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Research Article

# Optimization of the oil sludge collection process based on analysis of composition and sedimentation behavior

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## ABSTRACT

Treatment of industrial wastewater prior to discharge into the environment is essential due to the presence of toxic compounds, high organic load, and complex pollutants. This study investigates the characteristics of oily sludges and examines practical methods for their collection in the ponds of the Mahshahr refinery. Effluent samples were collected after the primary sedimentation stage, and their BOD and COD parameters were measured under environmental conditions of 22.6 °C temperature, 43.9% humidity, and 756 mm Hg pressure. The results indicated that wastewater treatment and waste management processes in refineries are fundamentally similar, allowing the use of a unified treatment approach for both. The application of sludge pumps proved effective in improving environmental cleanliness and operational efficiency. For sludge recovery, the thermal pyrolysis method was employed, which not only reduced sludge volume but also enabled the production of reusable liquid fuel and combustible gases. Overall, the findings suggest that the application of thermal technologies can serve as an efficient and sustainable approach for managing oily refinery sludges.

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## Introduction

Oil sludge is a persistent problem in the oil refining industry, causing corrosion, reducing storage capacity, and imposing heavy removal and disposal costs, which have significant economic and environmental impacts. These sludges consist of polycyclic aliphatic and aromatic hydrocarbon compounds and, if disposed of improperly, can cause severe environmental pollution [1-3].

In refineries, especially in Mahshahr, a significant portion of this sludge accumulates in storage ponds. Manual or pumped discharge of these wastes is associated with many technical problems and health risks due to the high concentration and toxic nature of the materials. Today, the use of industrial suction units (sludge extractors) with high vacuum power is considered a safe and efficient alternative to traditional methods and, in addition to increasing the speed and quality of operations, prevents illness and injury to employees [4, 5].

After collection, the sludge treatment stage is carried out, which, depending on the type of compounds, includes processes such as concentration, stabilization, drying, waste incineration, stabilization, freezing, composting, or the use of biological cells [5, 6]. In this study, the use of biological treatment using the activated sludge method is proposed. This method, using microorganisms, can be applied in both aerobic and anaerobic modes and, due to its high efficiency and adaptability to different operating conditions, is considered an effective method for reducing pollution and recycling oil sludge.

The main objective of this study is to improve the methods of collecting and treating oil sludge in the ponds of the Mahshahr refinery in order to prevent stagnation and re-pollution of the environment and to enable the reuse of the treated wastewater in the industrial cycle.

## 2. Experimental

### *2.1. Materials, Equipment, and Method*

In this study, biological treatment of wastewater was carried out by examining BOD and COD parameters. The wastewater sample used from the Mahshahr refinery ponds was collected after initial sedimentation and transferred to the laboratory under ambient conditions of 22.6 °C, 43.9% humidity, and 756 mm Hg pressure

COD: After homogenization with a mixer, the sample was placed in a vial containing COD reagent. The control vial was prepared with distilled water. Both vials were placed in a COD reactor preheated at 150 °C for 2 hours and then cooled. The COD level of the sample was measured using a spectrophotometer at a wavelength of 350 nm.

The BOD sample was transferred to a BOD track bottle after cooling at 2 °C. Bacterial buffer and magnetic stirrer were added to the bottle and the surface of the bottle was greased with oil. Lithium hydroxide was added in such a way that it did not mix with the sample. The bottle was placed in the BOD track device and the test was carried out in the incubator for 5 days. After the end of the time, the BOD value was read from the device. Finally, the sludge resulting from the biological wastewater treatment process was collected, treated, and recycled.

## 3. Results and Discussion

### *3.1. Investigation of pyrolysis kinetics and recycling of oil sludge from Mahshahr refinery*

In recent years, the use of thermal decomposition methods, especially pyrolysis, has been considered as one of the accurate and advanced methods in investigating the thermal behavior of fossil fuels and oil sludge. In this study, oil sludge from the residue of the Mahshahr refinery, known as Cracked Fuel Oil (CFO), was investigated [7, 8]. Oil sludge is converted into intermediate materials and ultimately into petroleum coke through the processes of thermal cracking and thermal polymerization of heavy hydrocarbons present in the oil feed.

