COMPLEX WATER TREATMENT OF AGROINDUSTRIAL COMPLEXES BEFORE WASTEWATERS DISCHARGE INTO BASINS OF RIVERS

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ABSTRACT

In the general complex of natural resources of region one of primary places belongs to the water resources. As a result of man-made pollution of Western Bug is global and irreversible and causes pollution of basin of the Baltic Sea. Investigation is devoted to the issue of water treatment. The aim of this work was to study the process of phosphate adsorption on natural and synthesized adsorbents such as aluminosilicates. Sorption properties of natural zeolite (clinoptilolite of Sokyrnytsia mineral deposits) to phosphate in static and dynamic conditions are checked. Found that phosphates are absorbed better in an acidic environment. Adsorption capacity of clinoptilolite to unsubstituted phosphates is higher and decreases with substitution of orthophosphoric acid by alkali metal ions. Essential influence of pH on the sorption properties of clinoptilolite P_2O_5 was shown. Research data and the known theoretical relations calculated kinetic coefficients of adsorption process were identified. The mathematical modelling of process of absorption of active component by grainy sorbents describes unstationary diffusive-kinetic processes in the multicomponent distributed systems. Zeolites on the basis of fly ashes of Dobrotvir heat power plant are synthesized and modified. Properties of zeolite on the basis of termogravimetric analysis are investigated. Adsorption properties of natural zeolite are tested to the contaminating components of flow waters of meat-packing plants, from ammonium and phosphates. The equilibrium values of adsorption capacity are expected and the proper isotherms are built at a temperature 20^{o}C. It is set, that phosphates are taken in better, than ammonia nitrogen. It is explored, that adsorption ability of clinoptilolite in relation to the monophase systems is higher and diminishes at the process of adsorption simultaneously two components from solution. Taking into account the exhaustive supplies of natural zeolites the synthesis of synthetic zeolites and is their application for cleaning of wastewaters carried out.

KEYWORDS: phosphates, ammonium, zeolite, equilibrium, adsorption, wastewaters

INTRODUCTION

As a result of heterogeneity of contaminations of industrial wastewaters there is the necessity of application methods for complex water treating of industrial wastewaters. To that end, in particular, methods mechanical, biological, chemical and physical and chemical are carried out. In many cases there is a necessity in their combination. During realization processes of water treatment by an adsorption method the natural and synthetic are used. Therefore are actual problems of investigation of adsorption mechanisms for ascertaining the expedience of subsequent sorbent regeneration. And also choice of optimum method of realization of adsorption and desorption processes is essential requirement in technological processes of water treatment.

Earlier researches in the field of investigation of adsorption of organic and inorganic substances waters were carried out by use of natural and synthetic adsorbents, however the received results give the information only about adsorption of one-component systems and only at the initial stage disregarding the description of mechanisms of joint adsorption.

For sewage treatment it is important to investigate mechanisms of adsorption for optimum realisation of processes of wastewaters treatment. Besides that is necessary to investigate ways of reception effective adsorbents for wastewaters treatment, in particular, applying fly ashes of heat power plants.

METHODOLOGY

Zeolites synthesizing from fly ashes.

The experiment was carried out in the teflon crucibles with the use of the stove equipped by a temperature regulator and in thermostatically the bath-house equipped by mixer. Specimens of fly ashes (40 g) were mixing up with solution NaOH (160 ml), whereupon the mixture was crystallized at interval 90˚C …107˚C. The precipitate was filtered, washed by the distilled water to pH =10 and dried out at 105°C during 12h. In such a way we received zeolite marked 3m12h.

Investigation morphology of surface and chemical composition of synthesized zeolites.

Specimens of zeolites which were obtained according to 1.1 were investigated by applying the scanning electronic microscope. The diameter of electronic bunch was 1 mcm, potential acceleration was 15 KV. The element analysis was carried out for different specimens with specific surface of 100 mcm^2 by using the scanning electronic probe, whereupon obtained results has been averaged out.

