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Regularities of Sorption-based Removal of Petroleum Products from Model Aqueous Solutions using Saponite Clay of Ukrainian Origin

Abstract: Industrial wastewater contains petroleum products, heavy metal ions, and a wide range of chemical compounds. Harmful chemical elements and substances enter water bodies, degrading their sanitary condition; therefore, thorough treatment is necessary before the water can be used for domestic, drinking, and certain industrial purposes. Many the most obvious trends in changes to the quality of natural waters under the influence of human economic activity can be identified. Petroleum products entering the environment negatively impact the “water body–soil–flora and fauna–human” ecosystem and are among the most dangerous components of wastewater pollution. They have a harmful effect on biochemical and physiological processes in living organisms. The use of natural minerals, such as saponite clay, for sorption-based wastewater treatment to remove petroleum products is acceptable from both environmental and economic perspectives; however, such materials often lack the necessary sorption properties and require chemical modification. The modification allows for the production of sorbents, whose surface differs from that of the original mineral and combines the beneficial properties of the source material and synthetic sorbents. In this study, the influence of various factors on the efficiency of sorption-based removal of petroleum products using native saponite clay samples was investigated, since their use (without prior modification) is more economically feasible. The influence of parameters such as sorbent dose, pH, temperature, and concentration of petroleum products on the efficiency of sorption extraction of petroleum products was analysed. Optimal conditions for the sorption process were established.

Keywords: sorption, petroleum products, saponite clay, recovery rate, optimal conditions.

Introduction

Petroleum refining waste (oil sludge) consists of amphoteric or fine-crystalline masses containing 20–80% water. The chemical composition of oil sludge is extremely complex and

includes aliphatic and aromatic hydrocarbons, carboxylic acids, asphaltenes, tar, metal ions, mechanical impurities, and radioactive elements.

A significant portion of petroleum products and a wide range of organic compounds originate from lubricating and cooling fluids (oil-based and water-miscible) and degreasing solutions.

Oil-based coolants consist of mineral oils (70–90%) with or without additives serving various functional purposes. Water-miscible coolants include three types: emulsifiable, semi-synthetic, and synthetic (*Kosheleva et al., 2022*).

Emulsifiable coolants (emulsions) are specially formulated (balanced) mixtures of mineral oils, emulsifiers, binding agents (water, alcohols, glycols, etc.), corrosion inhibitors, biocides, defoamers, and various additives. So-called water-miscible coolants—semi-synthetic (containing insignificant amounts of petroleum oils) and synthetic (containing no petroleum oils)—are finding increasingly widespread use in addition to emulsions; these mix well with water and form stable colloidal emulsions or solutions.

The most important components of coolants are vegetable oils (rapeseed, coriander, castor, and cottonseed), animal fats, and fat substitutes (synthetic fatty acids, naphthenic acids) (*Maia Cardoso et al., 2021*).

Modern coolants contain additives with various functional purposes (0.5–15%). These are primarily anti-wear, anti-seize, and antioxidant additives. The additives used include phosphates and dialkyl phosphates, dialkyldithiophosphates and dialkyldithiocarbamates of metals, salts of amines and amides of dialkylphosphoric acids, sulfurized fats, organic sulphides and polysulfides, chlorinated paraffins, antioxidants such as aromatic amines, alkanolamines, and polydimethylsiloxane fluids (anti-foaming additives).

Biocides are added to coolants to protect them from microbiological degradation. Triazines are used as biocides in coolants; oxazolines, thiazolines, formalin, fibracillin, hexachlorophene, vasin, and others are also recommended. All components of coolants can have a negative impact on the environment (*Bingari et al., 2024*).

The classification of waste by hazard class is based on indicators characterizing the impact of toxic pollutants on ecosystems, including humans: toxicity, cumulative effects, and the ability to cause long-term effects.

Petroleum hydrocarbons belong to hazard class III. Some substances in the coolant belong to class IV (triethanolamine, carbamol, oleic acid) (*Emerike et al., 2022; Zamparas et al., 2020*).

Methods

Natural samples of saponite clay from the Varvarivskyi deposit (Ukraine) were used as the subject of the study.

The sorption properties of saponite clay were studied using model aqueous solutions (emulsions) of petroleum products with concentrations, mg/L: 20, 50, 100, 200, 250, 500. The dependence of the degree of petroleum product removal on the following parameters was investigated: sorbent dose (0,1; 0,5; 1; 1,5; 2; 2,5 g), pH (3, 5, 6, 7, 9), temperature (20, 25, 30, 35, 40°C).

