V. Sabadash*, J. Gumnitsky, O. Lyuta, A. Hyvlyud

Lviv National Polytechnic University, Viacheslav Chornovil Institute of Sustainable Development, Department of Ecology and Sustainable Environmental Management, 79013, Lviv, Ukraine

* *virasabadash@gmail.com*

REGULARITIES OF ADSORPTION OF α -OXYPROPIONIC ACID BY NATURAL ZEOLITE

ABSTRACT

Wastewaters from dairy processing factories contaminated with α -oxypropionic acid were monitored. Theoretical analysis of industrial wastewater treatment methods on zeolites of Sokyrnytsia deposit was carried out. The process of sorption of α -oxypropionic (α -oxypropionic) acid by natural zeolite of Sokyrnytsia deposit was considered. It was established that the most economically advantageous and safe is the method of adsorption using a natural sorbent - zeolite, which provides the lowest concentration of contaminants in treated wastewaters from dairies. An assessment of their number, localization features and measures of toxicological impact on the environment was done. The existing theoretical apparatus of description of adsorption processes was analyzed. The sorption properties of natural zeolite (clinoptilolite of Sokyrnytsia deposit) and activated carbon to α -oxypropionic acid were tested. Equilibrium values of adsorption capacity were calculated and corresponding isotherms at a temperature of 20 °C were constructed. The porosity of the sorbent and its influence on the sorption properties were studied by the methods of physicochemical analysis. Infrared spectroscopic and electron microscopic studies confirmed the presence of the process of sorption by the surface of the internal pores of the zeolite of α -oxypropionic acid molecules. Experimental studies have confirmed the possibility of using natural zeolite for wastewater treatment of dairy factories. It was experimentally confirmed by physicochemical methods of analysis (electron microscopy, IR spectroscopy, microprobe analysis, mercury porosimetry) and was established that the process takes place both by the mechanism of ion exchange and physical adsorption. The content of carbon radicals in the zeolite matrix after the sorption process was confirmed by X-ray spectral microanalysis. The ability of zeolite to adsorb organic carboxylic acid radicals was confirmed by the results of IR spectroscopic studies. On the IR spectra there are strips of deformation and valence oscillations of the groups of the crystal lattice of the zeolite Si-O, Si-O-SiOH: 452, 990–1210, 1638, 3368 cm⁻¹. The oscillation spectra of free OH groups in the region of 2600 cm⁻¹ were revealed.

Keywords: *α -oxypropionic acid; wastewaters; adsorption; zeolite*

INTRODUCTION

A rather urgent problem in many countries is the issue of wastewater treatment of meat and dairy industries [1]. On the one hand, this is an internal problem of environmental protection of Ukraine, on the other - a necessary condition for the promotion of products of

food industry enterprises of Ukraine on the foreign market. The chemical composition of wastewater from dairy plants is quite heterogeneous [1, 2]. The need to develop new wastewater treatment technologies is also justified by the change in the nature and phase-dispersed state of pollution in the dairy wastewaters [3]. Over the past 10 years, there has been a change in the phase-dispersed composition of dairy wastewaters, associated with increasing demand for fermented milk products and declining production of pasteurized milk, therefore, the concentration of undissolved organic particles compared to dissolved compounds increased [4]. According to the literature, this greatly complicates the choice of an effective method of wastewater treatment. It is known that wastewaters from the dairy industry belong to the highly concentrated microbiological contaminants that can be treated using biological methods [5]. Analysis of the state of wastewater treatment in the dairy industry and numerous literature sources shows that the technical solutions used in our country for wastewater treatment do not provide effective removal of biological contaminants to the required maximum allowable concentration for discharge into the reservoir [1, 5]. Such waters, discharged without proper treatment into natural reservoirs, can lead to their eutrophication. In addition, organic acids (especially α -oxypropionic), formed during the fermentation of milk and other fermented milk products, acidify wastewater to a pH of about 3 [6]. It is known that the effluents of dairy enterprises have COD 900–9004 mg/l, BOD 480–6090 mg/l, total nitrogen (TN) 8–230 mg/l and suspended solid (SS) 134–804 mg/l, which complicates the choice of an effective mode of wastewater treatment [7]. This is due to the interaction during the oxidation of organic components with dissolved oxygen.

Since the composition and pH of wastewater in the dairy industry changes greatly, there is a need to use a set of methods for industrial wastewater treatment [6]. It is mentioned in the literature that mechanical, biological, chemical and physicochemical methods are widely used for wastewater treatment in the dairy industry [8]. For this purpose, in particular, methods of coagulation, adsorption [9] and membrane separation are used [7, 9]. The need to find and develop new technologies for wastewater treatment of dairies is justified by the low efficiency of existing treatment facilities [10]. The usage of classical biological treatment technologies is characterized by the presence of recirculation flows and is associated with relatively high energy costs for wastewater treatment and the formation of a significant amount of excess biomass. The need to stabilize of the formed sediments requires additional costs [3].

