ENVIRONMENTAL PROBLEMS

Vol. 9, No. 4, 2024

APPLICATION OF LIQUID EXTRACTION FOR WASTEWATER TREATMENT

Vasyl Dyachok, Liubov Venher

Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013, Ukraine
liubov.o.venher@lpnu.ua

https://doi.org/10.23939/ep2024.04.213

Received: 22.09.2024

Abstract. This article presents the results of studies of the structure of the emulsion formed in the wastewater of edible oil production. The process of refining edible oils produces stable emulsions that are released into wastewater and pose a threat to the hydrosphere. The main pollutants in these wastewaters are organic substances, mainly of a fatty nature, which existing wastewater treatment plants are unable to treat to the level of sanitary requirements. This creates a significant environmental problem as it causes pollution of surface waters with organic substances. This paper presents the results of studies of the structure of the emulsion formed in the wastewater of edible oil production. The type of emulsifier was determined, and an effective reactive method of emulsion destruction based on the established composition was substantiated. The proposed method of emulsion destruction ensures high-quality wastewater treatment and does not lead to the formation of additional polutants. To achieve a given degree of purification, traditional diagrams have been constructed to determine the number of transfer units that will correspond to the corresponding value of the MPC of polutants. The proposed method of wastewater treatment of edible oil production enterprises makes it possible to solve the problems of reducing environmental pollution and can be implemented in a wide range of changes in the composition of wastewater.

Keywords: wastewater, emulsion, emulsifier, diffusion.

1. Introduction

The increase in the capacity of edible oil production enterprises at the current stage of development of the food industry leads to the generation of huge amounts of waste water, which forms the wastewater of the production process (Dyachok et al., 2016). The main pollutants in these wastewaters are organic substances, mainly of a fatty nature, which existing wastewater treatment plants are not able to treat to the level of sanitary requirements. This creates a significant environmental problem as it causes pollution of surface waters with organic substances. The main source of these pollutants is the wastewater from edible oil production. These pollutants cause the processes of decay, blooming of water, infection with pathogenic bacteria, and ultimately have a negative impact on fauna and flora (Holodovska et al., 2016; G Mazzola et al., 2008; Ali et al., 2015). For many companies in the industry, appropriate wastewater treatment is a serious problem. Our proposed method of wastewater treatment of edible oil production enterprises makes it possible to solve the problems of reducing environmental pollution and can be implemented in a wide range of changes in the composition of wastewater (Food Process Engineering and Technology, 2018; Lajoie et al., 2022).

The aim of the work is to find an effective way to eliminate pollutants from the wastewater of edible oil production enterprises. Based on the experimental results of the research, to propose an effective technology for eliminating the main pollutants.

2. Experimental part

Neutral fats, phospholipids, organic acids and other substances of organic origin are the main pollutants in the wastewater of edible oil production plants. These contaminants are insoluble in water and

For citation: Dyachok, V., Venher, L. (2024). Application of liquid extraction for wastewater treatment. *Journal Environmental Problems*, *9*(4), 213–217. DOI: https://doi.org/10.23939/ep2024.04.213

cause the formation of stable emulsions, which in turn contribute to the accumulation of a significant amount of mechanical contamination in the form of suspended solids. Many of the known treatment methods are ineffective, and some of them cause additional water pollution. The studied wastewater was a microheterogeneous system that can be qualified as an emulsion in which the dispersed phase and the dispersed medium are in a liquid state. Such systems can exist for a long time only if they are formed by liquids that do not dissolve in each other. In our case, the stability of such an emulsion is determined by the ratio of the phase densities. The density of the dispersion medium is close to the density of the dispersion phase, so such an emulsion is stable in terms of sedimentation. This has been confirmed experimentally, the emulsion remains for a long time not only in the field of gravity, when standing, but also in the field of centrifugal forces. Centrifugation at 3000 rpm. For 20 minutes, the desired results were not achieved, which indicates the ineffectiveness of mechanical methods of wastewater treatment with such properties.