Determination of adsorption capacity of zeolites relatively to the ammonium ions

For investigation the adsorption capacity of zeolite in relation to the ammonium in glass retorts was placed a 200 cm^3 solution the ammonium chloride prepared in the distilled water, at different initial concentrations (C = 0.0125 – 5 g/dm^3), and immersed zeolite (~1 g). The range of concentrations was conformable to concentration of NH_4^+ in the real waste waters. Retorts hermetically closed and abandoned at periodic interfusion on two days at a temperature +20°C. Sorbent was separated from solution which was analysed on a presence of NH^{4+} on photocolorimeter after the known method.

Determination of adsorption capacity of zeolites relatively to the phosphates

For investigation of adsorption capacity of zeolite in relation to phosphate-ions in glass retorts placed on 200 cm^3 solutions 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), and added identical to the specimens of zeolite (~1 g).

Essence of method consists in the hydrolysis of phosphates to orthophosphoric acid, receipt of the painted complex substance of this acid with ammonium molibdate and ammonium vanadate and determination of optical density of the painted solution.

Specimens were diluted in 0-50 times in a volumetric flask on 100ml, added to the 25ml of reagent And were analyzed on photocolorimeter CFC-2-2.

Determination of adsorption capacity of zeolites relatively to the phosphates at joint presence of ammonium and albumin

Research of absorbing properties of zeolite at simultaneous presence at a solution of two polluting components was a following stage. Initial concentration of substances were same, as well as initial concentration of substances in the previous researches in which studied absorbing ability of zeolite in relation to one component solution. Absorbing ability of zeolite concerning phosphates in the presence of ammonium and albumin was carried out according to the technique, described in 1.5., with corresponding initial concentration of ions of ammonium (Cn = 10-60 mg/dm3) and phosphates (Cn = 5-30 mg/dm^3); with corresponding initial concentrations of ions of ammonium (Cn = 10-60 mg/dm^3), phosphates (Cn = 5-30 mg/dm^3) and 0.1-1 % albumin at 20°C and pH ~ 7.

RESULTS AND DISCUSSIONS

Synthesis of zeolites on the basis of fly ashes of Dobrotvir heat power plant

Synthetic zeolites for adsorption pollutants from solutions which are modelling waste waters were obtained according to methodology.

Morphology of surface and chemical composition of the got standards was studied with scanning electronic microscope according to 1.2. Electronic microscopic images of surface of particles of synthesized zeolites on the base of fly ashes got by use of the scanning electronic microscope are shown on fig. 1.

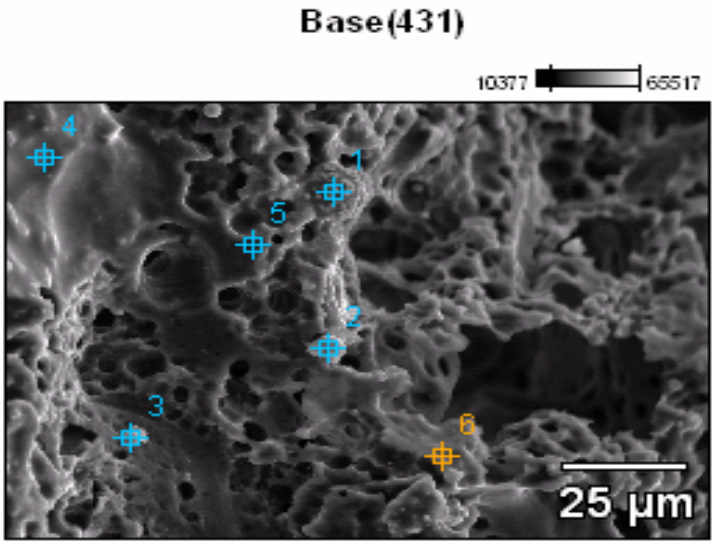


Figure 1. Electronic microscopic images of surface of particles of synthesized zeolites

Places on Fig. 1. are marked by numbers according to numbers of spectrums. Decoding of spectrums, with the conforming number, show to us the chemical composition of places of surface of particles of synthesized zeolites, which are shown in Table 1.

