Oil-extracting plants wastewater purification: research results

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Abstract. The problem of environmental pollution becomes more and more actual nowadays. The pollution of water basins is a particularly serious current environmental issue. Water basins pollution is one of the most pressing technical, ecological, biological and social problems of mankind. Despite the fact that food industry enterprises tend to use modern methods of processing raw materials, they are still harmful to the environment. Oil-extracting plants also exert a significant negative impact upon the environment: upon the atmosphere and water facilities, in particular. The study aim is to estimate the harmful effect oil-extracting industry produces on water bodies, measure the overall purification effect produced by treating agents and examine their types, doses and input modes. The oil-extracting plant under investigation is located in the residential area, in the town of Bezenchuk, so there is a need for constant control over the nearby environment.

1. Introduction
Wastewater flowing from industrial plants contains a large amount of organic pollutants. Usually they are vegetable oils and animal fats, surface-active substances, etc. In particular, industrial wastewater of food production and of consumer service enterprises contain up to 20000 mg/l of oils, fats and other organic substances [1]. When combined, these contaminants mix and mingle which result in the formation of a stable emulsion.

Fats and oils in wastewater exist in two aggregate states, that is solid, liquid and colloidal. Depending on the conditions of formation and wastewater composition, fats and oils take on the form of a fat-phase, thus making a fatty film on the surface of the water. This fatty film consists of particles dispersed in the water (emulsion) and is in a dissolved state [2]. In wastewater, fats and oils usually exist in all these three states at the same time. This fact significantly complicates the determination of their concentration.

2. Problem Review
Papers [3,4] describe several methods of determining fat concentration in wastewater. The describes are based on the extraction of fats and oils by means of organic solvents.

The most widespread method is a gravimetric method which involves the use of a Soxhlet extractor, diethyl or petroleum ether being an extraction solvent [5]. The gravimetric analysis is based on the exact measurement of the determined substance or its constituent parts mass, obtained as a result of analytical reaction and existing in chemically pure state or in the form of corresponding compounds.
The method of the refractometric analysis is based on the change of refractive index of the analyzed liquid substance (or its solution). The beam of light, passing from one transparent medium (air) to another (liquid), falls inclined to the surface of the section and changes its original direction, that is the beam refracts. The refractive index has different characteristics for each individual substance. It depends on the wavelength of the incident light, on pressure and concentration (in case it is a solution).

This study reveals the results of determination of fats and oils content in sewage water (model solution). The results are obtained by means of a photometric method, which is based on changes of the intensity of light that passes through a solution [6]. This measurement has been carried out with the help of special optical devices known as photocolorimeters. A part of a light stream passing through a solution is absorbed. After the light stream passed through a solution, it falls on a photocell. The light stream causes an electric current (photoelectric) in the photocell and its force is measured with a galvanometer. Current intensity here is in direct proportion to the intensity of the light falling on the photocell.

Papers [7,8] demonstrate that oil-containing wastewater of fat-and-oil industry is most frequently purified through the use of various treating agents.

3. Problem Solution
In this paper the researchers investigate industrial wastewater discharged from the oil-extracting plant CJSC "Samaraagroprompererabotka", located in the town of Bezenchuk.

The results of the control have shown that fat-and-oil industry wastewater is muddy, grey and contains flocculated suspended solids. Fats there usually take the form of vegetable oils. There small quantities cover the surface of the water, making it difficult to reaerate and dissolve oxygen. Passing through the sewer networks, these oils adhere to the walls of the channel. It causes contaminants agglutination, which reduces the cross section of stream [9]. In addition, the wastewater contains organic acids and nitrogen substances. They decay after neutralizing thus forming hydrogen sulfide from decaying proteins and regenerative sulfates. Table 1 shows incoming wastewater parameters according to the controlled values.

| No. | Parameter                           | Unit of measurement | Values    |
|-----|------------------------------------|---------------------|-----------|
| 1   | Suspended substances               | mg/dm³              | 180±9.1   |
| 2   | BOD                                | mg/dm³              | 8.60±0.12 |
| 3   | Synthetic surfactants              | mg/dm³              | 0.017±0.006 |
| 4   | Nitrate ion                        | mg/dm³              | 2.35±0.71 |
| 5   | Ammonium ion                       | mg/dm³              | 3.63±0.76 |
| 6   | Nitrite ion                        | mg/dm³              | 0.38±0.023 |
| 7   | Phosphorus phosphate               | mg/dm³              | 0.28±0.042 |
| 8   | Chloride ion                       | mg/dm³              | 950.08±39.70 |
| 9   | Iron Total                         | mg/dm³              | 0.78±0.23 |
| 10  | Nickel                             | mg/dm³              | <0.08     |
| 11  | Copper                             | mg/dm³              | 0.002±0.0012 |
| 12  | Chromium                           | mg/dm³              | <0.01     |
| 13  | Petroleum products                 | mg/dm³              | 0.42±0.147 |
| 14  | Phenol                             | mg/dm³              | 0.002±0.001 |
| 15  | Fats and oils                      | mg/dm³              | 400.2±7.4 |

Then the researchers examined the received data and prepared a model solution for further analysis. Vegetable oil was used as the main ingredient for the solution. The tap water was brought to the
temperature of 40-60\textdegree{} C. The researchers added pollutants in the form of vegetable oil to this water and calculated the amount of the pollutant according to certain chemical parameters. Then the model solution was cooled to 20-22\textdegree{} C.

