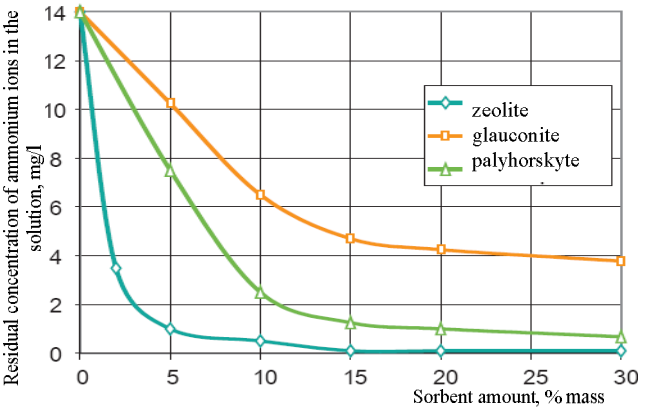

Fig. 1. Residual concentration of ammonium ions *vs* sorbent amount

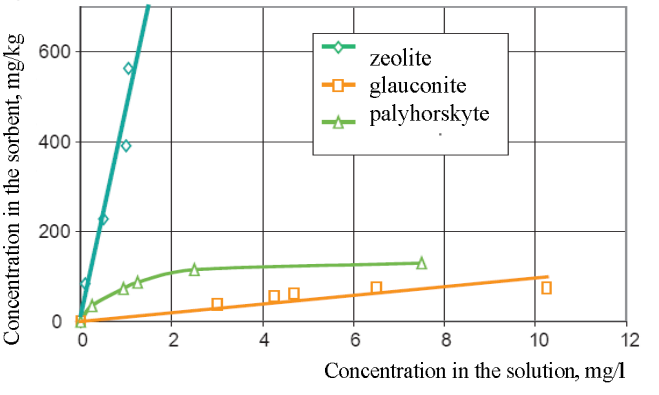

Fig. 2. Adsorption isotherms of ammonium ions in the solution

For the identification we chose 4 theoretical models: Langmuir model, Nikolskyi model, bi-Langmuir model and Freundlich model. The identification was done in turn according to these models and approximation was chosen at the first stage using algebraic functions in relation to Markwart method.

For the choice of above-mentioned models and determination of the most correct one it was necessary to analyze the statistical estimations of identification [7]. We selected Fisher criterion for the estimation of two dispersions similarity (experimental data and calculation model) and t-Student criterion – for the estimation of of calculated mass-exchange coefficients significance, which were compared with standard values of t-Student criterion with confidence interval of 95 %.

Table 2

Calculated parameters of theoretical data identification to the experimental results

Parameters	Parameter values	t-Student criterion	Standard value of t-Student criterion (confidence interval 95 %)	Fisher criterion
Langmuir model				
P_1	2.812E+0001	2.583E+0000	5.844E+0000	25.82
P_2	9.259E-0001	1.139E-0001	2.577E-0001	
bi-Langmuir model				
P_1	2.713E+0001	2.577E+0000	5.828E+0000	19.17
P_2	9.235E-0001			
P_3	1	2.577E+0000	2.659E-0001	
P_4	1			
Nikolsky model				
P_1	7.666E+0008	2.258E+0016	5.206E+0016	22.95
P_2	2.726E+0007	8.027E+0014	1.851E+0015	
P_3	2.524E+0007	7.432E+0014	1.714E+0015	

The calculated parameters for the analyzed theoretical models are given in Table 2. The analysis of Fisher criterion for the theoretical isotherms allows to assert that Langmuir model describes the adsorption process in the most correct way. At the same time we may affirm that three isotherms (Nikolskyi, bi-Langmuir and Langmuir) may be used to describe the process with sufficient degree of precision. The calculated values of mass exchange constants presented in Table 1 may be used for the calculation of the real process. Their significance is confirmed by calculated values of t-Student criterion which were in all cases at the level of standard values with the confidence interval of 95 %.

4. Conclusions

The work deals with the experimental results of ammonium ions adsorption over natural sorbents: (zeolites, palyhorskyties and glauconites). It is shown that within the range of investigated temperatures (293–308 K) zeolite has the best sorption properties. Since the temperature has the insignificant effect on the mass-exchange process, the experimental data for these temperatures may be described by the same dependence.

On the basis of experimental results it was established that using zeolite and glauconite as adsorbents, the experimental data may be described by the isotherm straight-line section (Henry isotherm). The kinetic coefficients were determined.

The experimental data of ammonium ions adsorption over palyhorskyte using the developed program were identified to the known theoretical isotherms – Langmuir, Nikolskyi, bi-Langmuir and Freundlich. Using calculated values of Fisher criterion it was established that Langmuir isotherm describes the process best of all. The values of mass-exchange constants were calculated for all investigated theoretical isotherms and may be used for the calculation of actual processes.

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СОРБЦІЙНЕ ОЧИЩЕННЯ ВОДИ ВІД АМОНІЙНОГО ЗАБРУДНЕННЯ

Анотація. *Досліджено процеси сорбційного очищення води від амонійного забруднення. Охарактеризовано сорбційну здатність природного глинистих сорбентів. Побудовано ізотерми адсорбції йонів амонію природними цеолітами, палигорськітами та глауконітами. Визначено, що процес очищення води від йонів амонію переважно відповідає моделям поверхневої дифузії при нелінійній ізотермі.*

Ключові слова: *амонійне забруднення, глинисті сорбенти, адсорбція.*