Table 1. Chemical composition of places of surface of particles of synthesized zeolites

Weight %

	C-K	O-K	Na-K	Mg-K	Al-K	Si-K	P-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Mn-K	Fe-K
Base(431)_pt1	27.83	34.35		1.06	4.20	1.54					0.35		0.95	29.73
Base(431)_pt2	38.06	39.79	0.43	0.33	7.55	10.04	0.05	0.12	0.11	1.35	0.25	0.28		1.63
Base(431)_pt3	35.53	43.04	0.53	0.31	6.86	9.77				1.50		0.44		2.02
Base(431)_pt4	88.21	9.63	0.15	0.11	0.27	0.30		0.42			0.56			0.35
Base(431)_pt5	99.81							0.19						
Base(431)_pt6	95.69	3.79		0.08	0.10	0.13		0.15			0.06			

Atom %

	C-K	O-K	Na-K	Mg-K	Al-K	Si-K	P-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Mn-K	Fe-K
Base(431)_pt1	43.91	40.69		0.83	2.95	1.04					0.17		0.33	10.09
Base(431)_pt2	49.44	38.79	0.29	0.21	4.37	5.58	0.02	0.06	0.05	0.54	0.10	0.09		0.45
Base(431)_pt3	46.44	42.23	0.36	0.20	3.99	5.46				0.60		0.14		0.57
Base(431)_pt4	91.67	7.51	0.08	0.06	0.12	0.13		0.16			0.17			0.08
Base(431)_pt5	99.93							0.07						
Base(431)_pt6	96.90	2.88		0.04	0.04	0.06		0.06			0.02			

Taking into account results which are represented on Fig. 1 and Table 1 we can assert that we has obtained zeolites with microporous structure which are able to adsorption of inorganic substances such as ammonium and phosphates. Because of large amounts of carbon in synthesised zeolites they are able to adsorption of organic substances likewise to activated charcoal.

Adsorption recovery of ammonium by the use of natural and synthetic zeolites

Agroindustrial complexes are one of greatest water users, abstractors and simultaneously pollutants of waters superficial and ground. In particular, meat-packing plants for the activity need the great amounts of fresh water, 95% of which are merging as very muddy wastewaters. The effective way for sewage treatment is application of zeolites.

Adsorption properties of natural zeolite of the Socirnitsa deposit are explored in relation to the contaminating components of flow waters of meat-packing plants from ammonium, concentration of which in sewage is supervised by corresponding norms.

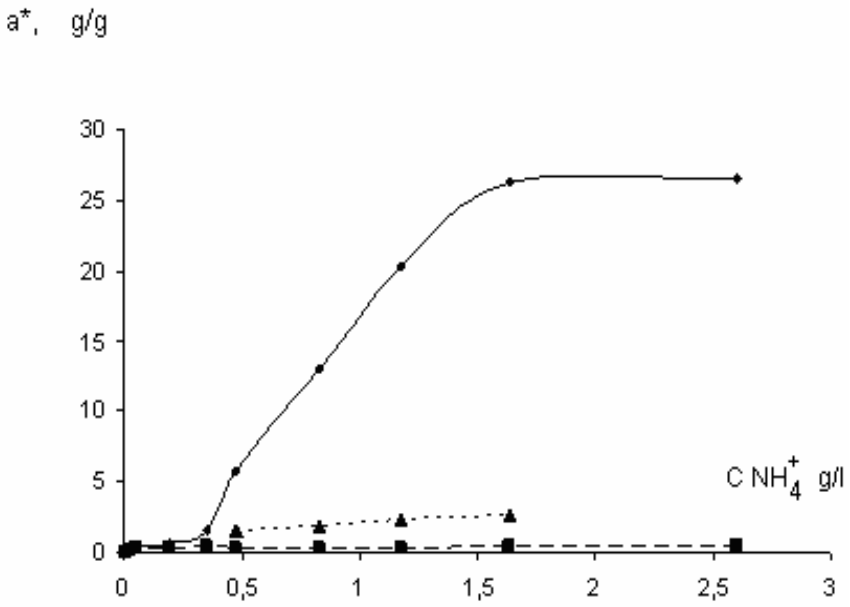
In work the adsorption capacity of zeolite of the Socirnitsa deposit in relation to the ammonium ions was explored according to the methodology. The mechanism of ammonium ions adsorption by zeolite is accompanied by replacement of compensating ions such as calcium and sodium, and also ions H^+ that are localized on bond on ammonium ions.

