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FINAL-TREATMENT OF WASTEWATER FROM THE PRODUCTION OF EDIBLE OILS

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Abstract. The adsorption method of after-treatment of wastewater from the production of vegetable oils was investigated. The reasons of choice the activated carbon as adsorbent was justified. The statics and the kinetics of the adsorption process by activated carbon the organic component from the wastewater of oil production after extraction cleaning was investigated. The experimental data based on the theory of Freundlich and Langmuir were processed and the main constants of the process were defined.

Key words: wastewater, adsorption, activated carbon, isotherm, statics, kinetics.

Statement of the problem

Today the problem of wastewater treatment of the edible oil's production, along with the quality of the final product of production is an important task. It is also conditioned by the introduction of more modern and efficient technological processes, and the development of new approaches to the organization of non-waste or low-cost resource and energy-saving technologies. All this justifies a more serious attitude to the problems of the disposal of waste products [3, 4].

The production of edible oil's increases year by year in proportion to the demand, more and more enterprises of this profile emerge, thus the total amount of emissions including wastewater increasing. For Ukraine, the topic of wastewater from the production of oils is relevant because our country occupies the first place in the world ranking of growing sunflowers, consequently, the production of oil. As Ukraine is one of the major sunflower producers and their processors, the issue of wastewater treatment of the oil's production is very relevant today.

In the process of vegetable oil's production, a large amount of wastewater arises in the form of emulsions. Such systems are stable over a long period of time. They are not destroyed by the mechanical method [5, 6]. They are poorly biodegradable due to large volumes of wastewater and a significant amount of organic components in them [2–4]. In such circumstances, it is appropriate to use liquid extraction to clean such wastewater [1, 7]. The feasibility of using extraction for wastewater treatment is determined by the concentration of organic impurities in them. In the general case, for most substances, it can be assumed that at the concentrations of more than 3-4 g/l, it is more expedient to withdraw them by extraction than adsorption. At concentrations, less than 1 g/l the extraction should be used in special cases.

The absolutely insoluble liquids are absent in water, that's why in the process of extraction , the part of the extractant dissolves in wastewater and becomes a new pollutant. Therefore, it is necessary to remove the extractant from the conditionally purified water. This also needs to be done to reduce the consumption of the extractant. In addition, extraction cleaning is not always appropriate to achieve high purification efficiency. In these cases, the adsorption method of purification is used. The advantage of the method is the high efficiency, – and the possibility of purification of wastewater, which contains several substances and recovery from these substances.

The analysis of recent researches and publications

In most enterprises of oil production in Ukraine, industrial effluents cannot be purified and hundreds of tons of pollutants are dumped into water bodies. Treatment facilities, as a rule, have been built long ago and are designed according to the requirements of domestic wastewater treatment. Such facilities partially reduce the size of the general BOD (biochemical oxygen demand), or just pass through wastewater, and at worst case, rots in them and further poisoning before dumping into water bodies. Such industrial wastewater is mostly contaminated with organic substances, as the result treatment facilities are unable to clean them up to the level of sanitary requirements. Significant environmental hazards create pollution of surface water with organic substances from wastewater of edible oil's production. These substances, getting into the body of water, contribute to contamination with pathogens, algal bloom and, - have a negative impact on flora and fauna. For many companies, proper treatment of wastewater is a serious problem. Increasingly, companies have the problem of finding treatment facilities efficient and reliable in use, which guarantee a stable, high quality of cleaning.

The literature contains data about liquid-extraction wastewater treatment, which significantly reduces the level of pollution of wastewater from the vegetable oil's production, but there is always a certain amount of extractant. Therefore, to resolve the problem, it is advisable to use adsorption purification.

The aim of this work is to study the statics and kinetics of adsorption purification of wastewater at companies of vegetable oil's production.

Theoretical part

The adsorption method is used for the deep purification of wastewater from dissolved organic substances, as well as in local installations if the concentration of these substances in water is low or they are highly toxic. The most universal from adsorbents is activated carbon, but it must have certain properties.

The activated carbon, as a rule, poorly interacts with water molecules and well – with molecules of organic substances. It has a relatively coarse pore with an effective radius in the range of 0.8–5.0 mm, or 8–50 A, so its surface is available for large and complex organic molecules. With a small time of contact with wastewater, activated carbon has a large adsorptive capacity, high selectivity, and low containment during regeneration. Actually, the latter condition ensures limited costs for the adsorbent regeneration. Coal is mechanically strong, quickly getting wet with water, has a definite granulometric composition. In the process of purification, fine-grained adsorbents with particles of 0.25–0.5 mm in size and less highly dispersed coal with particles of 40 microns are used.