Adsorption methods are widely used for wastewater treatment [11]. The efficiency of this process is ensured by the correct selection of the sorbent. Typically, hydrophilic sorbents are used to remove polar compounds. Organic compounds are effectively adsorbed by carbon and polymeric adsorbents [12]. Perspective adsorbents are polymer nanocomposites [13, 14]. Natural and synthetic zeolites are used to remove toxic substances from wastewater. The efficiency of ion sorption depends on many factors, including external and intradiffusion transfer. With increasing concentration, the process of adsorption begins to predominate. It is known that zeolites have the ability to adsorb ions not only by the mechanism of physical adsorption, but also by the mechanism of ion exchange and manifest themselves as ion exchangers. The literature describes the sorption processes, gives the isotherms of adsorption of various substances on zeolites and other aluminosilicates [15, 16]. In our previous works, we reported that α -oxypropionic acid is well adsorbed by zeolite [17]. It was found that the use of natural zeolite from Sokyrnytsia deposit for adsorption of oxypropionic acid from wastewaters of dairy plants are very effective. The adsorption properties of natural zeolites and activated carbon were compared [18]. Studies have shown that activated carbon adsorbs lactic acid better than zeolite. It was found that the sorption capacity of the zeolite relative to α -oxypropionic acid was 2.5 mg-eq/g.

Preliminary studies of the sorption process of α -oxypropionic acid by natural zeolite, conducted in an apparatus with a propeller-type stirrer, have shown that the adsorption efficiency was affected by the intensity of mixing [19]. The maximum intensification of the adsorption process corresponded to the internal diffusion region. It was found that the coefficient of internal diffusion of α -oxypropionic acid in the zeolite was $D_{ef} = 2.62 \cdot 10^{-12} \text{ m}^2/\text{s}$. But the mechanism of the process needs to be studied in more details [20]. The aim of the work is to study the structure of natural zeolite of Sokyrnytsia deposit after adsorption of α -oxypropionic acid and the possibility of its usage as an adsorbent for wastewater treatment of dairy factories.

EXPERIMENTAL

Chemicals

α -oxypropionic acid 80% ISO 4621:2006, model solution of α -oxypropionic acid with a concentration of $C_0=0.002 \text{ mg/dm}^3$, 1,2-dichloroethane and chloroform were used to extract the polylactide, zeolite of the Sokyrnytsia deposit (CNP, diameter 2-3 mm), TC U 14.5-00292540.001-2001 is characterized by the following chemical composition: SiO_2 71.5 %, Al_2O_3 13.1 %, Fe_2O_3 0.9 %, TiO_2 0.5 %, CaO 3.44 %, MgO 0.68%, P_2O_5 0.014 %, $\text{K}_2\text{O} + \text{Na}_2\text{O}$ 3.03 %, F 0.025 %, As 0.0015 %, Pb 0.002 %, Cu 0.02 %.

The content of trace elements in the zeolite: Mn-242 g/t, Zn-45 g/t, Ga-20 g/t, Th-12 g/t, Rb-110 g/t, Y-22 g/t, Zr-235 g/t, Nb-22 g/t, Ba-232 g/t, Ce-52 g/t.

Instrumentation

To study the morphology of the zeolite surface and microprobe X-ray spectral analysis was used the Nova 200 NanoSEM scanning electronic microscope. The chemical and oxide composition of the material was determined by X-ray spectrometer ARL 9800 XP. Spectrometric studies were performed using a SPECORD-75 IR spectrophotometer. The porosity of the material was determined using an instrument Autopore 9500 IV (mercury porometer) in the pressure range of mercury 0.036 - 413 MPa, which allows you to determine the radius of the pores in the range of 0.0015 - 47 μm .

The samples of natural zeolite and α -oxypropionic acid - loaded zeolite were taken for the analysis.

Methodology

Method for determining the adsorption capacity of sorbents relative to lactic acid under mechanical mixing.

Experimental researches of α -oxypropionic acid adsorption were performed under dynamic conditions. To study the adsorption capacity of sorbents relative to lactic acid under conditions of mechanical stirring. The study was performed in an apparatus with a propeller-type stirrer, the speed of which varied in the range of 200-800 rpm. A model solution with a concentration of $C_0=0.002 \text{ mg/dm}^3$ and a previously determined optimal amount of sorbent 50 g per 1 dm^3 of solution were prepared for experiments. The kinetics of the process was studied under conditions of mixing a solution of lactic acid (8) with zeolite (9) at different speeds.