Almost all carbon-containing materials have the ability to be converted into coke in two stages: first, pyrolysis reactions and the production of intermediate compounds; and second, coke formation due to further heating [8, 9]. The main reactions involved in this process include: 1. C–C and C–H bond cleavage and free radical generation 2. Molecular rearrangement 3. Thermal polymerization 4. Aromatic condensation 5. Side branch removal and dehydrogenation reactions These reactions occur simultaneously and continuously during the pyrolysis process and lead to the formation of a porous structure in the final coke [10, 11].

The thermal cracking process usually starts at a temperature of about 350°C, in which heavy petroleum compounds with more than a thousand different compounds are converted into coke. Thermogravimetric analysis (TGA) was used to investigate the thermal behavior of

CFO [11-14]. In this method, a sample with a mass of approximately 27 mg was heated in an aluminum crucible in a nitrogen atmosphere with a flow rate of 80 ml/min, with a linear heating rate of 5°/min, from 45°C to 700°C. The resulting data, including weight change (TG) and derivative (DTG) plots, were examined to analyze the kinetics of pyrolysis and thermal reactions.

Two figs (1) and (2) show the changes in BOD and COD parameters compared to the standard values. As can be seen, the increase in the values of these parameters is beyond the standard limit. This situation is mainly due to the following reasons:

1. Excessive injection of chemicals in the treatment process.

2. Extensive leakage of grease and oil into the ponds, which reduces the efficiency of the aeration system in the treatment units.

3. The old age of some process units, including distillation units, has a negative effect on the quality of the effluent.

Considering these factors and the information in the Figs, it can be concluded that the effluent output of the refinery is currently above the standard range and requires corrective measures and optimization of the treatment processes.

