FOOD INDUSTRY WASTEWATER TREATMENT

Dereyko K.*, Malovanyy M.*, Dyachok V.*, Sakhnevych Y.*, Marachovska S.*

* Department of Ecology and Environment Protection, Lviv National Polytechnic University, 79013 Bandery 12, Lviv, Ukraine (E-mail: dereykokhrystyna@gmail.com; mmal@polynet.lviv.ua)

Abstract The purpose of the present study is to assess the condition of wastewaters pertaining to the production of cooking oil and to develop an effective and low-cost method for purification of wastewaters and utilisation of other oil production-related wastes which would comply with environmental safety requirements. It was made a quality assessment in terms of content of polluting substances of cooking oil-production wastewater. For identification of fat content (phospholipids) of wastewaters, the thin-layer chromatography method was applied. The basis of the proposed method for purification of wastewaters was a preliminary separation of clarified and neutralized wastewater by dint of calcium carbonate, subsequently sodium hypochlorite for water clarification and its additional neutralization was used. The presented method allows reaching a high degree of wastewater purification, being effective and low-cost.

Keywords: Cooking oil production wastewater; phospholipids; thin-layer chromatography; wastewater purification; wastewater treatment

One of the main tendencies of development of food industry in the 21st century is the creation of useful and healthy products, the so-called functional food products. A specific feature of such products is that they contain ingredients which, besides their traditional nutrient and energy-supplying function, also possess a range of specific physiological functions which help human organism to combat negative influence of civilisation.

Food industry is one of the most resource-demanding branches of industry, therefore it is especially important to ensure rational usage of raw materials. In the processing sub-branches of agricultural complex where the net value of products is comprised of material and energy expenditures, it is increasingly crucial to decrease the consumption of materials. This can be achieved by dint of wide implementation of non-waste technologies, complex usage of raw materials and secondary (recycled) resources in combined industry. Another important aspect of the subject problem is ensuring of ecological safety of plants where the food products are produced as well as elimination of the influence of the wastes upon the environment. One of the most important problems which the food industry enterprises face is the problem of wastewater treatment (Koshel et al., 1998). In Ukraine, food-producing enterprises are mostly located in the West and the South-West which have a rich network of water bodies. This means that control over discharge of sewage water is to be exercised more strictly than usual and food-producing companies in these regions are to be prevented from polluting the water reservoirs.

Ukraine is one of the five main world producers of sunflower. Yearly output of sunflower amounted to more than 4 million tonnes in this year. Only Argentine (6.4 m tonnes) produced more.

In the latest years, Ukrainian vegetable oil market has become increasingly more integrated into the global vegetable oil market. This is due to the fact that processes of international division of labour get deepened and Ukraine is becoming one of the world's leading producers of sunflower seeds, sunflower oil, and groats.

However, the production of sunflower oil has for years been aimed at internal consumer. Summary production capacity of our plants at 100% load allows to process 3.2m tonnes of sunflower seeds per year (which is the same as the usual crop) and to receive about 1.4m tonnes of vegetable oil. Thereby, the level of consumption is around 1.3-1.4m tonnes. This means that we are producing about as much as we are consuming. Today, there are around 80 enterprises in Ukraine which are producing sunflower oil and its derivatives (vegetable fat and mayonnaise). The largest of the subject enterprises are located in Southern Ukraine where the sunflowers actually grow.

Therefore, we are facing a crucially important task which foresees a more detailed examination of peculiarities of such valuable product as sunflower oil, bringing this production closer to the ecologically clean technologies whilst minimising the wastes of production.

Sunflower oil, alongside other vegetable oils, possesses a number of useful properties which make its consumption a lot more preferable than consumption of animal fat (Ezau, 1980).

In the latest years we have been able to observe a process of technical re-equipment of food-producing enterprises, specifically producers of cooking oil. A change in technology causes a change in the quality of sewage waters which are formed thereby.

With the purpose of further study of ecological influence of production of the cooking oil, assessment of the condition of sewage water, we shall examine the technology of oil production.

