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Detection of oil pollution on the Tigris River in Iraq using Fluorescence and Reflecting Techniques

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Keywords

: Fluorescence, Oil Slick, Minerals Contamination, Detection, Broad Band Source, Tigris River Oil Pollution.

RESEARCH PAPER

Detection of Oil Pollution on the Tigris River in Iraq Using Fluorescence and Reflecting Techniques

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Abstract

In this study, a broadband light source (visible and ultraviolet) was used to name minerals via fluorescence spectra and estimate slick oil thickness, ranging from sub-millimetres, using the reflecting spectrum technique. Using a fluorescent technique, we obtained fluorescence spectra of the samples, converting and processing the signals to produce high-resolution data, which enabled the identification of the types of dissolved elements and oil slicks in the Tigris River, highlighting pollution sources and potential control measures. This system aims to show the faint signal in fluorescence samples collected from the cooling system outlet water throughout the refining process from AL-Dora (Baghdad) and Baiji (180 km north of Baghdad) refineries on the Tigris River. A simple optical technique is proposed for remote testing to figure out slick oil thickness and detect dissolved minerals in river water for the first time in Iraq. Accurate detection of minerals and slicks is achieved as mineral oil stimulated by UV light emits visible wavelengths, with a detection limit of 0.5 ppm. Laboratory measurements of sub-millimetre oil slick thickness were conducted, with fluorescence detected using systems running at various excitation wavelengths. The research focuses on measuring the thickness of oil slicks on water surfaces and differentiating between distinct types of mineral pollutants. This capability to distinguish pollutants based on their physical and chemical characteristics introduces a novel aspect to the study, highlighting the technique's versatility in analysing complex mixtures.

Keywords: Fluorescence, Oil slick, Minerals contamination, Detection, Broad band source, Tigris River oil pollution

1. Introduction

One of Mesopotamia's two great rivers, the Tigris, is essential to the survival of the country's inhabitants and ecosystems. Like many other bodies of water worldwide, the Tigris River faces environmental issues, such as pollution from several sources. Oil spills are a significant cause of river contamination and can have disastrous consequences for aquatic life, human health, and water quality. The oil industry is vital to Iraq's economy, but it also creates environmental dangers, mainly when there are oil spills. Our study focuses on two major refined oil sectors: AL-Dora Refined (found in Baghdad) and Baiji Refined (approximately 180 km north of Baghdad), as shown in Fig. 1. These two refined oil sectors have been linked to oil contamination in the Tigris. The detection and monitoring of such oil spills are critical for mitigating their effects and holding responsible parties accountable [1–3]. The accuracy and effectiveness of traditional approaches for finding oil pollution in aquatic bodies may be constrained by their reliance on chemical analysis or visual observations. Fluorescence techniques have become a practical method for the sensitive and quick identification of oil pollution in water in recent years. Fluorescence techniques use the unique fluorescence properties of various chemicals, especially oil molecules, to detect and quantify their presence in water samples. These methods come with several benefits, such as being extremely sensitive, allowing for real-time monitoring, and the ability to distinguish between several types of pollutants. Notably, fluorescence

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Fig. 1. Iraqi map highlights the locations of refineries and oil fields situated along the Tigris River [22].

techniques had been introduced to detect oil spills in sea and revers water in several research's [4–6].

Oil refining operations in Iraq have had a significant impact on rivers, leading to pollution in both water and air due to the buildup of oil waste from ongoing refining activities [3]. To address this issue, spectroscopic techniques, including fluorescent spectroscopy, are being used to detect oil contamination in water. These techniques encompass various methods such as laser-induced fluorescence spectroscopy [7–9], optical image profiling (OIP) [10], absorbance spectroscopy [11,12], fluorescence lidar [13], laser Raman spectroscopy [14], near-infrared spectroscopy [15], Differential Optical Absorption Spectroscopy (DOAS) [16], Optical Remote Sensing [17] and Fluorescence techniques [18–20].

In this study, we focused on using fluorescent spectroscopy. We designed a system that includes both a source and a detector, which works together to send and receive optical signals. This allows us to measure the types of minerals present, the thickness of oil slicks, and the concentrations of dissolved metals in the water. The system is also capable of detecting oil slicks leaking into river water because of wastewater from oil refining operations [17]. Our approach has proven effective in finding oil pollutants with high sensitivity and accuracy. This technique not only helps in detecting mineral pollutants and oil spills on the water's surface but also provides estimates of the size of these spills. Overall, this method is particularly efficient for assessing mineral contaminants in aquatic environments affected by oil spills, as it allows us to estimate slick thickness and characterize these pollutants using fluorescence spectroscopy [19–21].

This study aims to explore how effective fluorescence techniques are in detecting oil spills in the Tigris River in Iraq, specifically those linked to the AL-Dora and Baiji refining sectors. By using the unique fluorescence signatures of oil molecules, we hope to develop a reliable and efficient method for finding and monitoring oil spills in the river. This research marks the first time fluorescence techniques have been used for oil spill detection in the Tigris River, being a significant step forward in understanding water pollution in Iraq's rivers. Our study highlights several key advancements, particularly in the innovative application of fluorescence and reflectance spectroscopy to find mineral contaminants. Some of the notable benefits of these spectroscopic techniques over traditional methods include faster analysis, heightened sensitivity to trace pollutants, and the ability to conduct assessments directly in the field. By using spectral fingerprints, we are creating a novel approach to find the thickness of oil slicks and differentiate between several types of pollutants based on their physicochemical properties. The work sets up the foundation for future developments in crude oil analysis and environmental management in Iraq and provides a useful tool for the oil industry's pollution monitoring requirements, as well as its immediate application.