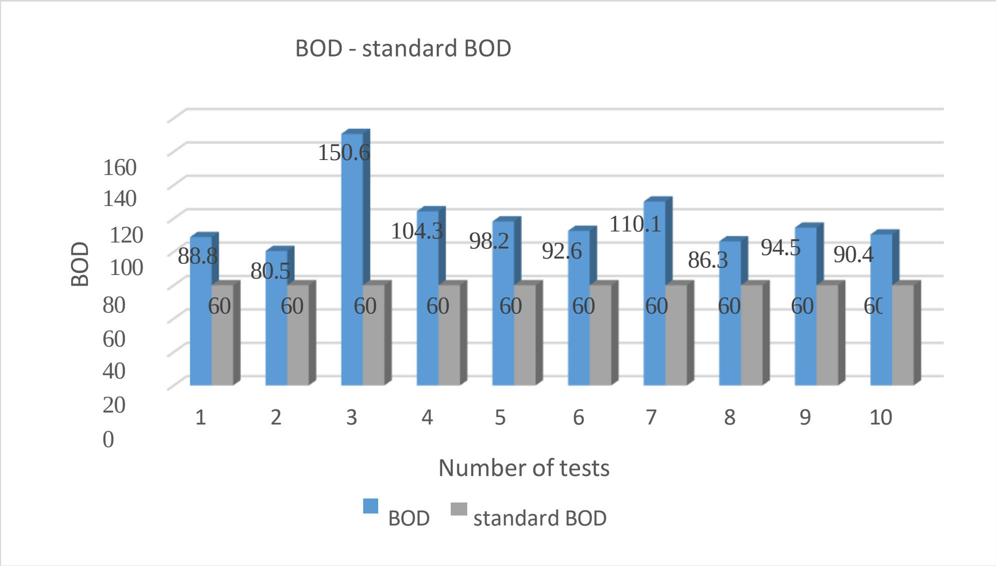


**Fig. 1.** Comparison of BOD results obtained with standard BOD

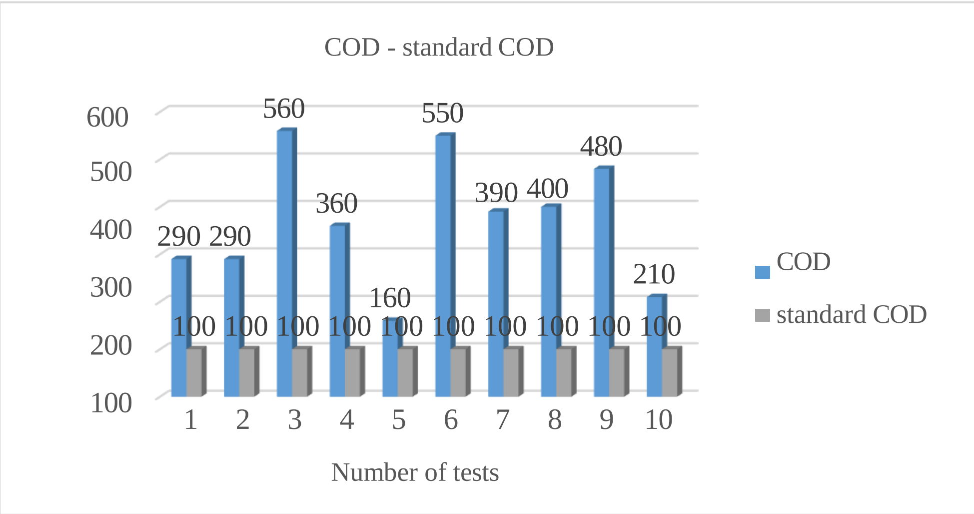


**Fig. 2.** Comparison of the obtained COD results with the standard COD

According to Figs (3) and (4), it can be concluded that the three parameters BOD, COD, and pH have a direct effect on each other. As is clear, the ratio of COD to BOD is approximately 2 times. Therefore, as the COD and BOD values decrease towards standard values, this decrease can also affect other wastewater parameters, including pH, because pH has a direct relationship with these two parameters and its change can help reduce BOD and COD.

If the test is performed in the environment, it is necessary to measure all four parameters: BOD, COD, pH, and temperature. However, if the test is performed in a laboratory environment, in addition to BOD and COD, it is also necessary to measure temperature. Here are the BOD-COD-Temperature Figs that show the changes in these parameters.