Different oils are named according to the designation of plants whose seeds, parts, or tissue is used for their production. Within each designation, dependent upon the manner of their separation (press, extraction) and purification (refinement) new kinds of oil are formed. In the world practice, there exist two methods of oil production: the mechanical/pressed method and the method of dilution of oil in volatile organic solvents, or extraction. In the production of vegetable oil, these two methods are applied either separately or jointly.

Pressed method. Seeds are cleaned from peelings, skin, then milled to the condition of pulp which is moistened and heated to 80° C for better separation of fat. This is called the *hot pressing method* as opposed to the *cold-pressing method* which does not include heating of the pulp. After the oil is removed from the raw material, the pulp, groats etc remain which contain a lot of albumen substances. The residues of the defatted raw material are used for the production of sunflower flour, concentrated sunflower albumen containing 67.1-71.0% of albumen as well as albumen isolates containing 85-97% of albumen.

Extraction method is applied owing to the solubility of fat in organic ether, hexane, and pentane. The fat which is produced in this manner must be cleansed of solvents and the fat is to be refined.

The oil produced by way of pressing may be refined or not refined. But given the increased usage of chemicals in the agriculture and the deterioration of the environment, the raw materials as well as the oil may contain pesticides, toxic metals, mycotoxins, and carcinogenic benzopyrene. Because of this, scientists and specialists deem it that all kinds of oil must necessarily be subject to refinement whilst raw material is to be subject to sanitary and hygienic control, verifying the presence or absence of these substances.

Oil refinement leads to full or partial removal of harmful substances. Depending upon the depth of purification, the following types of oil are produced:

- non-refined (cleaned from mechanical admixtures)
- hydrated (cleaned from phosphatides)
- refined non-deodorised (cleaned from phosphatides, free fat acids, colouring agents)
- refined deodorised (refined oil cleaned from aromatic and flavouring substances, pesticides and carcinogens). After the non-refined oil is separated from the raw material, it is to be filtered or left to settle, so that peelings, particles of seed coats, pulp etc can be removed. The non-refined oil possesses colour, flavour, and smell which are peculiar to its mother raw material as well as all the corresponding substances (including the biologically active ones) which are native to it.

Most of Ukrainian oil-producing enterprises do not provide for purification of industrial wastewaters, dumping thousands of tonnes of polluting substances into the water bodies. The purification facilities which exist in some places were constructed a long time ago and had been designed with regard to the requirements of domestic wastewater purification. Such facilities, at best, partially decrease the value of general BOD (biological oxygen demand) or simply let the wastewater flow through; whilst at worst, the wastewater is decomposing in these facilities and becomes even more poisonous when dumped into water bodies. Such industrial wastewaters are mostly polluted, especially with organic substances; therefore the purification facilities which are currently in operation are unable to clean them in compliance with sanitary requirements (Yacyk, 2007). A significant ecological danger comes from the pollution of surface waters with organic substances which the wastewaters flowing from cooking oil-producing facilities contain. These substances, when dumped into water bodies, prompt the development of decomposition processes, infect water bodies with pathogenic bacteria, cause water efflorescence and have an overall negative influence over fauna and flora (Fidley, Evanz, 1990). For many enterprises of the subject branch, purification of wastewaters presents a serious problem.

The enterprises are increasingly facing the necessity to look for effective, maintenance-reliable purification facilities which guarantee stable high quality of purification. Another option is to look for reconstruction and expansion of the already-existing ones. Increasing cost of fuel and energy resources forces Ukrainian producers to consider rational usage of energy resources, effective recycling and treatment of production wastes of which wastewaters are part.

The purpose of the present study is to assess the condition of wastewaters pertaining to the production of cooking oil and to develop an effective and low-cost method for purification of wastewaters and utilisation of other oil production-related wastes which would comply with environmental safety requirements.