Figure 1, preliminary drawn and graduated, was used to determine the concentration of fats and oils in the solution (the model solution having a concentration of fats and oils which is closest to the concentration of run-off).

![Figure 1](image)

**Figure 1.** Calibration graph for fats and oils calculation.

One of the most common methods of wastewater treatment is its purification with coagulants. The researchers carried out a series of experiments series to choose the optimal scheme of treating agent processing. The experiments helped to selected most suitable coagulants and determine specific expenses (doses) of treating agents.

The main process of coagulating treatment of industrial surface wastewater is called heterocoagulation. Heterocoagulation is a process of agglutination of colloidal and finely dispersed wastewater particles formed in sewer water coagulants [10].

Then the most rational way of introducing coagulants into purified water was chosen. The methods included:

1. The traditional one, when the solution of coagulants is added to purified water continuously, as a single addition.
2. Fractional coagulation (that is non-integral or partial method of coagulation) consists in adding the estimated amount of coagulant to water while taking two or more consecutive portions. Water treatment by different sequentially added coagulants can also be considered as fractionated coagulation.

The technological effect achieved at fractionation of coagulant can easily be explained from the kinetic point of view. As a result of hydrolysis of the first coagulant portions, the solid phase is formed. Then this solid phase acts as a center of flocculation at subsequent portions of coagulant hydrolysis. It is known, the speed of small particles adhering to large particles can exceed the rate of mutual coagulation of small particles by several times.

For each series of experiments, the water was poured into 6 cylinders with 1000 ml capacity. Then 10\% treating agent solution was injected into the cylinder in the following sequence:

1. with the use of aluminum sulfate, \( \text{Al}_2(\text{SO}_4)_3 \) – coagulant amount varied in the range of 100-400 mg/l;
2. with the use of 9-water aluminum nitrate \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) – coagulant amount varied in the range of 100-300 mg/l;
3. with the use of sodium hypochlorite, \( \text{NaOCl} \) – coagulant amount varied in the range of 100-300 mg/l.

Contents of all cylinders was intensively mixed with mixers for 30-40s. Then the samples were mixed slowly for the next 3-5 minutes. Then the samples were left for detention for 60 minutes to observe the processes of flocculation. After the coagulated wastewater settled, the researchers took a 100 ml sample of water from each cylinder, collecting water from the upper layer without stirring up the sediment. For these experiments, chloroform was chosen as an extraction solvent because of its specific physical and chemical properties.

At the next stage, 100 ml of the model solution was placed into the separating funnel. 15 ml of chloroform was also put into the funnel and the solution was shaken for 2-3 minutes. After separation of layers, the extract was poured into a cylinder. And dried with anhydrous sodium sulfate. Fats and oils content in the extract was determined with a photocolorimeter. Table 2 shows results of measurements during the first experiment when coagulant was added to the solution continuously, as a single portion.

Table 2. Fats and oils content in the extract after the introduction of one single portion.

| Treating agent dose (ml) (1 fraction) | Aluminium Sulfate \( \text{Al}_2(\text{SO}_4)_3 \) (mg/l) | Aluminium nitrate, 9-water \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) | Sodium hypochlorite, \( \text{NaOCl} \) |
|-------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Optical density | Concentration of fats and oils | Optical density | Concentration of fats and oils | Optical density | Concentration of fats and oils |
| 100 | Not determined, because the minimum portion is 150 mg/l | 0.131 | 52.5 | 0.159 | 79.3 |
| 150 | 0.62 | 330 | 0.05 | 20 | 0.82 | 61 |
| 200 | 0.526 | 280 | - | - | 0.1 | 48 |
| 250 | 0.42 | 230 | - | - | - | - |
| 300 | 0.324 | 180 | - | - | - | - |
| 350 | 0.16 | 90 | - | - | - | - |
| 400 | - | - | - | - | - | - |

Table 3. Fats and oils content in the extract after the introduction of one single portion.

| Treating agent dose (ml) (1 fraction) | Treating agent dose (ml) (2 fraction) | Concentration of fats and oils (1 fraction) | Concentration of fats and oils (2 fraction) |
|-------------------------------------|-------------------------------------|---------------------------------|---------------------------------|
| 100 | 50 | 325 | 70 | 50 |
| 125 | 75 | 276 | 70 | 50 |
| 200 | 100 | 224 | 100 | 50 |
| 230 | 120 | 174 | 100 | 50 |
| 280 | 120 | 81 | 100 | 50 |
| 300 | 150 | - | 100 | 50 |
Figure 2 shows wastewater treatment effect produced by various treating agents.

![Figure 2. Change of water turbidity during processing by various treating agents.](image)

Thus, the series of experiments involved the use of aluminium sulfate Al$_2$(SO$_4$)$_3$, 9-water aluminum nitrate Al(NO$_3$)$_3$*9H$_2$O, hypochlorite sodium, NaOCl. It turned out that the use of 9-water aluminium nitrate is the most effective treating agent.

### 4. Conclusion

The research yielded the following conclusions:

In industrial conditions high efficiency of wastewater main stream purification is achieved with the use of reagent method followed by separation of the solid phase. This technical solution allows to remove a large mass of contaminants from the run-off.

Local purification of highly polluted wastewater of fat-and-oil industry can be successfully carried out with the help of physico-chemical methods. The proposed technological solution is characterized by the most effective scheme of run-off reagent treatment.

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