As a result of experimental studies using the methylene blue dye and subsequent microscopy, it was found that these are emulsions of the first type, since colorless balls were observed on a blue background, which should be identified as oils. Such emulsions are also called straight emulsions, namely oil-in-water emulsions, where a non-polar or weakly polar dispersed phase is in a strongly polar dispersion medium. According to another classification, this is a concentrated emulsion, since the dispersed phase occupies more than 0.1 % of the total volume of the emulsion (Fedushchak et al., 2012).

It is important to determine which surfactants in the water under study can act as emulsifiers. It is known from the literature that phospholipids are related substances of edible oils. They form the membranes of the fatty reservoirs on the seeds (Food Process Engineering and Technology, 2018). Phospholipids, which are an integral part of all cells and form cell membranes (liver cell membranes consist of 65 %, in seeds – 0.25–2.0 %) (Walker et al., 2013) are also contained in oil, and their amount in oil varies depending on the amount of anthropogenic impact on seeds: the more intense the technological impact on seeds, the more phospholipids get into the oil. The higher the phospholipid content in oils, the higher it is in wastewater, which complicates the process of wastewater treatment.

We conducted chromatographic studies, namely thin-layer ascending chromatography on silica gel plates. “H” from Merck (Germany) with a layer thickness of 0.3 mm. Chromatography was performed in the following systems: 1st direction: chloroform – methanol – 25 % aqueous ammonia solution /65-25-2/; 2nd direction: chloroform – methanol – acetic acid – water /65-15-10-3/. It was developed with iodine vapor in an exciter. The following phospholipids were detected in the studied water-emulsion solution: lysophosphatidylcholine, phosphatidylcholine, phosphatidylinositol, phosphatidylserine, phosphatidylethanolamine, phosphatidylglycerol, phosphatidic acids, lysophosphatidylethanolamine, minoglycoside diglycerides, and neutral lipids. This result suggests that phospholipids, compounds of a diphilic structure with ammonium cation at the base of the polar part, play the role of emulsifiers in this system.

When surrounded by water, phospholipid molecules tend to organize themselves in such a way that the hydrophilic “heads” are directed outward and come into contact with water, while the “tails” are directed inward and come into contact only with the tails of neighboring phospholipids. This results in two types of formations: micelles – small spherical particles with tails pointing inward; bimolecular bilayers, where the tails are located between two layers of hydrophilic heads. Most likely, this structure causes extreme stability, which greatly complicates the search for effective, and most importantly, safe methods of wastewater treatment. Obviously, the presence of phospholipids, which were determined by thin-layer chromatography, is the reason for the formation of stable emulsions.

The task is not limited to the study of the structure of the dispersed phases of the emulsion, but also to the search for effective methods of destroying the latter. The process of destruction is much more complicated than the process of their formation. It is usually realized by using chemical or electrochemical methods. Electrochemical methods include electrophoresis, which is sometimes accompanied by slight heating. However, an attempt to implement this method of emulsion destruction was unsuccessful.

Chemical methods involve the use of chemical reagents, which often become additional polutants, which is certainly not always advisable. In our case, it is necessary to use reagents that would form simple and safe compounds after the chemical reaction, but that their use would cause the so-called phase reversal: the dispersed phase turns into a dispersion medium, and vice versa. This phenomenon is observed when substances are introduced into an emulsion that can change the nature of the emulsion. Thus, the process of

emulsion destruction becomes an integral part of the wastewater treatment process.

According to the results of the previously obtainned experimental data, chemicals capable of destroying the studied oil-water emulsion can be: isopropyl alcohol, sodium hypochlorite, and sulfuric acid. However, these reagents have a number of disadvantages, which were mentioned earlier, and this led us to search for other chemical reagents that are safer, more reliable, and more effective. Hydrogen peroxide turned out to be such a reagent. In an acidic environment, the addition of hydrogen peroxide caused the oxidation of the polar part of the phospholipid molecule, the destruction of their surface activity, which ultimately led to the destruction of the emulsion.

