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COMPLEX WATER TREATMENT OF AGROINDUSTRIAL COMPLEXES

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Abstract. The aim of this work was studying the process of phosphate adsorption on natural and synthesized adsorbents such as aluminosilicates. Sorption properties of natural zeolite concerning phosphates in static and dynamic conditions were investigated. It was found that phosphates were absorbed better in an acidic environment. Zeolites based on fly ashes of Dobrotvir heat power plant were synthesized and modified. The equilibrium values of adsorption capacity were established and the proper isotherms at a temperature 20 °C were built.

Key words: phosphates, ammonium, zeolite, equilibrium, adsorption, wastewaters

1. Introduction

As a result of heterogeneity of contaminations of industrial flow waters, after composition there is the necessity to apply a complex of methods for industrial wastewaters treating. For this purpose, in particular, mechanical, biological, chemical and physical – chemical methods are applied. However, in some cases there is a necessity to combine them. During water treatment by an adsorption method, natural and synthetic materials were used. Therefore problems of investigation of adsorption mechanisms are actual, to find the expedience of subsequent sorbent regeneration. The choice of the optimum method for implementation of adsorbtion-desorbtion processes is an essential requirement in technological processes of water treatment.

2. Experimental research

Research of phosphates adsorption by the zeolite of clinoptilolite type was carried out in static conditions using monobasic, dibasic and substituted by three atoms potassium phosphates and orthophosphoric acid.

Zeolites, which are synthesized from fly ashes**.** The experiment was carried out in Teflon crucibles with the use of the stove equipped with a temperature controller and in a thermostatic bath equipped with a mixer.

Specimens of fly ashes (40 g) were mixed with a solution of NaOH (160 ml), whereupon the mixture was crystallized at interval 90 °C …107 °C. Sediment was filtered, washed by the distilled water to pH =10 and dried out at 105 °C during 12 hours.

Determination of adsorption capacity of zeolites relatively to ammonium

To investigate the adsorption capacity of zeolite relatively to ammonium, 200 sm^3 of SM3 solution was placed in glass retorts. Ammonium chloride was removed in distilled water at different initial concentrations (C = 0.0125 – 5 g/dm^3), and zeolite (~1 г) was dipped. The range of concentrations was conformable to concentration of NH^{4+} in real wastewaters. Retorts were hermetically closed and left at periodic interfusion for two days at +20 °C. Sorbent was separated from the solution, which was analyzed for the presence of NH^{4+} on photo-colorimeter after the known method [1]

Determination of adsorption capacity of zeolites relatively to the phosphates

The essence of the method consists in the hydrolysis of phosphates into orthophosphoric acid, getting of the colored complex substance of this acid with ammonium molibdate-vanadate and determining of the colored solution optical density.

The specimens were diluted 0–50 times in a 100 ml volumetric flask, added to 25 ml of reagent and then analyzed on photo-colorimeter CFC-2-2.

3. Results and Discussion

Zeolites synthesis based on fly ashes of Dobrotvir heat power plant.

Morphology of the surface and chemical composition of the got specimens were studied by applying a scanning electronic microscope. The diameter of the electronic bunch was 1 mcm, potential acceleration was 15 cV. The elements analysis was carried out for different specimens with specific surface of 100 mcm^2 by using the scanning electronic probe, whereupon the obtained results have been averaged out. Electronic microscopic images of particles surface of fly ash and synthesized zeolites obtained by a scanning electron microscope are shown in Fig. 1.

Places marked by figures specify the numbers of spectra, chemical composition of which is shown in Table 1.