The equilibrium values of adsorption capacity are set and the proper isotherms of adsorption for a temperature 20° C are built. We have established that ammonium absorption passes partially on the mechanism of an ionic exchange. Volumes of replacement of exchange ions of sodium and calcium on ammonium ions are experimentally investigated.

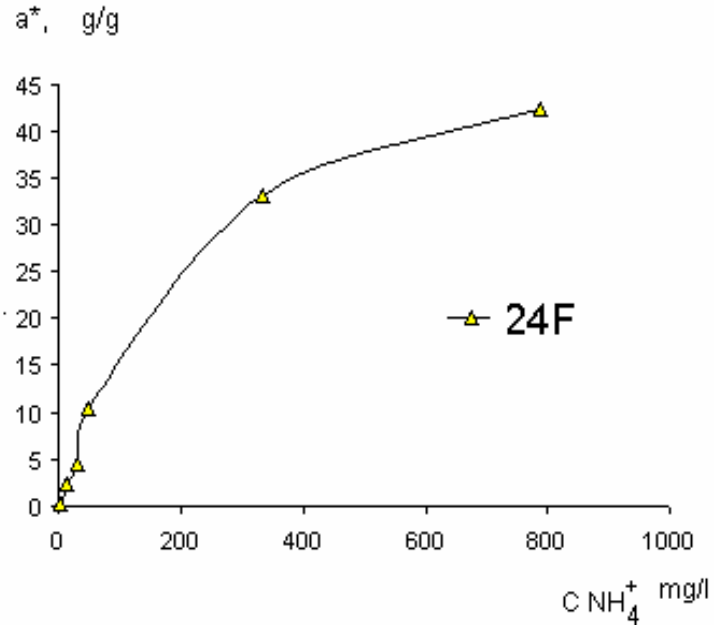
The received graphic dependences (Fig. 2.) show the general absorption of ammonium (a balance curve) and quantities of sodium (▲) and calcium (■) which have appeared in an investigated solution as a result of an ionic exchange. According to experimental data amount of adsorbed ammonium ions in 8.7 times exceeds amount of ions Ca^{2+} and Na^+ disengaged as a result of ionic exchange. Because of greatest amounts of ions Na^+ in synthesized zeolites, they are able to adsorption greatest amounts of ammonium.

During a hydrolysis of the ammonium chloride takes place the following reaction: an ion H^+ is adsorbed on the Lyois acid centers which were created as result of breaking of bonds between oxygen and aluminium. Pursuant to literary data the aluminium leaching from zeolite passes by substitution of aluminium by four hydroxyl groups.

As a result the processes of destruction of surface of zeolite and leaching of the ion Al^{3+} in solution take place. Thus $Na[AlCl_3]$appears in solution. This phenomenon was confirmed by the increase of optical density of test solution after adsorption of salts which contain the ammonium. $\Delta D = 0.15..0.2$, that testifies to the presence of dispersed and colloid particles in the explored solution. In the course of decomposition of the surface of zeolite by acid arise new adsorption centres which are located in deeper layers of adsorbent.