To prepare the model solution of lactic acid (8) was weighed on analytical scales 3.375 g of lactic acid, which was dissolved in 5 liters of distilled water. In the experiment a porcelain container with a capacity of 2 liters was used. At the beginning of the experiment, 0.5 l of lactic acid solution was added to the container. After turning on the stirrer with the appropriate speed we dropped 50 g of zeolite in container with solution and recorded the start time of the experiment.

On the propeller-type stirrer set (1) the number of revolutions, then under the propeller stirrer (4), which is fixed by a tripod (5) put a container with the prepared solution (3) and included the device (2). Samples were taken at regular intervals and analyzed for the content in the solution of oxypropionic acid. After 1 min, 3 min, 5 min, 7 min, 10 min, 15 min, 30 min, samples of the solution were taken from the tubes. The experiment was performed for the following stirrer speeds: 200, 300, 400, 500, 600, 700 and 800 rpm. The concentration of α -oxypropionic acid was determined by permanganatometric method, pH - using an ionomer IM-160. The experimental setup is shown in Fig.1

Fig. 1. Experimental installation for the adsorption process in dynamic conditions:
1 - digital stirrer controller; 2 - stirrer motor; 3 - container with a solution of lactic acid and zeolite;
4 - propeller stirrer; 5 - tripod; 6 – model solution; 7 – zeolite

RESULTS

The results of experimental studies of the kinetics of adsorption of α -oxypropionic acid are presented in Fig. 2.

The maximum intensification of the sorption process corresponds to the conditions of the process transition to the intradiffusion region. Increasing the number of revolutions above 600 rpm does not lead to a significant increase in the rate of adsorption of α -oxypropionic acid. This means that the adsorption process takes place in the intradiffusion region, in which external influences do not affect the sorption kinetics.

It is obvious that the purely external diffusion process takes place only in the initial time intervals, when the concentration of α -oxypropionic acid on the surface of the adsorbent is equal to zero, and in solution - equal to the initial one. Mass transfer during adsorption, regardless of the conditions of contact of the adsorbent with the adsorbed substance, consists

of the following stages: external transfer of sorbed substance molecules from the flow to the particle surface (mass transfer), internal diffusion of substance molecules from the surface to the middle of the grain through pores of different profile (mass conductivity) and stages of establishing adsorption equilibrium.

Fig. 2. The kinetics of sorption of α -oxypropionic acid
1 – 300 rpm, 2 – 400 rpm, 3 – 500 rpm, 4 – 600 rpm, 5 – 700 rpm, 6 – 800 rpm

Using experimental data we determined the effective coefficient of internal diffusion of α -oxypropionic acid in the zeolite $D_{\text{ef}} = 5.85 \cdot 10^{-9} \text{ m}^2/\text{s}$.

Equilibrium during adsorption is established almost instantly. Therefore, the total rate of mass transfer during adsorption depends on the rates of external and internal mass transfer and is limited by the slowest of these stages. For technological calculations, it is important to set a limiting stage and quantify it. Mass transfer during adsorption from solutions is the process of transferring a substance from the volume of the solution towards the outer surface of the particle, associated with the uneven distribution of the concentration of the substance in the liquid layer adjacent to the solid surface (boundary diffusion layer). The mechanism of external mass transfer of substance is associated with molecular and convective transfer [7]. Analysis of the intradiffusion stage of the sorption process of α -oxypropionic acid by natural zeolite.

The mechanism of adsorption of α -oxypropionic acid consists of two main stages:

- 1) diffusion of α -oxypropionic acid ions from solution to the surface of the adsorbent;
- 2) internal diffusion of α -oxypropionic acid ions in the sorbent grain.

The stage of the ion exchange reaction occurs very quickly, so only diffusion processes can be limiting: external or internal diffusion.

The external diffusion process (stage 1) depends on the hydrodynamic conditions. In the case of intense mixing, which took place in our experiments, the external diffusion resistance

is much lower than the intra-diffusion resistance, so the kinetics of the process is limited by stage 2 and mathematically described by differential equations of molecular diffusion in capillary-porous bodies, taking the form of adsorbent granules, the differential equation of molecular diffusion has the form:

$$\frac{\partial C_\alpha}{\partial t} = D^* \left(\frac{\partial^2 C_\alpha}{\partial r^2} + \frac{2}{r} \frac{\partial C_\alpha}{\partial r} \right) \quad (1)$$

where C_α — bulk concentration of $C_3H_6O_3$ inside the zeolite grain, kg / m³;

r — running radius of the grain, m;

t — time, s;

D^* — internal diffusion coefficient, m²/s.