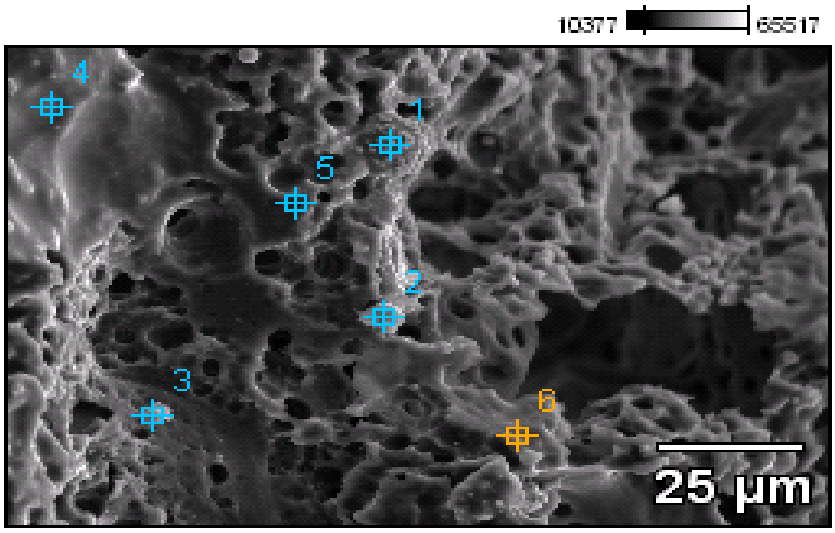


Fig. 1. Electronic microscopic images of the surface of the particles of synthesized zeolites

Table 1

Concentration of atoms, at. %

No. of spectra	Be-K	C-K	O-K	Na-K	Mg-K	Al-K	Si-K	Ca-K	Ti-K	K-K	Mn-K	Fe-K
1		45.19	32.92		0.36	0.91	1.27				0.30	19.06
2	24.07	36.19	29.36	0.07	0.41	1.00	1.66	0.19		0.12	0.15	6.77
3	26.65	32.67	29.13	0.18	0.34	2.63	6.79		0.08	0.70		0.84
4	50.19	26.71	9.17		0.15	1.22	1.81	0.30		0.25		10.21

Continuation of Table 1

Concentration of atoms, at. %

No. of spectra	C-K	O-K	Na-K	Mg-K	Al-K	Si-K	P-K	S-K	K-K	Ca-K	Ti-K	Mn-K	Fe-K
1	43.91	40.69		0.83	2.95	1.04				0.17		0.33	10.09
2	49.44	38.79	0.29	0.21	4.37	5.58	0.02	0.06	0.54	0.10	0.09		0.45
3	46.44	42.23	0.36	0.20	3.99	5.46			0.60		0.14		0.57
4	91.67	7.51	0.08	0.06	0.12	0.13		0.16		0.17			0.08
5	99.93							0.07					
6	96.90	2.88		0.04	0.04	0.06		0.06		0.02			

To determine the adsorption capacity of zeolite in relation to phosphate-ions, solutions of H_3PO_4, KH_2PO_4, K_2HPO_4 and K_3PO_4, prepared in the distilled water, at different initial concentrations (C = 25–750 mg/dm^3) were placed in 200 sm^3 glass retorts, and identical specimens of zeolite (~1 g) were added.

The experiment was carried out in Teflon crucibles with the use of the stove equipped with a temperature controller and in a thermostatic bath equipped with a mixer.

Samples of zeolite were obtained by mixing fly ashes (40 g) with NaOH (160 ml) solution of, whereupon a mixture was crystalized at 90 °C and 107 °C. Sediment was filtered, washed by the distilled water to pH =10 and dried out at 105 °C during 12 hours.

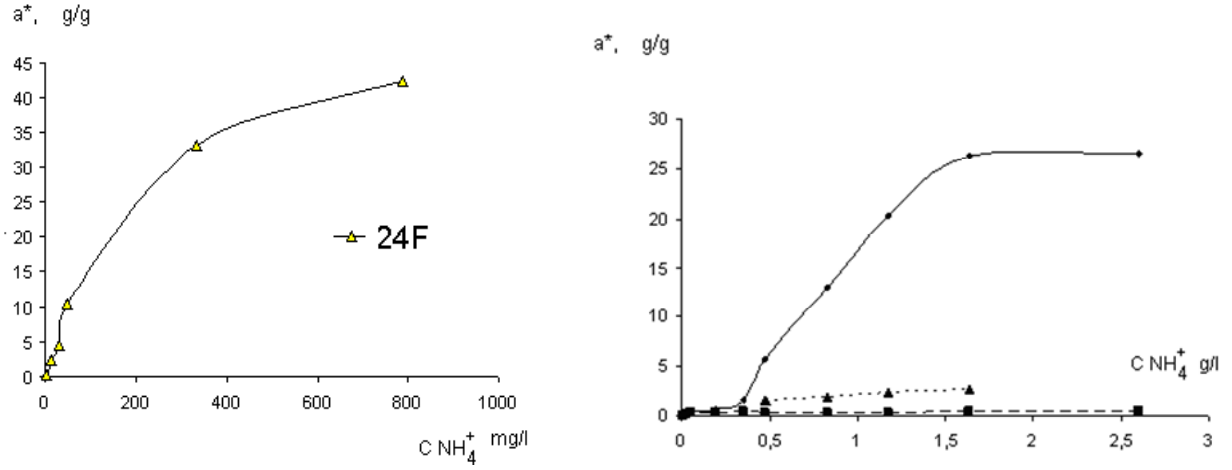
Adsorption removing of ammonium from wastewater using natural and synthetic zeolites.