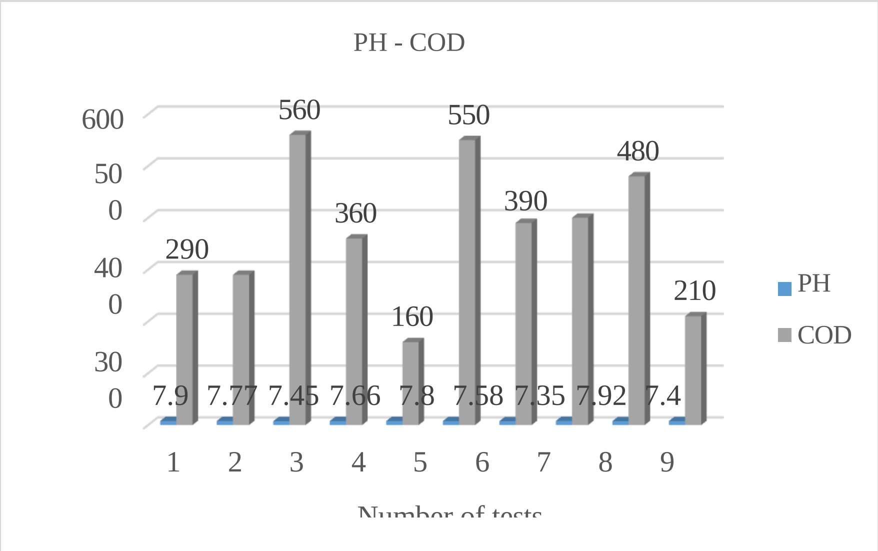


**Fig. 3.** Comparison of COD and pH results

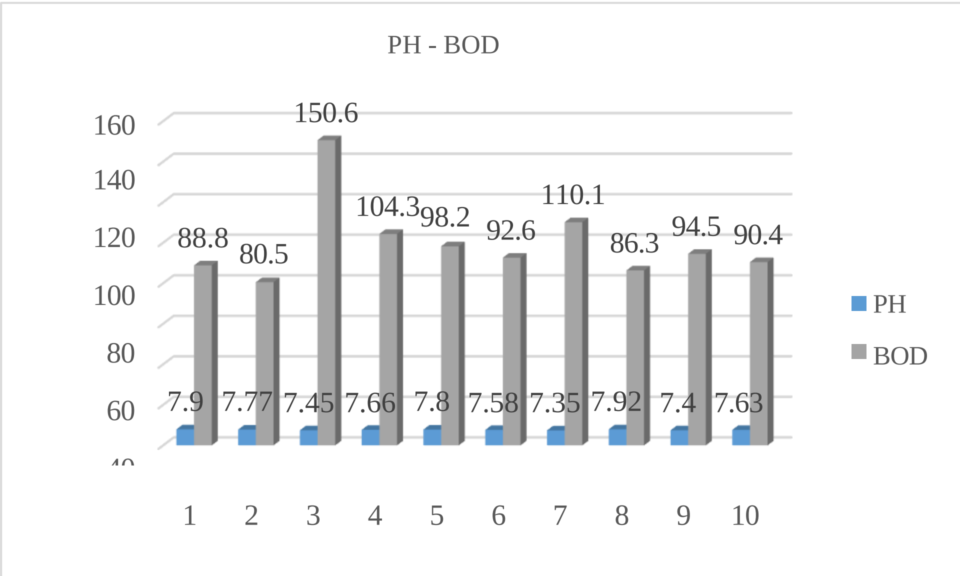


**Fig. 4.** Comparison of BOD and pH results

According to Figs (5) and (6), it can be concluded that increasing the temperature above 20°C leads to a decrease in the efficiency of BOD and COD removal. This is due to the decrease in the activity of microorganisms at temperatures above this limit, which means a decrease in the ability to remove contaminants. In the Mahshahr refinery, biological treatment was used in the past; but due to the bacteria not surviving during the treatment stages, this method was stopped. In the present project, an attempt has been made to provide conditions in which the bacteria remain alive until the end of the treatment stages by controlling parameters such as pH, temperature, providing suitable food for the bacteria, and sufficient aeration. In industrial wastewater treatment, two important principles are noteworthy: first, preventing waste and pollution as much as possible and separating the discharge channels based on the type of pollutants, and second, performing preliminary treatment of pollution at the production site. Based on the research conducted, the refinery wastewater treatment system should include preliminary and biological treatment stages.

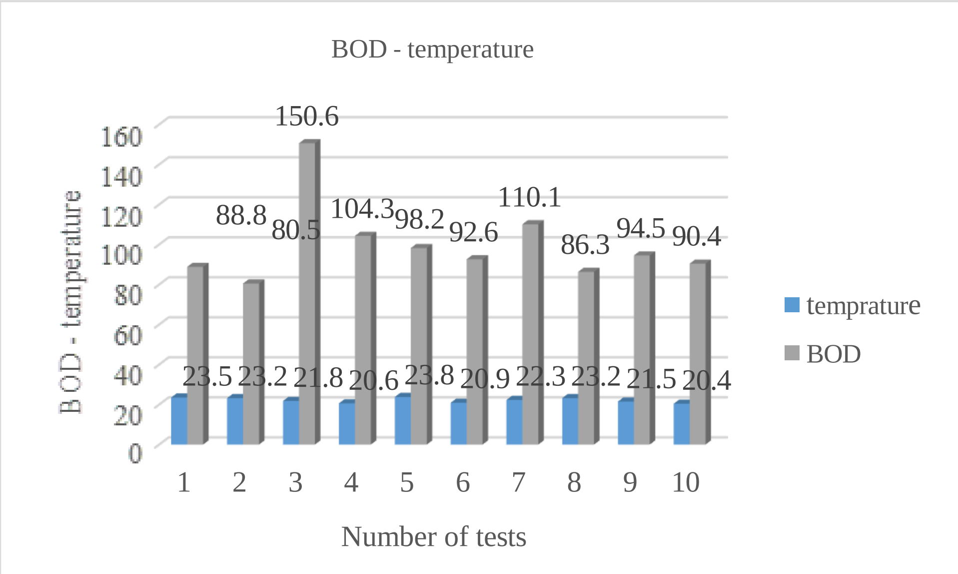


**Fig. 5.** Comparison of BOD and temperature results

Also, given that the treated wastewater is to be used for purposes such as cooling tower make-up water or agricultural irrigation, there is a need for some advanced treatment processes. The best use of treated wastewater is primarily in the refinery cooling system and secondarily in the irrigation of the refinery's green space. Also, the use of biological sludge as agricultural fertilizer is suggested as a suitable solution.