1) ♦- balance concentration of ammonium on natural zeolite; ▲-concentration of sodium; ■-concentration of calcium



2) Δ-balance concentration of ammonium on synthetic zeolite;

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

Adsorption recovery of phosphate ions by the use of natural and synthetic zeolites

These investigations are devoted to the problem of water treatment. The aim of this work was to study the process of phosphates adsorption on natural adsorbents such as aluminosilicates. Sorption properties of natural zeolite (clinoptilolite of Sokyrnytsia mineral deposits) to phosphate in static conditions are checked. Values of equilibrium adsorption capacity are obtained according to methodology. The isotherms of phosphates adsorption on natural and synthetic zeolites at

temperature of 20°C was built and represented on Fig 3. Analyzing Fig. 3 (1) it is possible to assert that zeolites are able for the better adsorption of phosphates in an 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 practically identical, however with the increase of concentration of initial solutions KH_2PO_4 is taken in less. Under initial concentration higher 100 mg/l the equilibrium was established. In the given range of concentrations there is practically the same tendency of phosphates adsorption from the solutions of K_2HPO_4 and K_3PO_4. For concentrations H_3PO_4 over 150 mg P_2O_5/dm^3 the sharp increase of adsorption capacity of

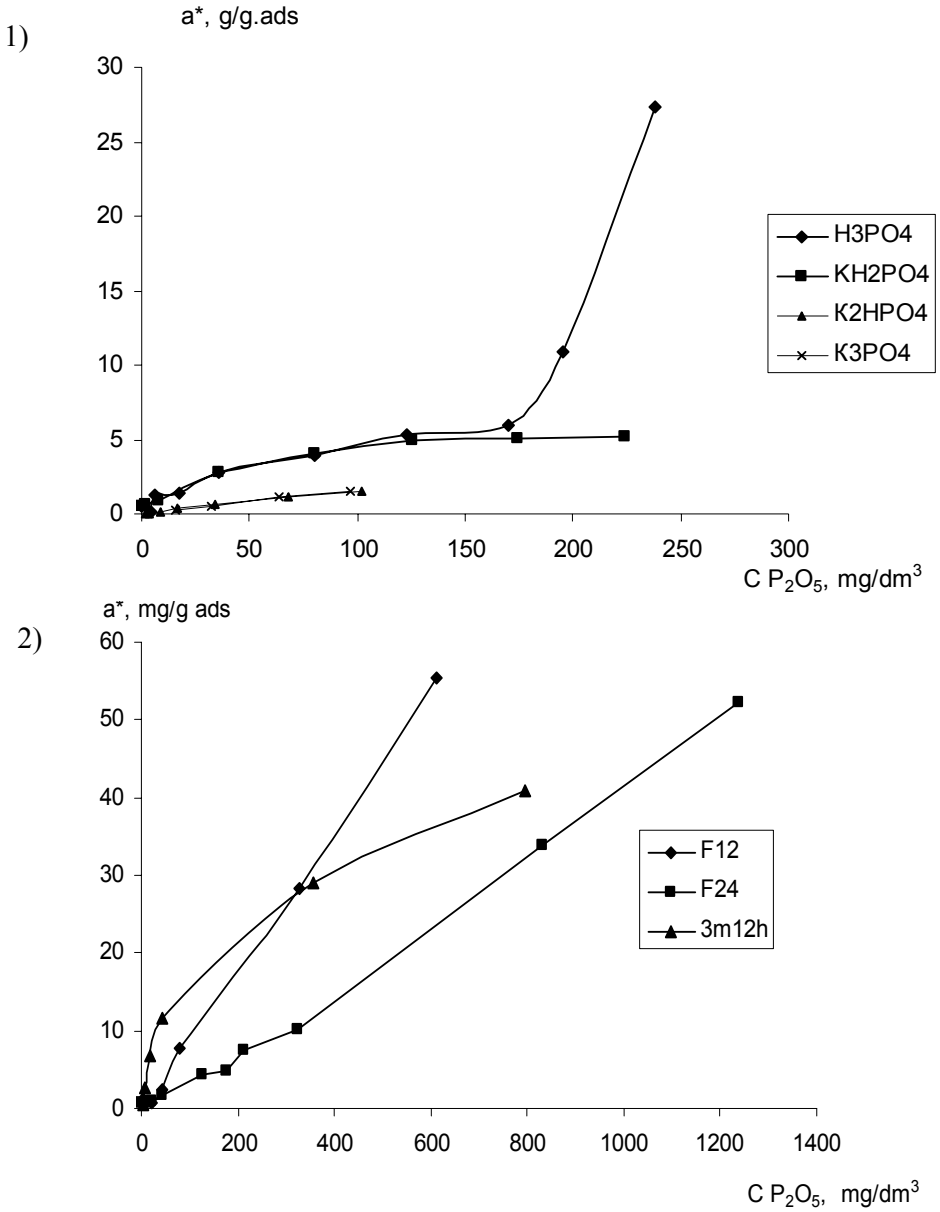


Figure 3. Isotherms of phosphates adsorption: On natural zeolite (1), KH_2PO_4 on synthetic zeolites (2)