Intensive mixing of the solution and transfer of the process to the intra-diffusion stage means that the concentrations of $C_3H_6O_3$ in the solution and on the outer surface of the zeolite grains are the same, and the number of $Bi = \infty$.

$$Bi = \frac{\beta \cdot d}{D^*} \quad (2)$$

In equation (1) C_α is the current concentration of $C_3H_6O_3$ on the radius r of the zeolite grain ($0 < r < R$, R is the radius of the grain) [27]. Experimentally, it is determined not by the running concentration on the running radius r , but by its average value, which is determined by the dependence:

$$\overline{C_\alpha} = \frac{3}{R^3} \int_0^R r^2 \cdot C_\alpha \cdot d \cdot r, \quad (3)$$

where R is the radius of the zeolite grain, m.

The relationship between the concentration of $C_3H_6O_3$ in solution and the average C_α concentration in the grains of the adsorbent is determined from the equation of material balance:

$$V(C_{10} - C_1) = m \cdot \rho \cdot C_\alpha, \quad (4)$$

where C_{10} — the initial concentration of the solution, kg / m³; C_1 — running concentration of the solution, kg / m³; m — the mass of zeolite, kg; ρ — the density of the zeolite; V — volume of solution, m³.

The problem is supplemented by initial and boundary conditions and a condition of symmetry of distribution of concentration on zeolite grain. Using dimensionless parameters:

$\varphi = \frac{r}{R}$; $Fo = \frac{D \cdot t}{R^2}$ — Fourier number, the problem can be written as:

$$\frac{\partial C_\alpha}{\partial Fo} = \frac{\partial^2 C_\alpha}{\partial \varphi^2} + \frac{2}{\varphi} \frac{\partial C_\alpha}{\partial \varphi} \quad (5)$$

The average concentration of the component in the grain in dimensionless parameters:

$$\overline{C_\alpha} = 3 \int_0^1 \varphi^2 \cdot C_\alpha \cdot d \cdot \varphi \quad (6)$$

The equation of material balance in dimensionless parameters has the form:

$$\alpha \left(1 - \frac{C_1}{C_{10}} \right) = \frac{\overline{C_\alpha}}{C_{\alpha\infty}}$$

$$\left(\frac{\partial C_\alpha}{\partial \varphi} \right) = 0$$

Initial conditions:

$$\begin{aligned} \varphi &= 0 \\ \partial C_\alpha(\varphi, Fo) &= 0; \quad C_1(Fo = 0) = C_{10} \\ C_1(\varphi \geq 1, \tau) &= C_1 \end{aligned} \quad (7)$$

In the system (7):

$$\alpha = \frac{V \cdot \rho_{\text{ад}} \cdot C_{10}}{m \cdot C_{\alpha\infty}} = \frac{V \cdot C_{10}}{m \cdot \alpha_\infty^*}; \quad \alpha_\infty^* = 0,271 \cdot C_{10}$$

The solution of this model was performed by an operational method based on the Laplace transform. In the images, the system has a zero root and a set of roots, which are determined from the characteristic equation:

$$\operatorname{tg} \mu = \frac{3 \cdot \mu}{3 + \alpha \cdot \mu^2} \quad (8)$$

Taking into account the zero root and the set of roots, the general solution of the model, presented due to changes in the concentration in the liquid phase of its change in the conditions of the periodic sorption process, has the form:

$$\frac{C_1}{C_{10}} = 1 - \frac{1}{1 + \alpha} \left[1 - \sum_{n=1}^{\infty} A_n \exp(-\mu_n^2 \cdot Fo) \right] \quad (9)$$

where A_n is the coefficient determined according to the dependence:

$$A_n = \frac{6\alpha(\alpha + 1)}{9 + 9\alpha + \alpha^2 \mu_n^2} \quad (10)$$

For large values of the root μ_n and a large time, the value of the exponent goes to zero, so we can limit ourselves to the first root of the characteristic equation μ_1 (regular mode region), and equation (9) can be reduced to:

$$\frac{\frac{C_1}{C_{10}} + \frac{\alpha}{1 + \alpha}}{\frac{\alpha}{1 + \alpha}} = A_1 e^{-\mu_1^2 Fo} \quad (11)$$

which is in the semi-logarithmic coordinated system $\ln \left(\left(\frac{C_1}{C_{10}} + \frac{\alpha}{1 + \alpha} \right) / \frac{\alpha}{1 + \alpha} \right) = f(t)$ and

gives a straight line.