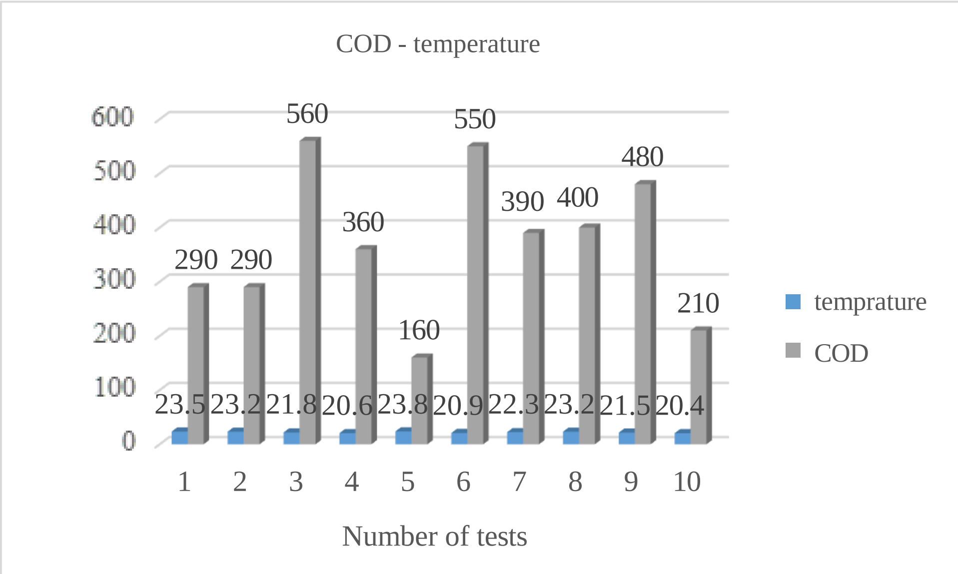


**Fig. 6.** Comparison of COD and temperature results

### *3.2. Results of thermal analysis (pyrolysis) experiments for oil sludge recovery*

The TG and DTG curves are shown in Fig (7) and the DTA curve from dynamic-thermal experiments on CFO feed with a heating rate of 5 °C/min is shown in Fig (8). According to Figure 1 and its comparison with similar processes presented in reputable articles, it is clear that the heating process of the feed in question cannot be examined as a single stage because coke production includes thousands of complex and simultaneous reactions. Therefore, in this study, the kinetics of the reactions in three separate thermal stages have been examined: The first stage (temperature less than 285 °C): In this temperature range, light and volatile materials are removed from the sample and the cracking reaction has not yet begun.

The second stage (temperature 320 to 450 °C): The initiation of thermal cracking reactions occurs in this temperature range. As mentioned in the theoretical section, coke formation begins when the asphaltene concentration reaches its maximum. Therefore, the onset of thermal cracking can be considered equivalent to asphaltene cracking. Third stage (temperature above 467 °C): As the cracking reactions progress and the temperature increases, secondary thermal cracking reactions also become important. In this stage, the viscosity of the system increases dramatically due to the formation of crosslinks and chemical reactions, and the fine coke particles are connected to each other and form a coke mass. Analysis of the thermal data showed that in the first stage, the reactions are consistent with the first-order equation. In the second stage, due to the onset of coke formation, the data were better matched with the second-order reaction equation, which is a reasonable prediction. In the third stage, the data were again consistent with the first-order equation, indicating the progress of thermal cracking reactions. The detailed results for all three thermal stages are presented in detail in Table (1).