Agro-industrial complexes are among the greatest water users, abstractors and simultaneously pollutants of surface and ground waters. In particular, meatpacking plants need a lot of fresh water for their activity, 95 % of which is discharged from production workshops as strongly muddy wastewaters. Adsorption properties of natural zeolite of the Socirnitsa deposit were investigated in relation to the contaminating components of wastewaters of meatpacking plants, especially amonium nitrogen, concentration of which is regulated by norms. [3, 4]

The equilibrium values of adsorption capacity were set and proper isotherms of adsorption at 20 °C were built. It was found that absorption of ammonium passes partly through the mechanism of ionic exchange. The volumes of substitution of exchange ions of sodium and calcium on an ammonium were experimentally explored.

The sorbtion capacity of zeolite of the Socirnitsa deposit in relation to ammonium ions was investigated. The mechanism of ionic adsorption of ammonium ions by zeolite is confirmed, that is accompanied with replacement of compensating ions of calcium and sodium, and also ions H^+ that are localized on bond Si-OH-Al on ammonium ions [5, 6].

It was found that the amount of adsorbed ammonium 8,7 times exceeds the amount of Ca^{2+} and Na^+ ions disengaged as a result of ionic exchange. Adsorption of ammonium ions on natural aluminosilicates was experimentally investigated. The obtained experimental results and calculation data were generalized.



1 2

Fig. 2. Isotherms of ammonium adsorption on natural zeolite (1) on synthetic zeolite (2)

During the hydrolysis of ammonium chloride the process passes the following reaction: an ion H^+ is adsorbed on the Lyois acid centers and results in the break of communications between oxygen and aluminum, Pursuant to literary data the leaching of aluminum ion from zeolite occurs by substitution of aluminum by four hydroxyl groups. As a result, there is a destruction of zeolite surface and leaching of ion Al^{3+} into the solution. Thus $Na[AlCl_3]$ appears in the solution. This phenomenon is confirmed by the increase of optical density of the tested solution after the adsorption of ammonium salts. ΔD = 0.15–0.2, that testifies the presence of dispersed and colloid particles in the explored solution. At destruction of the surface, new adsorption centers, contained in the adsorbent are freed.

Adsorption removing of phosphate ions from wastewaters using natural and synthetic zeolites.

Investigation is devoted to water treatment. The aim of this work was to study the process of phosphate adsorption on natural adsorbents such as aluminosilicates. Sorption properties of natural zeolite (clinoptilolite of Sokyrnytsia mineral deposits) of phosphate in static and dynamic conditions were investigated. Values of equilibrium adsorption capacity were calculated and the corresponding isotherm at 20 ºC was built. It was found that phosphates were absorbed better in acidic environment.

The carried out researches showed that the process of adsorption substantially relied on the degree of substitution of phosphate ions by alkaline metals [7]. Analyzing Fig. 1, it is possible to assert that phosphates were better adsorbed in acidic environment. Thus in the value area of initial concentrations 2,5–150 mg/l isotherms of sorption of orthophosphoric acid and potassium of digidrophosphfates are practically identical, however with increasing concentration of the initial KH_2PO_4 solutions is taken less. During the initial concentration above 100 mg/l equilibrium is set. In the given range of concentrations, there is practically the same tendency at the adsorption of K_2HPO_4 and K_3PO_4 solutions. For H_3PO_4 concentrations, over 150 mg P_2O_5/dm^3 there is a sharp increase in the adsorption capacity of zeolite.