As a result, the formation of two layers, water-oil, and their subsequent separation was observed. The process of emulsion destruction was facilitated by the use of cavitation and ultraviolet radiation. Since, under the cavitation effect on water, hydrogen peroxide is additionally formed in it, which in turn intensifies the purification process.

To neutralize the system, it was proposed to use calcium carbonate, since the reaction product is carbon dioxide, which improved phase separation. In addition, the use of hydrogen peroxide causes the release of oxygen, which also improved the separation.

After breaking the emulsion for the final extraction of contaminants from the wastewater, based on a thorough analysis of physicochemical treatment methods, we concluded that liquid extraction was the most appropriate as the final stage of wastewater treatment.

Liquid extraction is the process of removing one or more dissolved substances from a liquid phase (wastewater) with another that is practically immiscible with water. The distribution of the target component between the liquid phases is determined by equilibrium conditions. If we neglect the possible mutual solubility of the phases, then each of the phases will be a two-component solution and the equilibrium conditions are determined by the straight line equation. To achieve the maximum degree of wastewater treatment, it is important to choose the right extractant. The extractant must have selective solubility to contaminants. The extraction properties can be enhanced by mixing different extractants that form complexes in the mixture. Among the possible extractants, benzene, toluene, petroleum ether, halogen derivatives of aliphatic hydrocarbons can be used. However, the toxicity of such extractants does not allow their use. The most promising in terms of toxicity are acetic acid esters, in particular ethyl acetate and butyl acetate. In addition, based on experimental studies, it was found that a significant increase in the extraction properties of ethyl acetate and butyl acetate is achieved by mixing them with alcohols (methanol, ethanol, propanol, butanol, isobutanol). Thus, the degree of extraction of the ethyl acetate-alcohol and butyl acetate-alcohol mixture during the extraction of oil mill wastewater pollutants is significantly higher than in the case of using pure extractants separately.

One of the conditions for using liquid extraction is phase separation after extraction. It is important that the addition of alcohols that are highly soluble in water to increase the extraction capacity of the extractant does not lead to phase dissolution. For this purpose, three-dimensional diagrams of the studied solutions were used to determine the maximum concentration of the corresponding alcohol in the mixture (Holodovska et al., 2016, G Mazzola et al., 2008, Ali et al., 2015). According to (Fedushchak et al., 2012), the maximum permissible concentration of alcohols is within 20 %. Experimentally, it was found that with an increase in the molar mass of the alcohol added to the extractant, the degree of extraction increases (Fig. 1, Fig. 2).

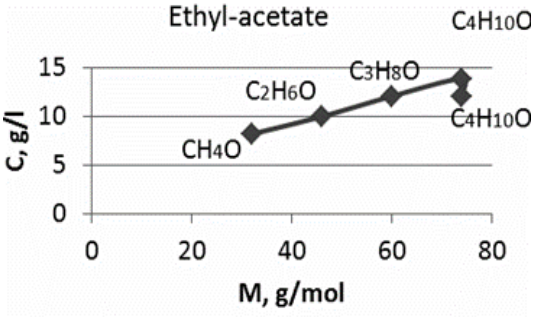

Fig. 1. Dependence of the molar mass of alcohols on the concentration of the contaminant in the extractant (mixture with ethyl acetate)

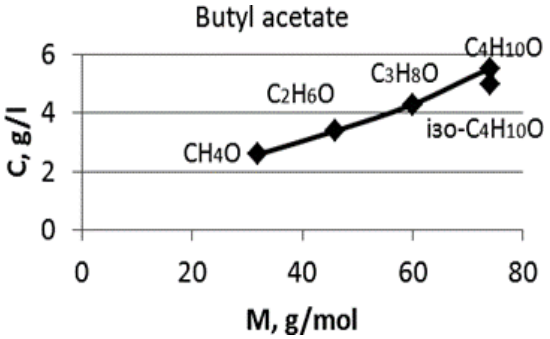

Fig. 2. Dependence of the molar mass of alcohols on the concentration of the contaminant in the extractant (mixture with butyl acetate)