Fig. 3 shows the data relating to the adsorption of lactic acid on the zeolite at a speed of 600 l / min in the area corresponding to the internal diffusion regime. Slope of the line represents values:

$$\operatorname{tg} \mu = \mu^2 \frac{D^*}{R^2} \quad (12)$$

Fig. 3. Kinetics of α -oxypropionic acid sorption by zeolite at different speeds, where: ◆ - 300 rpm; ■ - 500 rpm; ▲ - 800 rpm

The following equations were obtained from the Fig. 3:

$$y_{300} = -6 \cdot 10^{-6} - 0,0062$$

The value of the coefficient of determination at 300 rpm $R^2 = 0,9594$.

$$y_{500} = -9 \cdot 10^{-6} - 0,0056$$

The value of the coefficient of determination at 500 rpm $R^2 = 0,998$.

$$y_{800} = -9 \cdot 10^{-6} - 0,0064$$

The value of the coefficient of determination at 800 rpm $R^2 = 0,9773$.

The value of internal diffusion effective coefficient of lactic acid in zeolite was $D^* = 2.62 \cdot 10^{-12} \text{ m}^2/\text{s}$.

From the above data we can see that for the initial concentration of oxypropionic acid $C_0 = 25 \text{ mg} / \text{dm}^3$, the nature of the kinetic curves is different, and with increasing mixing intensity is achieved a greater rate of adsorption. This is evidence that the process changes from externally diffusion, or mixed, to intradiffusion, in which the number Bio goes to ∞ . Moreover, its greatest intensity was observed in the initial moments of time, where external diffusion kinetics was predominated [27].

To find out the mechanism of α -oxypropionic acid sorption by zeolite, we studied sorbents before and after adsorption. Zeolite rocks of the Sokyrnytsia deposit of the Zakarpattia region are represented by clinoptilolite with inclusions of montmorillonite-hydromica tufoargillite, feldspar quartzite. The average rock density is $1740 - 1920 \text{ kg/m}^3$, porosity is $20.2 - 8.1\%$, water adsorption is $12 - 14\%$, compressive strength is $40 - 80 \text{ MPa}$.

According to chemical analysis, the oxide composition of the zeolite is, wt. %: SiO_2 – 69.27; Al_2O_3 – 12.33; Fe_2O_3 – 1.4; CaO – 2.31; K_2O – 3.11; Na_2O – 2.18. Losses on calcination – 8.48%, the content of free quartz – 6 %. X-ray phase analysis in zeolite rock revealed diffraction maxima of clinoptilolite with $d/n = 0.898$; 0.395 and 0.296 nm and quartz with $d/n = 0.425$; 0.333; 0.228 nm. Zeolite has a porous structure with a clear spatial orientation. The composition of such aluminosilicate structures is expressed by the general formula $(\text{Na}, \text{K}, \text{Ca})_{2-3}\text{Al}_3 (\text{Al}, \text{Si})_{2\text{Si}_{13}\text{O}} \cdot 12\text{H}_2\text{O}$. Clinoptilolite crystals have a plastic habit, although it belongs to the frame aluminosilicates, ie. its structure is three-dimensional with a rigid system of channels and windows. This discrepancy between the shape of the crystals and the structure of clinoptilolite is due to the heterogeneity of chemical bonds in certain crystallographic directions, which leads to the formation of weakly bound alumina layers in its structure and manifests itself in the form of lamellar crystals.

Zeolite from a crystal chemical point of view is a silicon- and aluminum-containing spatial structure with a certain porosity and is characterized by a corresponding pore size. Since the clinoptilolite lattice (Fig. 4) has a negative charge, hydrated ions Na^+ , K^+ , Ca^{2+} , Mg^{2+} , which can participate in ion exchange processes, occupy places in the pores, which is an important factor in adsorption processes.

In this case, these hydrated ions occupy certain places in the structure, which creates micropores of appropriate size and spatial orientation, namely:

- I - Na- and Ca-ions are localized in a 10-fold ring of 0.44 x 0.72 nm;
- II - Na- and Ca-ions are localized in an 8-fold structural ring with a size of 0.41 x 0.47 nm;
- III - K-ions are localized in an 8-fold vertical structural ring with a size of 0.40 x 0.55 nm;
- IV - Mg-ions are localized in a 10-fold structural ring and are located in the center of the channel.

By the method of scanning electronic microscopy (Fig. 4a) it was found that the structure of the zeolite is represented by deformed plate crystals with a size of 1–5 μm with pores of various sizes and configurations. On the surface of the pores treated with α -oxypropionic acid zeolite (Fig. 4b) were revealed amorphous globules 0.01 – 0.1 μm in size, which confirms its high adsorption capacity [7].