zeolite was established. Thus adsorption capacity of zeolite relative to unsubstituted phosphates is higher and decreases with substitution of hydrogen ion in phosphoric acid by alkali metal ions.

Analysing results submitted on the Fig. 3 (2) we can establish the superiority of synthetic zeolites above natural. Specimens of zeolites which were obtained by a method of fusion of ashes with a crystal NaOH deserve the special attention.

Adsorption recovery of phosphates from modelling solution of sewage at joint presence of ammonium and albumin

It is known that adsorption on firm surfaces has competing character. With that end in view we investigated joint adsorptions of phosphates, ammonium and albumin from solutions which on the composition are close to sewage of meat-packing plants. Investigations were carried out according to methodology of determination of adsorption capacity of zeolites relatively to the phosphates at joint presence of ammonium and albumin.. Results of experiments are presented on Fig. 4.

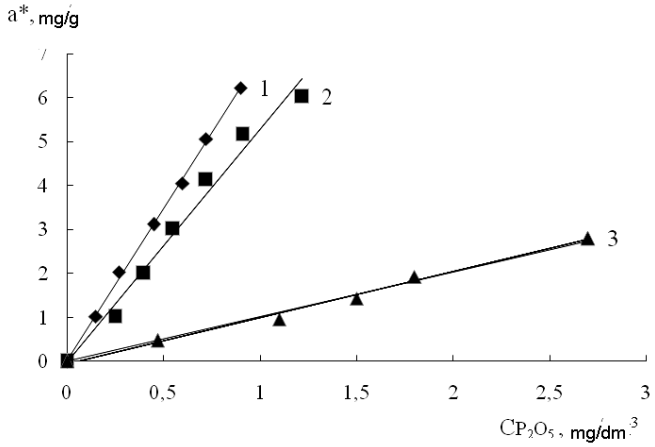


Figure 4. Isotherms of phosphates, (KH_2PO_4) adsorption on natural zeolite (1), jointly with ammonium nitrogen (2), jointly with ammonium nitrogen and albumin (3)

Analyzing graphic dependences it is possible to assert that phosphates from single-component solution are taken better, than at simultaneous presence of ammonium (2) and ammonium together with albumin (3). Graphic dependence (3) shows exclusively low degree of extraction of phosphates. The cause to it is adsorption of macromolecules of albumin on superficial active sites and simultaneous blockage by the adsorbed molecule of albumin of pores of zeolite.

CONCLUSIONS

Based on the present results such conclusions can be made:

- Adsorption properties of natural zeolites to remove contaminants that are contained in the wastewater of meat, in particular, ammonium and phosphates were investigated.
- Adsorption of ammonium ions on natural aluminosilicates has been experimentally explored.
- The equilibrium values of adsorption capacity of zeolites to the P_2O_5 and ammonium were obtained and the proper isotherms at the temperature 20^{o}C were built. It was found that zeolites adsorb more phosphates than ammonium.
- Essential influence of pH on the sorption properties of clinoptilolite to the P_2O_5 was shown.
- We have explored, that adsorption ability of clinoptilolite in relation to the single-phase systems is higher and diminishes at the process of adsorption simultaneously two

components from solution. Generalization of got experimental results and calculation data were carried out.

- Because of effectiveness of this natural sorbent is expediently to apply this zeolite for cleaning of wastewater of meat-packing plants from the given contaminations.
- Taking into account the exhaustive supplies of natural zeolites the technique for synthesis of synthetic adsorbents has been proposed. Work on their application for cleaning of wastewaters is carried out.
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