3. Results and Discussion

Based on the experimental studies of the degree of extraction of pollutants from wastewater, graphical dependencies of the molar mass of alcohol on the concentration of the pollutant in the extract were constructed. As can be seen from the graphs, with an increase in the molar mass of alcohol, the concentration of the pollutant that has passed into the extractant increases (Fig. 1, Fig. 2). This is due to the fact that with an increase in molar mass, the solubility of alcohols in water decreases and the solubility of organic wastewater pollutants such as glycerides, phosphatides, and neutral fats in the extractant increases

Analyzing the data, it should be noted that with an increase in the molar mass of the alcohol, the concentration of contaminants transferred to the extractant increases. From the list of alcohols studied, the experiment shows that butanol is the most appropriate (Fig. 1 and Fig. 2).

The distribution of the target component between the liquid phases is determined by equilibrium conditions. If we do not take into account the mutual solubility of the phases, the equilibrium conditions are determined by the straight line equation: $y=kx$, where y is the concentration of the target component in the extract; x is its concentration in the wastewater; k is the distribution coefficient. According to the law of distribution, the coefficient k is a constant value at a constant temperature. In fact, it depends on many factors: temperature, pressure, nature of the substance, concentration, etc. Therefore, the equilibrium line in the x-y coordinates under the studied conditions takes the form of the curve shown in Fig. 3 and Fig. 4. In this case, as can be seen from the figures, the equilibrium line is curved. The distribution coefficient is not a constant value (Fedushchak et al., 2012).

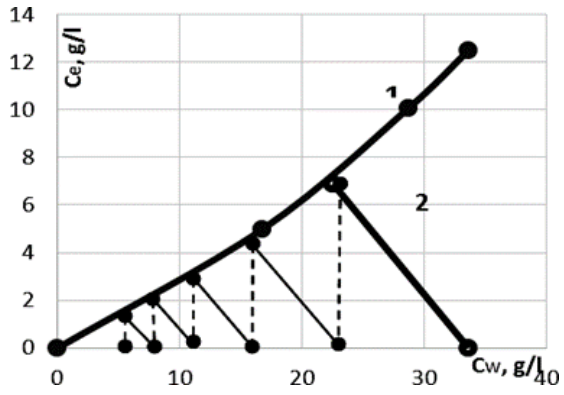

Fig. 3. Equilibrium line-1, working line-2 for ethyl acetate, batch process

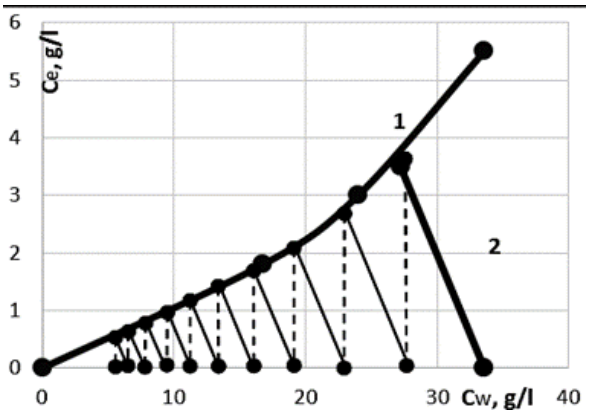

Fig. 4. Equilibrium line-1 and working line-2 for butyl acetate batch process

An equally important stage in the study of the liquid-extraction method of wastewater treatment is to obtain a process operating line. The operating line shows the concentration of the pollutant in the wastewater after equilibrium is reached. In Fig. 3 and Fig. 4 show the equilibrium line and the operating line for ethyl acetate and butyl acetate, respectively, and the degree of treatment within the given initial and final concentrations for the two liquids. As can be seen from the figures, to reduce the concentration of pollutants in wastewater by a factor of seven, five transfer stages are required for the case of ethyl acetate (Fig. 3) and twice as many for the case of butyl acetate (Fig. 4).