Fig. 4. Microstructure of zeolite before (a) and after adsorption (b) of α -oxypropionic acid (x1000)

The conducted X-ray spectral microanalysis (Fig. 4) confirmed the results of microscopic studies and chemical analysis of the zeolite.

For research was used zeolite of the clinoptilolite type of the Sokyrnytsia deposit and model solutions of α -oxypropionic acid. The process of sorption of α -oxypropionic acid by zeolite was carried out in an apparatus with a propeller-type stirrer in the range of 300 – 800 rpm. The initial concentration of α -oxypropionic acid was 25 mg/dm³. The sorption capacity of the zeolite was determined by changing its porosity during processing. After adsorption, the sorbent was dried at a temperature of 100-240 °C. 1,2-dichloroethane and chloroform were used to extract the polylactide. During the adsorption of α -oxypropionic acid on zeolite and activated carbon, a decrease in the acidity of the solutions was observed. This indicates that in the process of α -oxypropionic acid adsorption is adsorbed not only the carbon radical, but mainly the hydrogen proton, which is formed during the dissociation of the acid. If we consider the process of adsorption of α -oxypropionic acid on zeolite, it may be fair to say that the proton can be sorbed by the mechanism of ion exchange, as a result of which exchange cations enter the solution. Active Brønsted acid sites are involved in this process.

The process takes place according to the following scheme:

Table 1. Sorbent characteristics

Zeolite	The inner-space surface area of the pores, m ² /g	Specific surface area, m ² /g	The average pore radius, μm	Density, g/cm ³	Porosity, %
Natural zeolite	0.1842	14	0.027	1.534	28.2
α -oxypropionic acid – loaded zeolite	0.1599	14	0.023	1.604	25.6

The presence of adsorbed α -oxypropionic acid on the surface of the zeolite pores was confirmed by the results of IR spectroscopic researches (Fig. 5). The spectra contain adsorption strips in the region 452, 990 - 1210, 1638, 3368 cm⁻¹, which belong to the deformation and valence vibrations of Si-O, Si-O-Si and OH groups of the zeolite, as well as oscillations in the region 2600 cm⁻¹ free OH groups. The presence on the IR spectrum (Fig. 5) of the loaded zeolite additional adsorptions in the range of 1700 - 1720 cm⁻¹, which can be attributed to fluctuations of acid groups C = O, indicates the presence in the structure of the zeolite α -oxypropionic acid [8]. We performed quantum mechanical calculations for the zeolite- α -oxypropionic acid adsorption system. Quantum chemical calculation of the properties of the α -oxypropionic acid was carried out in the software environment ChemOffice, Chem3D. The aim of the study was to calculate the parameters of molecules by which we can predict the probability of adsorption of the α -oxypropionic acid on the outer or inner (pore) surface of the sorbent and to establish the limiting stage of the adsorption process. The values of charges on individual atoms were calculated. The effective charges on the oxygen atoms of the studied compounds range from -0.406 to -0.217.

The values of effective charges in the molecule range from -0.072 to -0.276. The charge of the O8 atom of the carboxyl group is -0.39, and that of the oxygen atom of the hydroxyl

group of O4 is -0.35. Charges of carbon atoms: methyl group C1 – 0.035 and carboxyl - C3 0.31. Dipole moments in the molecule of α -oxypropionic acid range from – 0.356 D to 1.355 D, magnitude – 1.402 D. Therefore, this compound is polar [9, 10]. Thus, due to the polarity of the molecule, α -oxypropionic acid can be adsorbed by hydrophilic and hydrophobic sorbents.

The bond lengths, the degree measure of the angles between the atoms in the molecule and the dihedral angles of the α -oxypropionic acid were calculated. The largest linear size of the molecule is 1.46 nm, the smallest – 0.89 nm. According to the calculated size of the α -oxypropionic acid molecule, this compound can be adsorbed in the pores of the sorbent with the smallest pore cross section of 1.46 nm, as well as on the outer surface of the sorbent.

Fig. 5. IR adsorption spectra of zeolite: a - natural zeolite; b - α -oxypropionic acid – loaded zeolite

So on the IR spectrum of the zeolite after adsorption of carboxylic acid, additional adsorptions in the range of 1700 - 1720 cm^{-1} were detected, which are characteristic for the carbonyl group $\text{C}=\text{O}$ and valence oscillations of the ether group $\text{C}-\text{O}-\text{C}$ in the range 1219 cm^{-1} . Therefore, α -oxypropionic acid radicals are present in the crystal structure of the zeolite.

