Extracting vegetable oils from model waters by sorbent on the base on carbonate sludge

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Abstract. The peculiarities of sorption interactions between TMSP$_{600}$ material obtained from carbonate sludge from sugar production and model sewage containing vegetable oils are investigated. It was found that in the absence of synthetic surfactants, TMSP effectively interacts with emulsions of vegetable oils and causes their rapid clarification. In the presence of sodium lauryl sulfate, efficiency is markedly reduced. The observed phenomenon is explained by the presence of a negative charge on the oil droplets, as a result of which they are repulsed from TMSP$_{600}$ particles. The purification efficiency remains quite high at a synthetic surfactant concentration of <0.01 mg/dm$^3$; therefore, TMSP$_{600}$ can be considered acceptable for treating sewage contaminated with vegetable oils at a low synthetic surfactant content in the system.

1. Introduction
Food production enterprises and agriculture are the source of the formation of large volumes of sewage of complex composition [1–3]. They are difficult to clean and they are a threat to water bodies, since biodegradable components lead to eutrophication [4–6].

Sunflower oil is the most popular type of vegetable oil among the population of the Russian Federation [7–9].

In the oil industry, a significant amount of water polluted by waste is formed, which is a threat to water bodies [10, 11].

Oily sewage is also produced in a number of other industries, such as
- production of fatty acids;
- drying oil melting;
- plants of synthetic detergents;
- various food production: meat, dairy, production of semi-finished products, etc.;
- cosmetic industry;
- other industries.

Synthetic surfactants are present in the vast majority of sewage, as they are inevitably used for washing equipment and containers. Under the conditions of colloidal dispersed systems, synthetic surfactants have a significant effect on the electrochemical properties of dispersed components. It is known that even small volumes of detergents lead to a sharp increase in the stability of emulsions [12–14], which creates difficulties in water purification.

Sunflower oil is a mixture of carboxylic acid triglycerides, the largest percentage of which are linoleic, oleic and palmitic [15–17]. Despite the pronounced hydrophobic properties, it is able to form
stable emulsions in the aquatic environment, especially in the conditions of turbulent flows generated during equipment washing. This is due to the presence in the oil of a small amount of hydrolysis and oxidation products of triglycerides, phospholipids and other compounds [18–20], which are natural surfactants and cosurfactants [21–23].

The presence of synthetic surfactants in the system leads to the formation of a solvation shell at the oil/water interface. The hydrophilic parts of the molecules are facing water, and impart some electrostatic charge to the micelle, which determines its sedimentation stability [14].

The study of the peculiarities of the electrostatic interactions of the emulsion with sorption material in the presence of synthetic surfactants is important for determining the parameters at which the stability of the system will be violated, so that it is possible to establish optimal conditions for the purification of model waters.

The sorption material used – a thermally modified saturation precipitate of sugar production from sugar beet (TMSP) – was previously investigated for interaction with a number of pollutants. It was found that it exhibits high sorption properties with respect to certain hydrophobic substances, such as oil products and milk fats [24–26].

The carbon layer formed on the surface of fine dispersed particles (Figure 1) gives the material hydrophobic properties and increases its sorption capacity.

Figure 1. Micrograph of TMSP, carbon flakes on the surface of CaCO₃ are visible in the figure.

2. Materials and methods
Emulsions of vegetable oil were prepared as follows: the necessary volume of oil was added to tap water, and then the tank was installed on an automatic mixer for 24 hours.

After the specified time, a stable emulsion was formed, which did not delaminate for several days. To study the effect of synthetic surfactants on the efficiency of extracting oils from model emulsions, synthetic surfactants were added to the tank with oil and water, after which mixing was carried out in a similar way.

Sodium lauryl sulfate (C₁₂H₂₅SO₄Na) was used as a synthetic surfactant, as one of the most common detergent components in the Russian Federation [27].

The sorption material used in the work was a thermally modified waste from the sugar industry contains ~ 95% CaCO₃ and ~ 2% amorphous carbon [24–26].

The purification efficiency was monitored by two parameters: the turbidity of the emulsion, which was determined using a HI 98703 turbidimeter and a COD using an Expert-003-COD photometric analyzer.

Zeta potential was measured by Zetatrac analyzer (Microtrac, USA).
3. Results and discussion
Studies have shown (Figure 2) that TMSP effectively interacts with emulsions of vegetable oils and causes their rapid clarification.

![Figure 2. Purification efficiency of model emulsions of sunflower oil with chalk (1) and TMSP_{600} (2).](image)

The results of studies of the influence of surfactant concentration on the purification efficiency of oil-containing model effluents are presented in Figure 3. The initial concentration of sunflower oil was 500 mg/dm$^3$.

![Figure 3. The effect of the concentration of synthetic surfactants and the mass of the additive TMSP_{600} on the efficiency of the purification of oil-containing model effluents.](image)

From the results of the studies it is seen that with an increase in the concentration of surfactants, the purification efficiency of emulsions decreases, but when the concentration of sodium lauryl sulfate is up to 0.005 mg/dm$^3$, it remains at a level of more than 80%. Consequently, at high concentrations of detergents in sewage, the use of sorption material will be irrational, but acceptable with a low content of synthetic surfactants.

When cleaning emulsions with a synthetic surfactant content of 0.01 mg/dm$^3$ and C$_{Oil} = 500$ mg/dm$^3$, a rational addition of sorption material is 25–30 g/dm$^3$.

The most effective purification of such emulsions occurs at pH 5-6. In this regard, it was of interest to study the peculiarities of changes in the electrokinetic potential and the systems under study.

Figure 4 shows the results of studies of the influence of synthetic surfactants on the value of the zeta potential of fat droplets in oil-containing emulsions.
An oil particle can acquire a charge due to the sorption of electrolytes from an aqueous solution, which is observed on the left side of the figure. When sodium lauryl sulfate is added to the emulsion, the zeta potential acquires a negative value.

This is due to the presence of the SO$_3^2$-group in sodium lauryl sulfate, where R is the hydrophobic radical (figure 5).

Figure 4. The influence of synthetic surfactants on the value of the zeta potential of fat droplets in emulsions of sunflower oil.

![Figure 4](image)

Figure 5. Schematic representation of the mechanism of interaction of sodium lauryl sulfate with a drop of oil.

![Figure 5](image)

Figure 6. Kinetics of the change in the zeta potential of the surface of TMSP$_{600}$ particles with changing environmental pH.
This explains the decrease in the purification efficiency of emulsions in the presence of synthetic surfactants, since the particles of sorption material in this pH range (about 7) also have a negative charge (figure 6), which causes electrostatic repulsion of oil particles and TMSP\textsubscript{600}.

Thus, TMSP\textsubscript{600} is an effective sorbent for the purification of both pure and surfactant-stabilized emulsions, and the interaction proceeds due to various mechanisms of electrostatic interaction and the properties of hydrophobic particles.

4. Conclusion
It was confirmed that TMSP\textsubscript{600} can be used as a sorbent for emulsified vegetable oils; the purification efficiency of model emulsions is more than 98%.

When sodium lauryl sulfate is added to the model system, the purification efficiency decreases, however, it remains quite high with synthetic surfactants concentration \(C<0.01 \text{ mg/dm}^3\). The decrease in purification efficiency is due to the presence of a negative charge in micro droplets of oils surrounded by molecules of sodium lauryl sulfate since the particles of sorption material at pH 7 also have a negative charge and electrostatic repulsion of oil particles and TMSP\textsubscript{600} occur.

It can be concluded that TMSP\textsubscript{600} is a promising sorption material for sewage treatment containing vegetable oil residues.

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