As basis of our study, we have chosen the wastewaters dumped by those Ukrainian vegetable oil-producing enterprises whose purification facilities are all but unused due to their technical deficiency. As a result of this, the polluted wastewaters, which do not correspond to the requirements of the Law of Ukraine “About protection of environment” and “Regulations for Protection of Surface Waters from Wastewater Pollution”, are dumped into open water bodies. As of today, the main problem of such facilities is the vast amount of wastewaters which are discharged in the process of production. These wastewaters flowing from extraction and refinement workshops are heavily polluted with organic substances (neutral fats, phospholipids, organic acids etc), both in dissolved condition and in the form of suspended solids and emulsion (Sozanskyy, 1998; Yacyk, 2007). It is not possible to dump such wastewaters into open water bodies without prior purification. The enterprise regarded it as economically unsound to neutralise discharges using sodium hydroxide because a lot of sodium hydroxide is needed while the water body would get even more polluted. Wastewaters are characterised by high degree of turbidity (dimness); the appearance of the substance resembles shaken emulsion of suspended substances in the form of tiny flakes having a sharp unpleasant smell of rancid fat exposed to rotting processes.

Experimental part

In order to design a method for purification of the aforementioned wastewaters, we have conducted a series of experimental investigation. A quality assessment (in terms of content of polluting substances) of cooking oil-production wastewater was made using physical and chemical methods of analysis. A degree of pollution of wastewater was determined in terms of the following indicators (Table 1).

In order to determine BOD-5, a neutralisation of the examined water sample was made and the water sample was dissolved using a specially prepared, oxygen-saturated water containing

Table 1. Quality indicators of wastewaters from the examined oil-producing facilities

No.	Wastewater quality indicator	Measuring unit	Values (de facto)	Values (normal)
1	Iron (general)	mg/dm³	1.62	0.3
2	Ammonia	mg/dm³	10.0	2.0
3	Phosphates	mg/dm³	102.79	3.5
4	Suspended substances	mg/dm³	104.4	15
5	Dry residue	mg/dm³	1571.0	200
6	Synthetic surface active substances (anionic)	mg/dm³	0.88	0.5
7	Fats	mg/dm³	13.0	1.0
8	Biological oxygen demand-5 (BOD-5)	mg/dm³	36.5	15
9	pH value		2.1	6.5-8.5

nutrients; incubation of the sample lasting a certain period of time (5 days) at $t° = 20±1°C$ without air and light access in an entirely filled and corked bottle; concentration of dissolved oxygen before and after the incubation period was determined by the method of voluminal iodometric titration; turbidity of the water sample was determined using the photometric method of analysis (turbidimetric method) (Stroyev, 1986; Boyechko F.F., Boyechko L.O., 1993).

For identification of fat content of wastewaters, the thin-layer chromatography method was applied with silica gel “H” plates produced by Merk company, layer thickness = 0.3 mm. Chromatography was made in the following systems:

Direction 1: chloroform: methanol: 25 % aqueous solution of ammonium in the following proportions: 65-25-2.

Direction 2: chloroform: methanol: acetic acid: water; proportions: 85-15-10-3.

After preliminary neutralisation and deposition of sulphates, the wastewater (qty = 50 mcL) was applied on the plate in right lower angle. After drying, the plate was inserted into the chromatographic chamber filled with a system of solvents for Direction 1. After the F1 Solvent Front was passed, the plate was removed and air-dried. Then it was turned over 90° clockwise compared to its initial placing, and again inserted into the chromatographic chamber filled with a system of solvents for Direction 2. After passing of F2 Solvent Front, the plate was removed and air-dried. Then it was developed in an exsiccator saturated with iodine steam for about 15 minutes. The phospholipids manifested themselves on the chromatogram in the form of yellow stains.

For identification, evidence was used (individual phospholipids and data from the literature) (Koifman et al., 1974; Muravyova, 1978; Pleshkov, 1985; Dyachok and Ivankiv, 2002).