The content of petroleum products in water was determined by IR spectroscopy using an IRAffinity-1S (Shimadzu) IR spectrophotometer in accordance with MBB Method No. 081/12-0877-13 “Reclaimed, surface, and groundwater”.

The determination of the content of petroleum products in water consists of four stages according to the methodology:

1. Extraction: Petroleum products are extracted from the water sample using a nonpolar solvent (e.g., carbon tetrachloride, tetrachloroethylene, or hexane).
2. Purification: The extract is passed through a column containing a sorbent (aluminum oxide or silica gel) to separate petroleum products from polar compounds, such as natural fats and vegetable oils.
3. Measurement: The purified solution is placed in an IR spectrometer or infrared photometer. The instrument records the degree of light absorption at a wavelength of approximately $3.4 \mu\text{m}$ (2930 cm^{-1}), which corresponds to the valence vibrations of C-H bonds.

Calculation: The concentration is determined using a calibration curve constructed from standard solutions of reference petroleum products.

Literature Review

Wastewater Treatment at Oil Refineries. Effective treatment of wastewater containing petroleum products is an essential step in refinery production cycles, as water is used as:

- a coolant for equipment, units, and finished products;
- a source of condensate and steam;
- a solvent for mixing reagents (*Melnykov et al., 2026*).

After water is used in these processes, the wastewater may have varying degrees of contamination and differ in the composition of pollutants. It may contain:

- urea and ammonium ions;
- cyclic organic hydrocarbons and phenol;
- surfactants and paraffins;
- fatty acids, petroleum products, sulphates, and other contaminants (*Chruszcz-Lipska, 2024*).

Installing oil separators or wastewater treatment systems for petroleum products allows the wastewater to be treated to a safe condition. Afterward, it can be discharged into sewer systems, onto the ground, into water bodies, or reused.

Technologies for Removing Oil Products from Water. There are two main technologies for treating oil-contaminated wastewater:

- mechanical.
- physicochemical (*Bekchanov et al., 2023; Łach et al., 2023*).

Mechanical removal of petroleum products from wastewater. This method of treating wastewater from oil refineries allows for the removal of up to 65% of contaminants from the effluent. The mechanical wastewater treatment process involves settling in oil separators. Wastewater is placed in tanks, where it is treated to remove petroleum products over a period of 6–24 hours. These tanks can be either static or dynamic. In the former case, the wastewater remains stationary; in the latter, it moves vertically or horizontally (*Tekeyeh et al., 2025; Zaker et al., 2025*).

Physicochemical treatment of wastewater from oil refineries. This technology removes suspended solids and water-soluble impurities from the effluent. The most effective methods for removing petroleum products from water are:

1. Flotation is removal of colloidal and dispersed contaminants from the medium using gas bubbles.
2. Sorption is adsorption of contaminants from the medium by the surfaces of adsorbents (solid materials). The following can be used for this purpose: activated carbon, alumogel, silica gel, zeolites.
3. Ion exchange is ion-exchange materials remove ions from the medium, replacing them with an equal number of ions from the ionite.
4. Hyperfiltration is treatment of oil-containing wastewater using reverse osmosis systems. The wastewater is fed under high pressure through semipermeable membranes, which purify the water at the molecular level.
5. Neutralization is removal of alkalis and acids from the treated medium.
6. Extraction is the redistribution of contaminants in a mixture of two mutually insoluble liquids.
7. Evaporation is a method of treating wastewater from oil refineries by passing steam heated to 100°C through the contaminated medium (*Hrynysbyn & Znak, 2024*).

Sorption is one of the most promising methods for removing petroleum products from water, both in terms of cost and efficiency.

Saponite is one of the most promising natural sorbents. The removal of petroleum products from water using saponite is based on its unique natural properties: it is a magnesium aluminosilicate that acts as a powerful adsorbent and ion exchanger. The mineral effectively binds hydrocarbons, heavy metals, and toxins, but has its own technological characteristics.

How saponite works?

Purification mechanism: Oil product molecules adhere to the highly developed internal and external surfaces of the mineral (adsorption).

Form of application: It is used in powder form (saponite flour) for treating stains, or as a filter media in industrial and local treatment facilities.

Advantage over other clays: Saponite forms a denser and more easily collectable sediment, thanks to its layered structure and lack of significant swelling in water (unlike bentonite).

Water purification methods:

1. Filtration method (for wastewater): Water is passed through multi-layer filters, where saponite acts as the main sorption layer. Once saturated, the filter is regenerated.
2. Direct application (for open water bodies/oil spills): The powder is sprayed over the water's surface, binds oil products into flakes, and settles to the bottom for subsequent mechanical collection (*Romanovsky et al., 2025*).