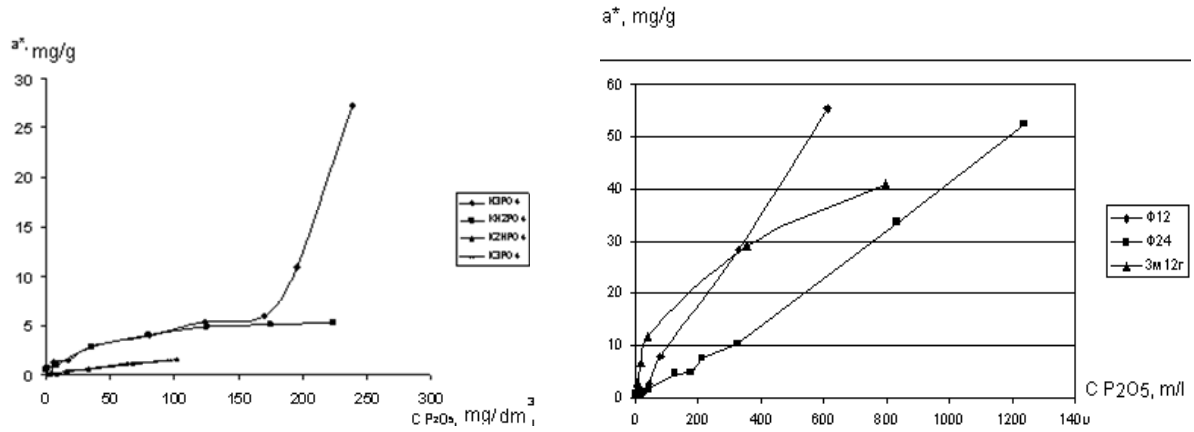


Fig. 3. Isotherms of phosphates adsorption: On natural zeolite (1), KH_2PO_4 on synthetic zeolites (2)

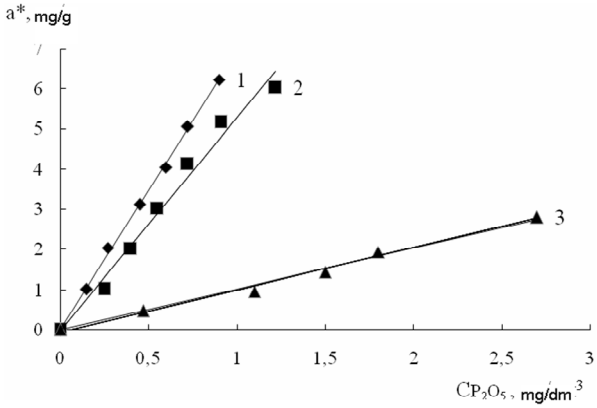


Fig. 4. Isotherms of phosphates, (KH_2PO_4) adsorption on natural zeolite (1), jointly with ammonium nitrogen (2), jointly with ammonium nitrogen and albumin (3)

Adsorption capacity of clinoptilolite relative to un-substituted phosphates is higher and decreases with substitution of orthophosphoric acid by alkali metal ions.

Essential influence of pH on the sorption properties of clinoptilolite to P_2O_5 was shown.

Research data and the known theoretical relations were identified. Kinetic coefficients of adsorption process were calculated. Coefficients of the Langmuir equation for adsorption of phosphates by zeolites were calculated by graphical and numerical methods.

Diffusion coefficient of P_2O_5 in the pores of zeolite in dynamic conditions under intensive mixing was estimated.

Conclusions

Adsorption properties of natural zeolite were investigated concerning the contaminating components of flow waters of meatpacking plants, from ammonium and phosphates.

The equilibrium values of adsorption capacity were expected and the proper isotherms were built at 20°C. It was found, that phosphates are taken in better than ammonium nitrogen.

It was explored, that adsorption ability of clinoptilolite in relation to single-phase systems is higher and diminishes in the process of simultaneous adsorption of two components from the solution.

Taking into account large supplies and cheapness of this natural sorbent, it may be used for wastewater treatment of meatpacking plants from the given contaminations. Work on their application for wastewaters treatment was carried out.

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