It was detected that oil production-related wastewaters contain the following phospholipids (Figure 1):

1 - neutral lipids;
2 - phosphatidylethanolamine;
3 - phosphatidyl-glycerol;
4 - phosphatidyl inositol;
5 - phosphatidic acids;

6,7 - lysophosphatidylcholine;
8 - sphingomyelins;

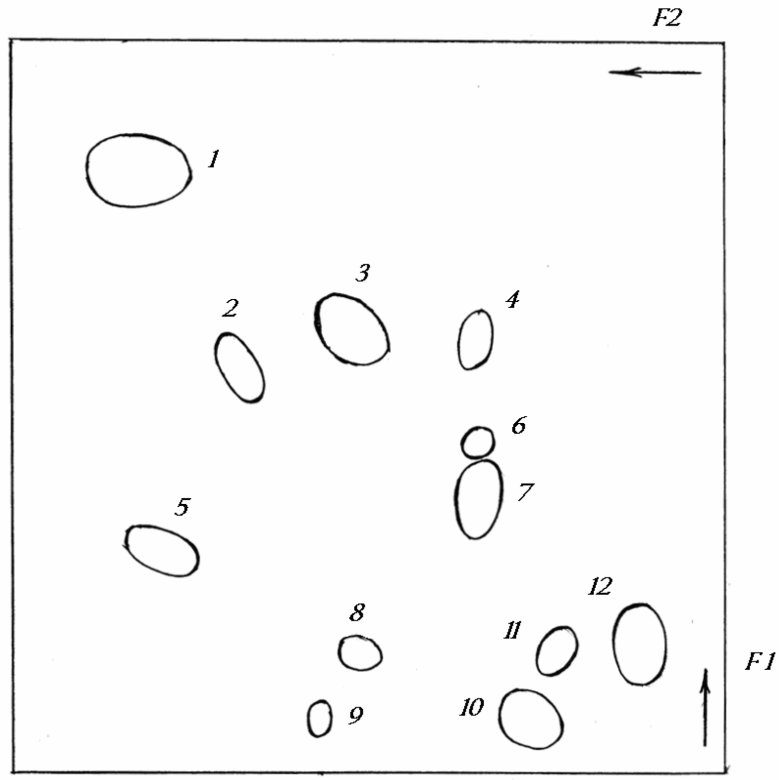

Figure 1. Chromatogram of phospholipids in oil production wastewaters

9 - phosphatidylserine;
10 - lysophosphatidylinositol;
11,12 - lysophosphatidylserine.

On the stage of primary water treatment, reagent methods were used, which included neutralisation of oil industry's wastewaters using calcium carbonate (chalk) which is a cheap and easily accessible material. The technology of water purification by chemical deposition presupposes its preliminary purification from colloidal-dispersed and suspended substances using coagulation with subsequent separation of the deposition as a result of filtering, settlement or flotation. As a result of chalk injection — 0.5 g into the wastewater (V = 0.5 ml), intense discharge of carbonic acid is observed whereby a thick foamy layer is formed and salts related to sulphate acid (which is used in the production process) subside into deposit. When the mix is heated, the mentioned process accelerates, which testifies to the fact that neutraliser can be injected into the wastewater received immediately after production without prior cooling of this wastewater; this also has its advantages with regard to rational usage of clean water for technological purposes. As a result of the process described above, we have reached a pH value of 5.1, having injected 1.5 g of calcium carbonate into 50 ml of wastewater.

On the examination stage of wastewater purification from organic fraction we have proposed the usage of oxidants, specifically hydrogen peroxide H_2O_2, oxygen O_2, ozone O_3, and sodium hypochlorite which is a multi-tonnage production waste at OJSV "Lukor" (Kalush town). The subject experimental investigations aim to determine the quantities of oxidant expenditure which are sufficient for complete cleaning of wastewaters from organic polluters on the one hand and to prevent over-expenditure of oxidants, on the other hand. In order to achieve this aim, a series of studies was conducted, the target of which was purification of wastewaters with different amounts of oxidants injected into them. The criteria of purification effectiveness are the actual water quality indicators.

The conducted studies have shown that among all the oxidants which were used, the most effective one is sodium hypochlorite. Therefore, the basis of the proposed method for purification of wastewaters was a preliminary separation of clarified and neutralized wastewater by dint of calcium carbonate, subsequently sodium hypochlorite for water clarification and its additional neutralization was used. This is the most simple and technologically feasible method. It has several advantages, specifically:

- it can easily be conducted and its reactant supply is not expensive;
- the reactant (sodium hypochlorite) is available in Kalush town where it is produced as a by-product of the production process;
- the reactant expenditure is not substantial; quantities of formed wastes are not large (only oxidised, disinfected organic polluters are produced);
- it can be used after enhancement of existing purification facilities;
- wastes can be used as an effective organic and mineral fertiliser (Rashevska, 1998).