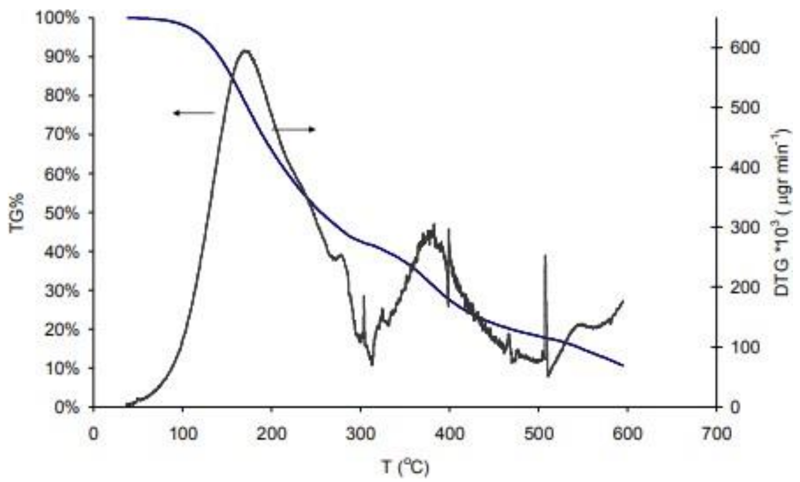


**Fig. 7.** TG and DTG curves of CFO feed

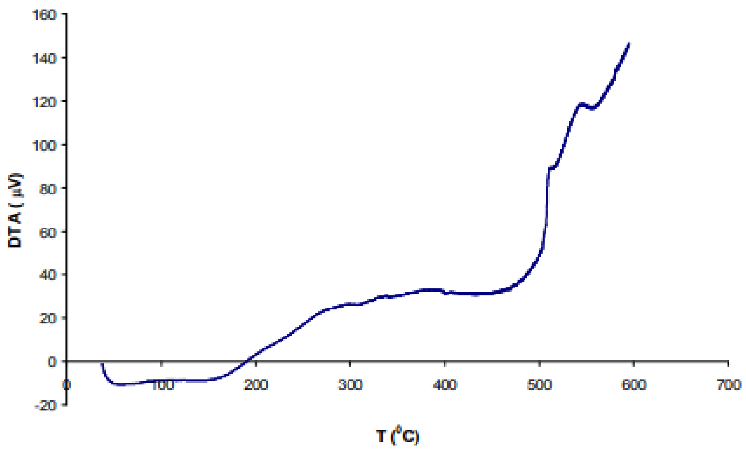


**Fig. 8.** CFO Feed DTA Curve

**Table 1.** Kinetic parameters in different temperature ranges

| 45°C – 295°C | | | | 340°C – 480°C | | | | 470°C – 700°C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n$ | $E_a$ $(kj/mol)$ | $A$ $(min^{-1})$ | $R^2$ | $n$ | $E_a$ $(kj/mol)$ | $A$ $(min^{-1})$ | $R^2$ | $n$ | $E_a$ $(kj/mol)$ | $A$ $(min^{-1})$ | $R^2$ |
| 1 | 38.824 | 657.792 | 0.9454 | 2 | 30.797 | 46.752 | 0.9551 | 1 | 58.131 | 437.924 | 0.9499 |

The pyrolysis kinetics of CFO feed were studied in three different temperature ranges including 295-45°C, 480-340°C, and 700-470°C. The results showed that the reaction equations in these temperature ranges followed first-order, second-order, and first-order reactions, respectively. Based on the determined reaction order and data obtained from thermal analysis, the activation energy and exponential function coefficient values were calculated for each stage and their differences were investigated.

## 4. Conclusion

In industrial wastewater treatment, two important principles can be mentioned: first, preventing (as much as possible) the creation of waste and pollution and separating the channel according to the type of pollution and second, preliminary treatment of pollution at the production unit site. According to research, in order for the refinery wastewater to be treated in a systematic manner and the remaining waste to be subjected to the correct process, the refinery wastewater treatment system should not only include preliminary and biological treatment stages, but also, given that the wastewater treated in refineries is intended to be used as make-up water for cooling towers or for agriculture and irrigation, some advanced treatment operations should be performed on it.

The best use of the treated wastewater is primarily in the cooling system and secondly in the irrigation system for the green space of the refinery, and the best use of biological sludge is recommended as agricultural fertilizer.

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