Further tasks for the study will be to find ways to complex purification from raw lactide and to develop the technology of regeneration and disposal of waste of polylactide production.

DISCUSSION

This paper analyzes the problems of wastewater treatment of dairy enterprises and existing wastewater treatment technologies used in this field [1, 2, 3]. We found that the application of the adsorption method allows to remove trace amounts of α -oxypropionic acid. This effect can also be achieved by the membrane method, but it is more energy-intensive than the adsorption process [4, 5]. In fact, the production of polylactide will allow to obtain polymeric materials capable to biological destruction [21, 22]. Currently, polylactide is synthesized by homogeneous catalysis, which has certain disadvantages [23, 24]. It is also known that the adsorption of most compounds is not affected by the high acidity of the solutions [7, 8]. In the literature it is indicated that the modification of the sorbent can provide effective extraction of α -oxypropionic acid [7, 8, 13, 14, 15]. It is established that adsorption is a very effective method, because in biological wastewater treatment there are following problems: energy consumption of production, the need to use resistant strains of microorganisms ect. [7]. A significant disadvantage of the biological method is the creation of biomass, which also requires disposal and the need to comply with the temperature regime. The authors believe that this problem can be solved by using several strains that are stable in certain pH ranges. But it is known that the acidity of such wastewater and their chemical composition can differ by two orders of magnitude [7, 8]. Another significant disadvantage is the duration of processes and the complexity of their automation. The cavitation method is proposed as an option for wastewater disinfection [25]. But the cavitation method also does not solve the problem of reducing the aggressiveness of the environment, BOD and COD. The issue of reducing the microbial count under the action of cavitation is also debatable. The authors [15, 16] indicate the selectivity of zeolites for organic acids. There are data in the literature on the use of adsorption methods for wastewater treatment of dairy enterprises [9, 12]. But in these works the peculiarities of the adsorption mechanism are not considered. However, we determined by the method of IR spectroscopy the presence of zeolite not only organic radicals, but also the ether group C-O-C in the range 1219 cm^{-1} . Thus, it is proved that the lactic acid radical is adsorbed by the sorbent. We also extracted low molecular weight polylactide. The probability of formation of polylactide on zeolites is confirmed in catalysis works, where there is information on the production of polylactide using zeolites [26].

CONCLUSIONS

The structural features of the natural zeolite of the Sokyrnytsia deposit of the Zakarpattia region were determined by the methods of physical and chemical analysis. The nature of zeolite pores and their sizes have been established, which gives foundations to use it for wastewater treatment of dairy processing factories due to adsorption of α -oxypropionic acid. Infrared spectroscopy revealed the introduction of an ether group and hydrocarbon radicals into the pores of the zeolite, which indicates the possibility of the zeolite to adsorb the organic anion of the acid. The studied mechanism of adsorption can be cancelled for the synthesis of polylactic - a thermoplastic polymer capable to biodegradation.

