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ADSORPTION OF OXYPROPIONIC ACID BY SOKYRNYTSKE'S DEPOSIT CLINOPTILOLITE

The present article substantiates the theoretical bases lactic acid adsorption on mineral and carbon adsorbents. Monitoring of wastewater contaminated with wastes of dairy plants, estimation of quantities, peculiarities of wastes localization and estimation of toxicological impacts on the environment was carried out. The existing theoretical apparatus for adsorption processes description was analyzed. Adsorption process mechanism and methods for identification of experimental data in theoretical models was developed. Sorption capacity of zeolite to lactic acid in static conditions was experimentally investigated. Influence of acidity on equilibrium and speed of absorption of lactic acid was determined. Experimental data and theoretical models of adsorption were identified. Adsorption capasity of adsorbents was set. It has been established that carbon adsorbents are more selective to lactic acid then zeolites.

Key words: zeolite, activated carbon, lactic acid, wastewater, external diffusion.

Обґрунтовано теоретичні основи адсорбції оксіпропіонової (молочної) кислоти на мінеральних і вуглецевих адсорбентах. Проведено моніторинг стічних вод, забруднених відходами молокозаводів, здійснено оцінку обсягів, особливостей локалізації відходів та оцінку токсикологічних впливів на навколишнє середовище. Проаналізовано теоретичний апарат , що використовується для опису процесів адсорбції. Встановлено механізм адсорбції та розроблено методи для ідентифікації експериментальних даних у теоретичних моделях процесу. Експериментально досліджено сорбційну ємність цеоліту щодо оксіпропіонової кислоти в статичних умовах. Вивчено вплив кислотності на рівновагу і швидкість поглинання молочної кислоти. Зіставлено експериментальні дані та теоретичні моделі адсорбції. Встановлено адсорбційну ємність адсорбентів. Встановлено, що вуглецеві адсорбенти більш споріднені щодо молочної кислоти, ніж цеоліти.

Ключові слова: цеоліт, активоване вугілля, молочна кислота, стічні води, зовнішня дифузія .

The statement of the problem and its relationship to important scientific and practical tasks. Dairy industries wastewater highly concentrated by the contents of microbiological contaminants can be cleaned using biological methods. Such water discharged without proper cleaning into natural water resources can lead to eutrophication. This is due to the interaction of organic components with dissolved oxygenduring the oxidation. In addition , organic acids (mainly lactic), resulting from the souring milk and other dairy products, acidified wastewater to pH about 3. During the production of dairy production large quantities of serum. COD of whey and waste water is respectively about 70,000 and 3,000 mg / l. The technology of adsorption treatment of wastewater milk processing plants allows to solve the problem of reducing the aggressiveness of the environment, has low power consumption and can be implemented in a wide range of changes in the composition of wastewater.

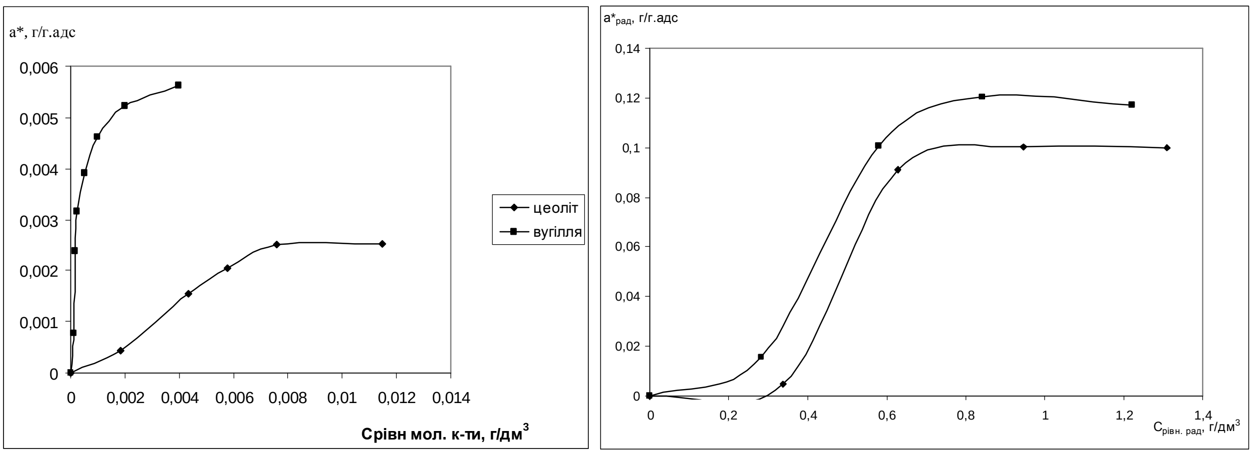
The Purpose. The aim of the work was the theoretical substantiation and experimental study of natural clinoptilolite and activated carbon for effluent milk processing plants from lactic acid, adsorption technology development of wastewater from lactic acid, which in turn ensures the environmental safety of water resources.