It is important that coal has a small catalytic activity in relation to oxidation, condensation, and other reactions, because some organic substances that are contained in wastewater tend to oxidizing and gumming. These processes are accelerated by catalysts. After gumming, the substances clog the pores of the adsorbent, which complicates its low-temperature regeneration. Finally, activated carbon has a low cost, and does not decrease its adsorption capacity after regeneration, which guarantees a large number of cycles of operation. The raw material for the manufacture of activated carbon can be any carbonaceous material: coal, wood, polymers, food waste and pulp and paper industries and others.

The adsorption capacity of activated carbon is a consequence of a highly developed surface and high porosity. If there are several components in wastewater, then for determining the possibility of their joint adsorption for each substance, find the values of the standard differential free energy ΔF° and determine the difference between the maximum and minimum values. Assuming $\Delta F^{\circ}_{max} - \Delta F^{\circ}_{min} < 0.5$ kJ / mole, the joint adsorption of all components is possible. If this condition is not respected, the treatment is carried out sequentially in several stages.

The rate of adsorption process depends on the concentration of the pollutant in wastewater, the nature and the structure of pollutants, the temperature of wastewater, the type, and properties of activated carbon. Usually, the adsorption process consists of three stages: the transfer of pollutants from wastewater to the surface of the adsorbent grains (external diffusion area), the adsorption process, the transfer of pollutants inside the grains of the adsorbent (the internal diffusion area). It is believed that the speed of adsorption is large and does not limit the overall speed of the process. Therefore, the limiting stage may be external or internal diffusion. In some cases, the process is limited by both these stages.

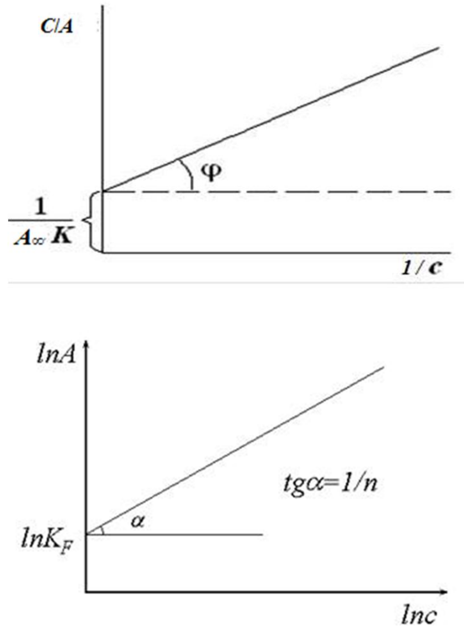

Fig. 1. Determination of Langmuir and Freundlich adsorption isotherms constants

In the external diffusion area, the rate of mass transfer is mainly determined by the turbulence intensity of the stream, which depends on the rate of wastewater. In the medium diffusion area, the intensity of the mass transfer depends on the type and the pores size of adsorbent, the shape and diameter of its grains, the size of the adsorbent molecules, and the mass transfer coefficient. All these circumstances determine the conditions in which adsorption treatment of wastewater goes with optimal speed. The process should be carried out in such hydrodynamic regimes, that it is limited in the internal diffusion area, the resistance of which can be reduced with changing the structure of the adsorbent and reducing the diameter of the grain.

Substances that are well adsorbed from aqueous solutions by activated carbons have a convex isotherm of adsorption, and poor adsorbing – concave. The isotherm of adsorption of substances in wastewater is determined by experimental methods [1, 8].

The most important stage in the process of adsorption purification is the regeneration of activated carbon. Biological methods of coal regeneration, in which the adsorbed substances are biochemically oxidized, are increasingly developed today. This method of regeneration significantly extends the use of the sorbent.

The methodology of research

To study the adsorption capacity of activated carbon for wastewater contaminants of vegetable oil's production, 200 cm^3 of wastewater after chemical purification (the destruction of stable emulsion "oil-water" by chemical substances) were placed in glass flasks, at different initial concentrations (C = 0.025–35 g/dm^3), and added the same amount of sorbent (~ 10g). The range of pollutants concentrations was the same as in industrial wastewater. The flasks were hermetically sealed and left in the mixing regime for two days at a temperature of + 20 °C. The sorbent was separated from the solution, which was analyzed for the content of pollutants by photocolorimetric method at a wavelength of 490 nm according to the known method [9].

The main material and discussion of the results

The adsorption method of extraction residual amount of the pollutant and the extractant was chosen for research. This method allows to removing of residual concentrations of pollutions. The activated carbon was selected as a sorbent. It has the ability to absorb pollutants of organic origin. In mixing the adsorbent with wastewater, activated carbon was used in the form of particles of 0.1 mm and less.