REFERENCES

1. Karadag D., Koroğlu O. E., Ozkaya B., Cakmakci M.: A review on anaerobic biofilm reactors for the treatment of dairy industry wastewater. *Process Biochemistry*. 50.2 (2015) 262-271.
2. Iervolino G., Zammit I., Vaiano V., Rizzo L.: Limitations and prospects for wastewater treatment by UV and visible-light-active heterogeneous photocatalysis: a critical review. *Topics in Current Chemistry*. 378(1) (2020). 7.
3. Chezeau B., Boudriche L., Vial C., Boudjemaa A.: Treatment of dairy wastewater by electrocoagulation process: Advantages of combined iron/aluminum electrodes. *Separation Science and Technology*. 55(14) (2020) 2510-2527.
4. Trujillo-Rodríguez M. J., Pacheco-Fernández I., Taima-Mancera I., Díaz J. H. A., Pino V.: Evolution and current advances in sorbent-based microextraction configurations. *Journal of Chromatography A*. (2020). 461670.
5. Garcia-Rodríguez A., Matamoros V., Fontàs C., Salvad, V.: The ability of biologically based wastewater treatment systems to remove emerging organic contaminants—a review. *Environmental Science and Pollution Research*. 21(20) (2014) 11708-11728.
6. Kolev Slavov A.: General characteristics and treatment possibilities of dairy wastewater—a review. *Food Technology and Biotechnology*. 55(1) (2017) 14-28.
7. Farizoglu B., Uzuner S.: The investigation of dairy industry wastewater treatment in a biological high performance membrane system. *Biochemical Engineering Journal*. 57 (2011) 46-54.
8. Ahmad T., Aadil R. M., Ahmed, H. i in.: Treatment and utilization of dairy industrial waste: A review. *Trends in Food Science & Technology*. 88 (2019) 361-372.
9. Lohse M. S., Stassin T., Naudin G., Wuttke S., Ameloot R., De Vos D., Bein T.: Sequential pore wall modification in a covalent organic framework for application in α -oxypropionic acid adsorption. *Chemistry of Materials*. 28 (2016) 626-631.
10. Ogunleye O. O., Adeniyi A. G., Durowoju M. O.: Factorial design based optimisation of crevice corrosion for type 304 stainless steel in chloride solutions. *Advances in Materials Science*. 16(2) (2016) 5-20.
11. Sabadash V., Gumnitsky J., Lyuta O. Combined Adsorption of the Copper and Chromium Cations by Clinoptilolite of the Sokyrnytsya Deposit. *Journal of Ecological Engineering*. 21 (2020) 42-46.
12. Polupan Y., Bashcheko M., Rieznykova N., Priyma S.: Genetic resources of dairy and beef cattle breeding in Ukraine. *Zhivotnov'dni Nauki/Bulgarian Journal of Animal Husbandry*. 57 (2020) 3-12.
13. Kausar A., Ullah W., Muhammad B., Siddiq M.: Novel mechanically stable, heat resistant and nonflammable functionalized polystyrene/expanded graphite nanocomposites. *Advances in Materials Science*. 14 (2014) 61-74.
14. Ates A., Akgül G.: Modification of natural zeolite with NaOH for removal of manganese in drinking water. *Powder Technology*. 287 (2016) 285-291.
15. Li Y., Li L., Yu J.: Applications of zeolites in sustainable chemistry. *Chem*. 3 (2017) 928-949.
16. Sakalova H., Malovanyy M., Vasylynych T., Palamarchuk O., Semchuk J.: Treatment of effluents from ions of heavy metals as display of environmentally responsible activity of modern businessman. *Journal of Ecological Engineering*, 20 (2019) 167-176.

17. Sabadash V.V., Givlyud A.M., Gumnitsky Y.M.: Investigation of α -oxypropionic acid adsorption under dynamic conditions. *Scientific Bulletin of NLTU of Ukraine*. 26 (3) (2016) 333-338.
18. Sabadash V.V., Givlyud A.N., Gumnitsky Y.M.: Investigation of intradiffusion kinetics of α -oxypropionic acid sorption by natural zeolite. *Bulletin of Vinnytsia Polytechnic Institute*. (2) (2016) 9-14.
19. Hyvlud A., Sabadash V., Gumnitsky, J., Ripak, N.: Statics and kinetics of albumin adsorption by natural zeolite. *Chemistry & Chemical Technology*. 1 (13) (2019) 95-100.
20. Sabadash V. V., Givlyud A. M., Gumnitsky Y. M.: Investigation of α -oxypropionic acid adsorption under dynamic conditions. *Scientific Bulletin of NLTU of Ukraine*. 26 (3) (2016) 333-338.
21. Shi G., Guan Y., Liu G., Müller A.J., Wang D.: Segmental Dynamics Govern the Cold Crystallization of Poly (α -oxypropionic acid) in Nanoporous Alumina. *Macromolecules* 52 (2019) 6904-6912.
22. Zhang L., Theng D.S., Du Y., Xi S., Huang L., Gao F., Borgna A.: Selective conversion of α -oxypropionic acid to acrylic acid over alkali and alkaline-earth metal co-modified NaY zeolites. *Catalysis Science & Technology*. 7 (2017) 6101-6111.
23. Czekaj I., Sobuś N.: Cluster model DFT study of α -oxypropionic acid dehydration over Fe and Sn-BEA zeolite. *Current Chemistry Letters*. 8 (2019) 187-198.
24. Sobieszczyk S., Melaniuk M., Zieliński A.: Bioactive core material for porous load-bearing implants. *Advances in Materials Science*. 12(3) (2012) 25-36.
25. Gashchin O.R., Viten'ko T.N.: The combined effect of hydrodynamic cavitation, hydrogen peroxide, and silver ions on the *Escherichia coli* microorganisms. *Journal of Water Chemistry and Technology*. 33(4) (2011) 266.
26. Dusselier M., Van Wouwe P., Dewaele A., Jacobs P.A., Sels B.F. Shape-selective zeolite catalysis for bioplastics production. *Science*. 349(6243) (2015) 78-80.
27. Givlyud A., Sabadash V., Gumnitskij J. The kinetics of oxypropionic acid on natural zeolite. *Litteris et Artibus*. Lviv Polytechnic Publishing House. (2015) 450-451.