Experiments were conducted using samples of wastewater, the aim of which was its purification from organic substances with the usage of active chlorine which was injected as part of sodium hypochlorite. To the initial wastewater (V = 100 ml) possessing pH value of 2.3, sodium hypochlorite had been being added until the colouring changed from dark-brown to stramineous, necessary quantity V (NaClO) = 9.2 ml with concentration C (NaClO) = 10 % (vol.). Also, it is observed that flakes are formed as a result of the process taking place on the surface of the mix. These flakes subsequently deposit to the bottom. When sodium hypochlorite is added to the water which was pre-neutralised using calcium carbonate, the pH reaches the necessary neutral value.

Upon having conducted the neutralisation and upon having achieved the necessary pH of wastewater, as well as upon having conducted its clarification as per abovementioned description, we proceeded to the next step: separation of the formed deposition with further identification of substances, specifically phospholipids which are part of the fats' composition and which might either subside into deposits or remain in the clarified water layer. The subject detection of phospholipids in the deposition was made using a chromatographic analysis method. The filtered deposition received as a result of the abovementioned was dissolved in 2ml of ethyl alcohol and applied (qty = 50 mcL) onto the plate in right lower angle; then air-dries and inserted into the chromatographic chamber.

Therefore, upon completion of purification using sodium hypochlorite and upon having conducted a chromatographic analysis of phospholipids in the received deposition, a conclusion could be made that fat content of the deposition is similar to the fat content of output wastewater. This confirms the efficiency of the proposed technology for removal of organic polluters.

Conclusions

We can see that, as of the present day, the existing technologies for wastewater purification enable us to remove any polluter out of them. However, thereby it is also crucially important to consider the cost of such purification, especially taking into account the present condition of national economy. That is why we have chosen the subject purification method not only with regard to the efficiency of wastewater purification with which it is characterised but also with regard to its cheapness. If we analyse the data received as a result of the experiment, we can see that polluters are mostly concentrated in the deposit which was received as a result of water neutralisation and water clarification. This deposition can subsequently be recycled and used as an organic and mineral fertiliser containing N, P, K, and Na. The clarified water then goes to the next stage of additional purification. The details stated above testify to the fact that the presented method allows reaching a high degree of wastewater purification, being effective and low-cost.

References:

Boyechko F.F., Boyechko L.O. (1993). The main biochemical concepts, definitions and terms. Kiev, High School. – 528 pp.

Dyachok V., Ivankiv O. (2002). Kinetic equilibrium of phospholipids extraction from the organic substances. The second Lviv-Lublin conference of biochemical and research facility, Lublin. University of Marie Curie Skłodowska, Pharmacia. Lublin. Vol.XV, P. 371-373.

Ezau K. (1980). Seed-plants anatomy. Volume 2. Translation from English, Moscow, Mir.- 558 pp.

Fidley D, Evanz U. (under editorship) (1990). Biological membranes. Methods. / Translation from English. M.: Mir.- 423 pp.

Koifman T.M., Volotovskaya S.N. and others. (1974). Particle-size distribution studying with reference to flax seeds and oil phospholipids // Works of VNIIZH, No 2.- P. 86-90.

Koshel M., Shmatko T. and others. (1998). Effective clearance of wastewater // Food and processing industry. — No 6. – P. 27.

Muravyova D.A. (1978). Pharmacognosy. Moscow, Medicine. – 656 pp.

Pleshkov B.P. (1985). Phytochemistry practical course. Moscow, «Kolos». - 255 pp.

Rashevska T. (1998).Utilization of organic wastes // Food and processing industry. — No 5. – P. 20.

Sozanskyy S. (1998). Two-level clearance of wastewater // Food and processing industry. — No 2. – P. 23-24.

Stroyev Ye.A. (1986). Biological chemistry. Moscow, High school. - 479 pp.

Yacyk A.V. (November - December 2007). Water resources in the context of ecological safety and sustainable development of a state. Ecological bulletin. - P. 21-24.