The adsorption of activated carbon in the form of the isotherm is shown on the graphic (Fig. 2). The isotherm describes the equilibrium between the pollutant in wastewater which must be treated and the amount of pollutant in the activated carbon.

The adsorption equilibrium in the solid adsorbent-solution system describes the equations that are given in the literature [1, 8]. We used two models that describe adsorption isotherms. One of the models is represented by the Freundlich equation:

$$A = kc^{1/n} :$$

where A is a value of adsorption, *mg /g·ads;* C – equilibrium concentration of adsorbed substance in wastewater, g/dm^3; k, n are constants.

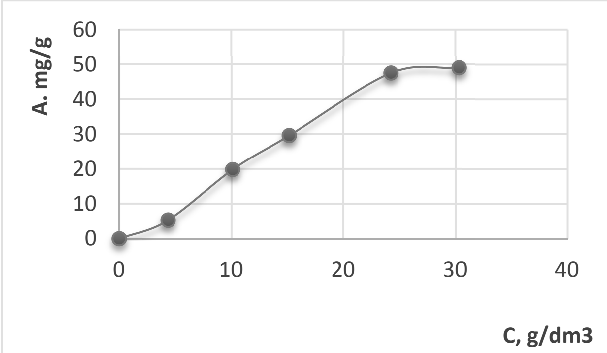

Fig. 2. The isotherm of adsorption wastewater pollutants in sunflower oil's production by activated carbon

To determine the constants of the Freundlich equation (*k, n*), the equation was given to the linear form by taking their logarithm:

$$\ln A = \ln k + 1/n \ln c;$$

From the graph built in the coordinates ln A = f (ln c), we find $tg\alpha = 1 / n$ and $\ln k$ as the distance which cuts the experimental straight line on the Y-axis. Experimental data in linear coordinates ln A = f (ln c) according to Freundlich equation are presented in Fig. 3.

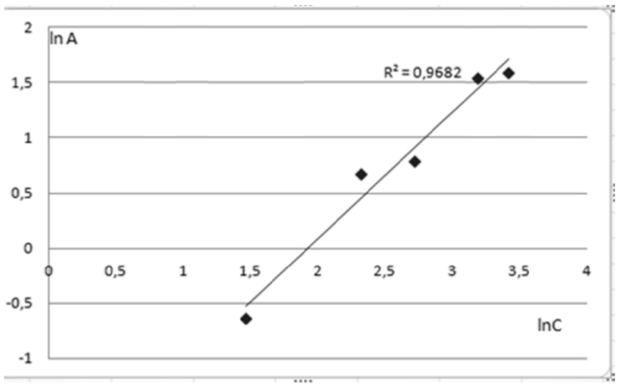

Fig. 3. The isotherm of adsorption in linear coordinates.

The experimental data on Fig. 3 represent a straight-line correlation and this indicates a satisfactory description of the isotherm of adsorption by the Freundlich equation. The correlation coefficient of experimental and theoretical data is 0.96, which indicating the reliability of experimental data.

The final form of the Freundlich equation for the adsorption process with using activated carbon:

$$A=1.045C^{1.1836};$$

However, we believe that there is sorption in the form of a monomolecular layer of adsorbate and this process is better described by the Langmuir equation. Therefore, we have analyzed the obtained isotherms of adsorption according to this theory.

$$A = A_{\infty}\frac{kC}{1+kC};$$

where A – is the static activity of the adsorbent which was determined, *mg/g·ads;* A_{∞}– the maximum possible value of adsorption (the value of adsorption at full saturation of the monolayer) k – the constant of adsorption equilibrium.

To calculate the limiting adsorption of the organic pollutant (A_∞) we use the linearity Langmuir equation [2, 3].

$$\frac{C}{A} = \frac{1}{A_\infty k} + \frac{1}{A_\infty C}:$$

where A_∞ - the static activity of the adsorbent, which determined:

$$A_\infty = \frac{C_{init.} - C_p}{m} V;$$

The graph in the coordinates C/A =f(1/C) was constructed and the angular coefficient of the slope of the line $k = \Delta C/\Delta(C/a^*)$, which is equal to the limit of the adsorption of was find.