4. Conclusion

Liquid extraction is used in cases where the concentration of a contaminant is quite high. When implementing the liquid-extraction purification process, the distribution of the target component between the liquid phases is determined by equilibrium conditions. Each phase represents a two-component solution and the equilibrium conditions are determined by the straight line equation. To achieve the maximum degree of wastewater treatment, an extractant with selective solubility to contaminants is selected. The extraction properties are enhanced by mixing different extractants that form complexes in the mixture. Such extractants are acetic acid esters, in particular ethyl acetate and butyl acetate. It has been found that a significant increase in the extraction properties of ethyl acetate and butyl acetate is achieved by mixing them with alcohols (methanol, ethanol, propanol, butanol, isobutanol). The degree of extraction of the ethyl acetate-alcohol and butyl acetate-alcohol mixture during the extraction of oil mill wastewater pollutants

is significantly higher than in the case of using pure extractants separately.

The structure of surfactants that act as an emulsifier in the formation of stable emulsions in wastewater at edible oil production facilities has been determined. An environmentally friendly method of their destruction is proposed, which ensures an adequate level of wastewater treatment in industrial conditions. A mixture of organic solvents that can be used as an extractant has been selected.

References

Ali, E., Mulyono, S., & Hadj-Kali, M. (2015). Scaling-Up Liquid-Liquid Extraction Experiments with Deep Eutectic Solvents. *New Developments in Biology, Biomedical Chemical Engineering and Materials Science*. *2015*, 91–95. Retrieved from https://www.inase.org/library/2015/vienna/bypaper/BICHE/BICHE-13.pdf

Dyachok, V. V., Guglych, S. I., & Marakhovska, A. O. (2016). Treatment of wastewater from edible oil production. *Bulletin of Vinnytsia Polytechnic Institute*, *1*, 23–26. Retrieved from https://visnyk.vntu.edu.ua/index.php/visnyk/article/download/1871/1871/1927

Food Process Engineering and Technology (2018). *Food Process Engineering and Technology (Third Edition)*, *Food Science and Technology* (Chapter 11, pp. 289–310). Retrieved from https://www.sciencedirect.com/science/book/9780128120187

Fedushchak, N. K., Bidnychenko, Yu. I., Kramarenko, S. Yu., & Kalibabchuk, V. O. (2012). *Analitychna khimii*. Vinnytsia: Nova knyha. Retrieved from https://www.kspu.edu/FileDownload.ashx/%D0%A5%D1%96%D0%BC%D1%96%D1%8F_%D0%90%D0%BD%D0%B0%D0%BB%D1%96%D1%82%D0%B8%D1%87%D0%BD%D0%B0.docx?id=5a40062c-3693-4552-af85-d5b2e64b1983

G Mazzola, P., M Lopes, A., A Hasmann F., F Jozala, A., CV Penna, T., O Magalhaes, P., O Rangel-Yagui, C., Pessoa Jr., A. (2008). Liquid–liquid extraction of biomolecules: an overview and update of the main techniques. *Chemistry Journals*, *83*(2), 143–157. doi: https://doi.org/10.1002/jctb.1794

Holodovska, O. Ya., Marakhovska, A. O., & Diachok, V. V. (2016). *UA Patent No. 111389*. Ukrainskyi instytut intelektualnoi vlasnosti (Ukrpatent).

Lajoie, L., Fabiano-Tixier, A.-S., & Chemat, F. (2022). Water as Green Solvent: Methods of Solubilisation and Extraction of Natural Products–Past, Present and Future Solutions. *Pharmaceuticals*, *15*(12), 1507. doi: https://doi.org/10.3390/ph15121507

Walker, J. F., Hanson, P. C., & Hunt, R. J. (2013). *Potential Effects of Climate Change on Inland Glacial Lakes and Implications for Lake Dependent Biota in Wisconsin. Hydrologic and Lake Quality Modeling.* U.S. Government: Environmental and Economic Research and Development Program of Wisconsin's.