Analysis of recent research and publications. Recycling of waste water is a major problem for dairy factories. The constant growth of production necessitates finding the newest, economically viable and energy efficient way of wastewater treatment [1,2]. As you know, dairy industry wastewater highly concentrated to the contents of microbiological contaminants can be cleaned using biological methods. Analysis of dairy industry wastewater treatment and numerous literature suggests that technical solutions applied in our country for wastewater treatment do not effectively remove biological contaminants to a maximum allowable concentration value for discharge into the reservoir. Such water discharged without proper cleaning to natural resources of water can lead to eutrophication. This is due to the interaction of organic components with dissolved oxygen . In addition, organic acids (including dairy), resulting from the souring milk and other dairy products , acidified wastewater to pH nearly 3.

To demonstrate the amount of damage that can be caused discharge of serum into the water this comparison: 1 $m^3$of serum pollutes pond so as it can polluted by 100 m^3 of domestic wastewater can be given. To reduce emissions of dairy processing enterprises in the process should be provided measures to reduce the loss of raw materials and production: collection and utilization of serum (through its thickening, drying, convertion into milk sugar or sale as feed) and the implementation of a closed water system and regeneration of the washing solutions [1].

Determination method. To determine the adsorption capacity of zeolite in accordance to oxypropionic acid 200 cm^3 of solution prepared in distilled water at different initial concentrations (C = 4 – 30 mg/ dm^3), and added the same sorbent sample (~ 1 g) in glass flasks were placed. The range of concentrations corresponded oksipropionovoyi acid content in wastewater dairies. Flasks sealed and left with periodic stirring for two days at a temperature of +20 ° C. Sorbent was separated from the solution , which was analyzed for the content of H + ions and carbon radical. The concentration of lactic acid was determined by permanganate method pH - Using Ionomers IM -160 and permanganate titration acid residue.

Experimental investigations. Experimental investigation of the adsorption of lactic acid was carried out in static conditions. The experimental data of lactic acid adsorption on activated carbon and zeolite of Sokyrnytske deposit are presented in Fig.1



a) *b)*

Fig. 1. Adsorption isotherms oxypropionic acid on clinoptilolite of Sokyrnytske deposit and activated coal a) adsorption of a proton acid, b) adsorption of carbon radical

As a result, studies have found that activated carbon adsorbs better lactic acid than zeolite. This is because the molecules of lactic acid have carbon radical, which exhibits affinity for non-polar sorbents, namely, the activated carbon [6]. On mineral sorbents, in particular clinoptilolite Sokyrnytske deposit adsorption with hydrophilic groups - OH and-COOH occurs. This is confirmed by the increase of pH of tested solutions [7].Since the mass fraction of hydrophobic radical is significantly higher than the functional groups, sorption on activated carbon is better. It should be noted that in this experiment and *a*¥ - limiting adsorption radical is 0.0011 g-eq /g zeolite and 0.0013 g-equiv /g of activated carbon adsorption, compared to the maximum proton acid - 0.0025 g-eq/g zeolite and 0.0056 g-equiv/g of activated carbon.

The calculation of the equation monomolecular Langmuir adsorption.

The process of adsorption of lactic acid on natural zeolite is good enough obeys monomolecular Langmuir adsorption theory.

To calculate the marginal adsorption of lactic acid ($a_{¥}$) using linearized Langmuir equation;

$$\frac{C}{a*} = \frac{1}{a_{\infty} K} + \frac{C}{a_{\infty}} \qquad (4)$$

where $a_{¥}$- limiting adsorption (adsorption value at full saturation monolayer), K - constant of adsorption equilibrium.

From Fig. 2. implies that the adsorption isotherm of hydrogen ions in zeolites and activated carbon is described by Langmuir:

For zeolites: $$a* = 0{,}003 \frac{186{,}43C}{1+186{,}43C} \qquad (5),$$

For activated carbon: $$a* = 0{,}003 \frac{5333C}{1+5333C} \qquad (6).$$

The correlation coefficient of experimental and theoretical data R^2 is 0.89 ... 0.97, which indicates the reliability of experimental data. The results of the research can be said about matching the experimental isotherm Langmuir isotherm.