Limitations and challenges are following. Water absorption. Saponite must be as dry as possible before being introduced into water like many natural clays. Otherwise, its pores will be blocked by its own moisture molecules, which will reduce its oil-holding capacity. Waste disposal. Spent mineral saturated with oil products is classified as hazardous waste. It cannot simply be discarded; it must be disposed of in accordance with environmental regulations (for example, incineration at specialized landfills, since the clay has refractory properties). Difficult regeneration. It is much more difficult to extract oil from saponite for reuse unlike some synthetic or carbon-based sorbents.

Results

The first experiment was devoted to investigating the dependence of the removal degree of oil product removal on the sorbent dose. Initial conditions: duration—15 min, pH 7, oil product solution concentration—100 mg/L, temperature 20°C, volume of the model aqueous solution—100 mL.

It was found that as the sorbent dose increased from 0.1 g to 2 g, the degree of oil product removal increased from 10% to 96%. The degree of oil product removal remained practically constant (not exceeding 97%) with a further increase in the sorbent dose (up to 2.5 g) (*Figure 1*).

The second experiment was devoted to investigating the dependence of the removal degree of oil product removal on the pH of the model aqueous solution. Initial conditions: duration – 15 min, oil product solution concentration—100 mg/L, temperature 20°C, volume of the model aqueous solution—100 mL, sorbent dose—2 g.

It was found that as the pH increased from 3 to 7, the degree of oil product removal increased from 21% to 96%. The degree of oil product removal decreased significantly (to 47%) with a further increase in pH (from 7 to 9) (*Figure 2*).

The third experiment was devoted to investigating the dependence of the removal degree of oil product removal on the temperature of the model aqueous solution. Initial conditions: duration—15 min, oil product solution concentration—100 mg/L, pH 7, volume of the model aqueous solution—100 mL, sorbent dose—2 g.

It was found that as the temperature increased from 20 to 40°C, a significant decrease in the degree of oil product removal was observed (from 99% to 38%) (*Figure 3*).

The fourth experiment was devoted to investigating the dependence of the degree of oil product removal on their concentration in the model aqueous solution. Initial conditions: duration—15 min, temperature 20°C, pH 7, volume of the model aqueous solution—100 mL, sorbent dose—2 g.

It was found that as the concentration of petroleum products increased from 20 mg/L to 500 mg/L, the degree of petroleum product removal decreased (from 99.9% to 72%) (*Figure 4*).

Thus, based on the studies conducted and the patterns identified, it can be concluded that the optimal conditions for the removal of petroleum products from model aqueous solutions are as follows: pH 7; sorbent dose—2 g per 100 mL of solution (further increases are impractical due to the extremely negligible increase in the degree of oil product removal); sorption process temperature—20°C (at higher temperatures, desorption processes evidently begin); concentration of petroleum products—100 mg/L (further increases require a proportional increase in the dose of saponite adsorbent).

Discussion

The following explanations for the observed patterns can be provided, based on the studies conducted.

The degree of petroleum product removal increases from 10% to 97% as the sorbent dose increases from 0.1 to 25 g per 100 mL of solution, which is due to an insufficient amount of sorbent in the range of 0.1 to 1.5 g per 100 mL of solution for effective removal of petroleum products. When the sorbent dose is increased to 2 g per 100 mL of solution, the removal efficiency increases to 96%. The extraction efficiency remains virtually unchanged, reaching 97% with a further

increase in the sorbent dose to 2.5 g per 100 mL of solution. This indicates that adding more than 2 g of sorbent per 100 mL of solution is economically unfeasible.

The degree of oil product removal also increases, reaching 96% as the pH of the solution increases from 3 to 7. However, the degree of oil product removal drops sharply and is 47% at pH 9 as the pH shifts toward the alkaline side. This is because acidic and, especially, neutral pH values contribute to the saponite surface acquiring a high affinity for petroleum products (the effect of a positively charged surface). The saponite surface apparently becomes negatively charged, preventing petroleum products from adhering to it at alkaline pH.

The degree of oil product removal decreases from 99% to 38% as the temperature increases from 20 to 40°C, which is associated with the predominance of desorption processes as the temperature rises (a well-known fact of the inversely proportional dependence of adsorption on temperature).

The degree of petroleum product removal remains nearly unchanged (98–99%) as the concentration of model aqueous solutions of petroleum products increases from 20 mg/L to 100 mg/L; however, it begins to decrease as the concentration of petroleum products continues to rise. This indicates that at petroleum product concentrations exceeding 100 mg/L, a sorbent dose of 2 g per 100 mL of solution is insufficient and must be increased in proportion to the rise in petroleum product concentration.