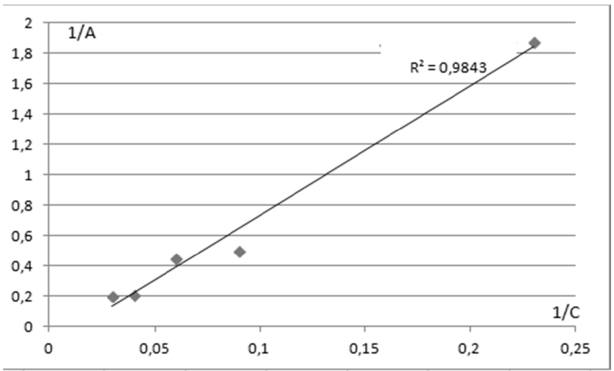

Fig. 4. The Langmuir isotherm of adsorption in linear coordinates

The isotherm of adsorption pollutants from wastewater of sunflower oil's production after chemical treatment (the destruction by chemical substances of a stable emulsion "oil-water"), by activated carbon is described by the Langmuir equation:

$$A = 49.1\frac{0.97C}{1+0.97C}$$

The correlation coefficient of the experimental and theoretical data R^2 is 0,96–0,98, which indicates a more reliable description of the experimental data by Langmuir isotherm. The selection criterion of the theoretical model was the maximum value of Fisher's criterion (F) and the maximum value of the determination coefficient.

To develop the technological process of sorption, it is necessary to determine the optimal contact time of the sorbent in the mixing reactor. The results of research about the kinetics of sorption by activated carbon are shown in Fig. 5/

The shape of the kinetic curves shows that the process of sorption most actively at the initial stage of the process, namely during the first hour of the experiment. The sharpest decrease of kinetic curves is observed after 30 minutes of the experiment, and from 30–60 minutes continue to fall. For 1 hour of sorption, the process is completed, as the linear origin of lines shows. Therefore, the optimal and most effective time for recovering the pollutants is 1 hour.

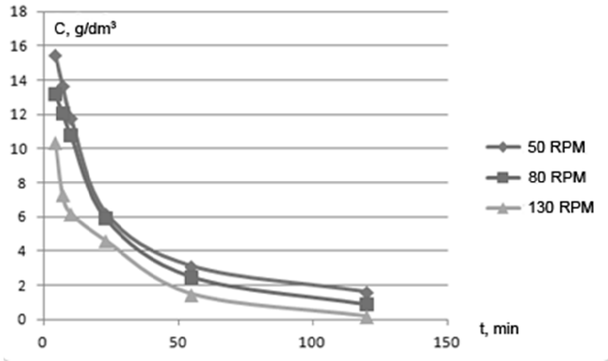

Fig. 5. Kinetics of absorption the pollutants from wastewater of vegetable oil's production.

As shown on Fig. 5, the kinetics of absorption the pollutant significantly depends on hydrodynamics. Intensification of the hydrodynamic conditions increases the absorption rate, which allows us to assert the external diffusion area of the sorption process.

Conclusion

The statics and kinetics of adsorption method of after-treatment of wastewater from the production of vegetable oil was studied. The study established that the experimental isotherm of adsorption is the best described by the Langmuir equation, and the process of adsorption proceeds by the external diffusion mechanism. In such circumstances, the degree of wastewater treatment corresponds to safe hygiene practices.

References

[1] Zapol`s`ky`j A. K., Kly`menko N. A., Astrelin I. M. ta in.: Fizy`ko-ximichni osnovy` texnologiyi ochy`shhennya stichny`x vod. Libra, Kyiv 2000, 552.

[2] Py`ly`penko A. T., Vaxny`n Y`. G., Goronovsky`j Y`. T. y` dr.: Kompleksnaya pererabotka my`neraly`zy`rovanny`x vod. Naukova dumka, Kyiv 1994, 284.

[3] Domarecz`ky`j V. A. Ostapchuk M. V., Ukrayinecz` A. I. za red. d-ra texnichny`x nauk, prof. A.I. Ukayincya: Texnologiya xarchovy`x produktiv. Pidruchny`k. NUXT, Kyiv, 2003, 572.

[4] Zapol`s`ky`j A. K. Ukrayinecz` A. V. Ekologizaciya xarchovy`x vy`robny`cztv. Vy`shha shkola, Kyiv, 2005, 423.

[5] Maraxovs`ka A. O., Visny`k NU "LP", 2013, 761, 297.

[6] Holodovs'ka O., Marakhovs'ka A., Dyachok V.: Pat. UA 111389, Publ. Oct. 11., 2016.

[7] Dyachok V., Marakhovska A., Marakhovska S., Chemistry & Chemical Technology, 2018, 12, 1, 114.

[8] Parfy`t G., Rochester K.: Adsorbcy`ya y`z rastvorov na poverxnostyax tverdy`x tel. My`r, Moskva, 1986, 488.

[9] Lur`e Yu. Yu. Analy`ty`cheskaya xy`my`ya promy`shlenny`x stochny`x vod. Xy`my`ya, Moskva, 1984, 447.