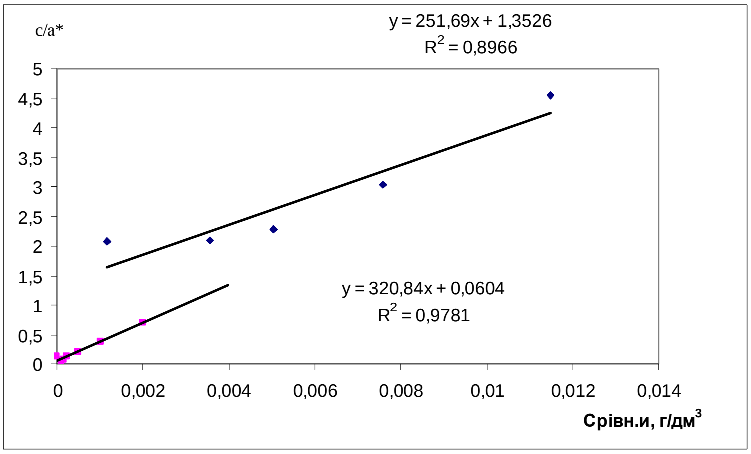


Fig. 2. Graphical determination of the coefficients of the Langmuir equation, where ■ - charcoal; ♦ - zeolite.

Experimental studies of changes in pH model wastewater after adsorption in static conditions. When lactic acid adsorption on activated carbon and zeolite decreased acidity of the solution . This suggests that during the adsorption of lactic acid is absorbed not only the carbon radical , but proton hydrogen , which is formed by dissociation of acid. If we consider the process of lactic acid adsorption on zeolite , may be just the statement that the proton can sorbate the mechanism of ion exchange , which resulted in the solution enters the exchange cautions. In this process involves active Brenstedovski centers.

$$CH_3 - CH(OH) - COOH \leftrightarrow$$
$$H^+ + CH_3 - CH(OH) - COO^- K_1 = 1{,}4 \cdot 10^{-4}$$
$$\text{C}L(Na) + H^+ + CH_3 - CH(OH) - COO^- \rightarrow$$
$$\text{C}L(H) + CH_3 - CH(OH) - COONa$$

When lactic acid adsorption on activated carbon, a decrease in pH due to the formation of the adsorption complex centers

$$Ads{-}C{=}O + H^+ \rightarrow Ads{-}C{-}OH$$

Analyzing the results of experimental studies presented in Fig. 1 and 3, it can be concluded that the adsorption capacity of sorbents on lactic acid correlated with a decrease in the acidity of model wastewater. Thus, the absorption of lactic acid zeolite and activated carbon is obviously the mechanism of physical adsorption.

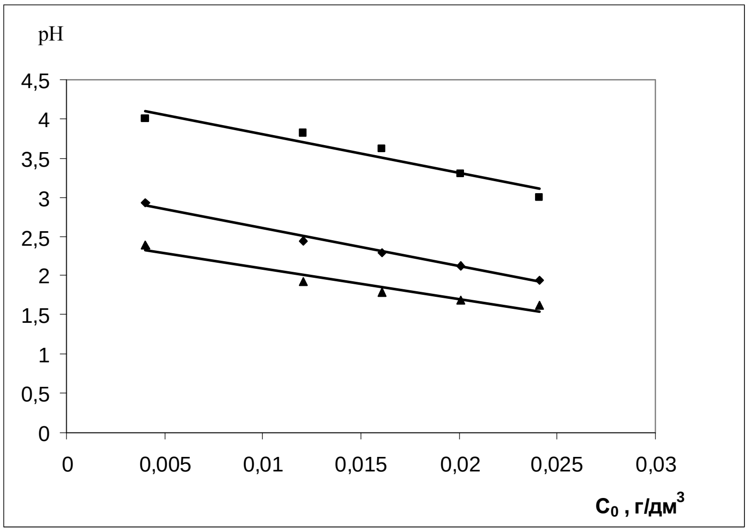


Fig. 3. Experimental studies of changes in pH model wastewater after adsorption in static conditions where ▲ - the initial pH of the wastewater; ■ - pH after adsorption on activated carbon; ♦ - pH after adsorption on clinoptilolite Sokyrnytske deposit

Conclusion. Retrieved sorption properties of natural zeolite and activated carbon on lactic acid. found that the use of natural zeolite deposits Sokyrnytske's and activated carbon as highly efficient sorbents are good for the treatment of industrial wastewater from dairy processors lactic acid as environmentally responsible and economically, given the low cost of the sorbent.

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