Conclusion

A literature review was conducted on the relevance of various methods for removing petroleum products from water. A comparative analysis revealed that sorption processes are among the most promising and effective methods for removing petroleum products from water, based on the literature review. The most promising sorbents, particularly from an economic standpoint, are natural clay minerals (e.g., saponite), which are abundant in Ukraine's subsoil.

A study was conducted on the effectiveness of sorption-based removal of petroleum products from model aqueous solutions using samples of natural saponite clay as a sorbent. The use of native saponite samples is motivated by the search for the most cost-effective method of removing petroleum products from large volumes of domestic and industrial wastewater. In addition, pre-modification of saponite clay leads to an increase in both the duration of the process and the need for additional reagents, which affect the cost of treated water and may be a source of secondary contamination.

It was established that to optimize sorption conditions, the following recommendations must be followed: the concentration of petroleum product solutions should not exceed 100 mg/L; the pH should be neutral; the process temperature should be as low as possible (at least 20°C); and the sorbent dosage should be 2 g per 100 mL of solution.

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Conflict of Interest

The author declares that there is no conflict of interest.

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Appendix

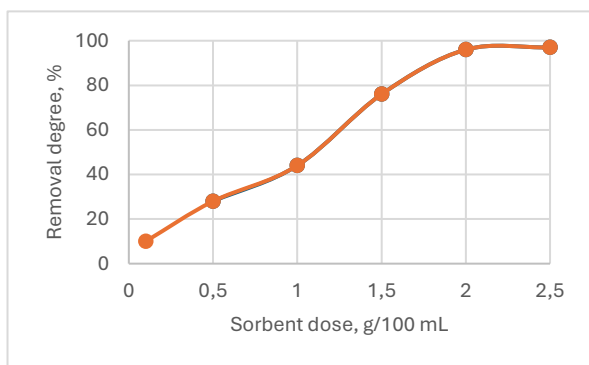


Figure 1. Dependence of the degree of petroleum product removal on the sorbent dose

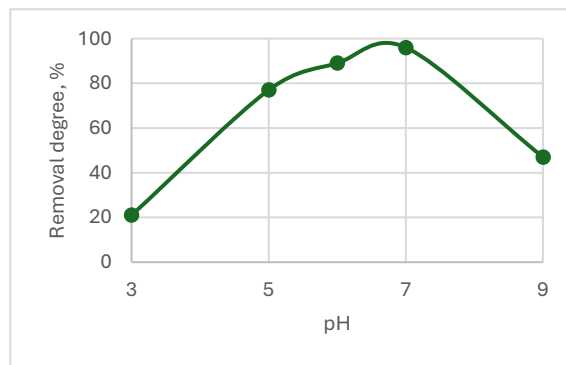


Figure 2. Dependence of the degree of oil product removal on the pH of the model aqueous solution

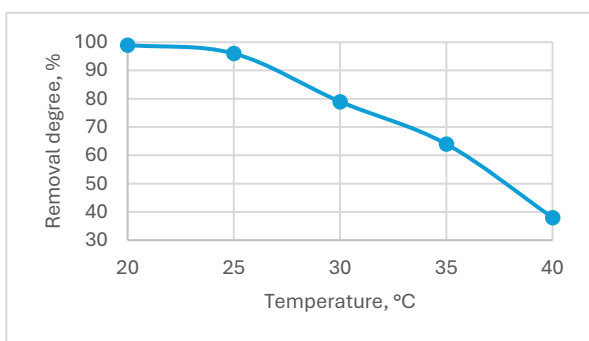


Figure 3. Dependence of the degree of oil product removal on the temperature of the model aqueous solution

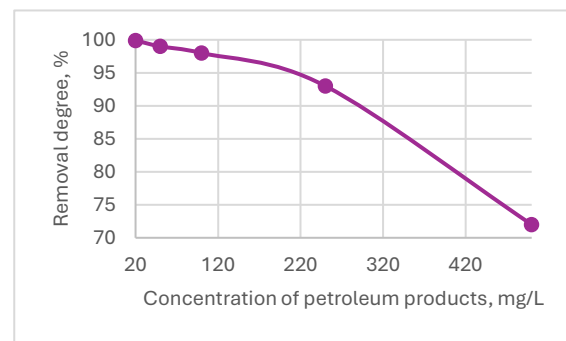


Figure 4. Dependence of the degree of oil product removal on the concentration of oil products