2. Experimental method

This study employed the fluorescence technique to find the spectral response of mineral oil slicks in the Tigris River water in Iraq. The emission spectra were collected by a quartz lens at an angle of 30°–35° and transmitted to a spectrometer for spectrally based analysis. Fig. 2 illustrates the fluorescent experimental setup. A broadband source-based free space sending was used to measure minerals of slick oil in water by fluorescence. The broadband source is deuterium-halogen Lamps (200–1100 nm); the specifications of the tools Lamp of a light source (Tungsten-Halogen), the largest wavelength of deuterium in the range (215–400) nm, and a tungsten-halogen range (360–1100) nm. A bulb life of

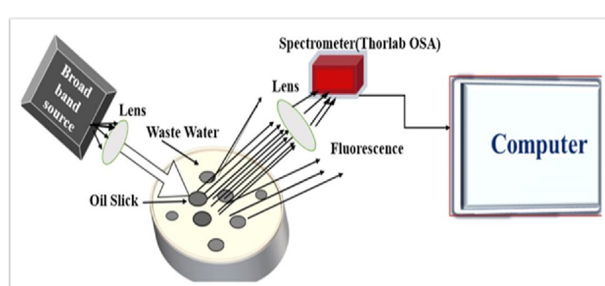


Fig. 2. The fluorescent experimental setup for the Laser Engineering laboratory.

1000 h, operating temperature (5−35) C°, was used to excite sample molecules. The spectrometer (THORLABS spectrometer) checked the fluorescent spectra for wavelengths ranging from 200 to 1000 nm. Al-Dora (south of Baghdad) and Baiji (180 km north of Baghdad) refineries provided the samples. The wastewater sample is from the oil refining cooling system (see Fig. 4). The samples are taken in a 1-L container with a related surface area of 10 cm^2. The fluorescence spectra response of the detector used for assessing mineral kinds and oil slick thickness in water remotely at varied distances from 1 m to 7 m maximum distance under laboratory circumstances is presented in Figs. 2 and 3.

Fig. (3) shows the slick oil thickness measurement at several meters (1−7) m. The relative reflectance intensity explained by Lambert−Beer's Law can be expressed in the following equation [17].

$$R_{oil} = T_{oil} \times R_{Dw} = 10^{-ad} \times R_{DW} \quad (1)$$

Where: R_{DW}: Reflectance of oil-free, optically deep water; T_{oil}, is oil slick transmittance; R_{oil} is oil slick reflectance, a is the oil slick absorption coefficient, d is the oil slick thickness.

3. Results and discussions

Tables 1 and 2 are inlet and Outlet water samples from the industrial water treatment (Cooling System, see Fig. 4) department at Al-Dura and Baji Refineries, where the samples were taken on September 5th, 2023, and April 3rd, 2023, respectively. Each refining plant's analytical laboratories measure the data in these tables. The PH, temperature, turbidity, conductivity, and other chemical characteristics of wastewater are all listed in these tables. The standard of the environmental limitations' column is from the Ministry of Environment in Iraq. These two tables are essential because they summarize the characteristics of the samples, from the refinery facilities' cooling system or the input water used in optical tests (the reflectance of the light and the fluorescence emission spectrum).

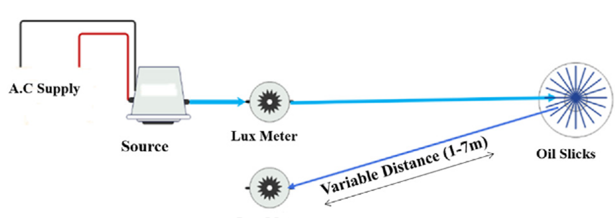


Fig. 3. A sketch of the experiment for slick oil thickness measurement.

Fig. 4. A picture of the cooling system oil refining.

Table 1. Test of inlet and Outlet water sample for treatment of industrial water in Cooling System dept. Al-Dura Refinery. Baghdad Iraq.

Item	Inlet Water	Outlet Water	Units
pH	7.9	7.4	
Temperature	29	23	C°
Total dissolved Salt (T.D.S)	960	465	ppm
Turbidity	71.5	5.97	NTU
Phenol	2.6	0.039	ppm
SO_4	363	369	ppm
Sulphide (S^{-2})	0.166	0.054	ppm
Suspended Solid	250	32	ppm
Oil	68.57	1.3	ppm
Chemical Oxygen Demand (COD)	341	50	Ppm
Biological Oxygen Demand (BOD)	74	13	Ppm
Phosphates (PO_4)	0.64	0.21	Ppm
Chloride ions	525	506	Ppm

Table 2. Test of inlet and Outlet water samples for the treatment of industrial water Cooling System, wastewater at Baji Refinery (180 km north of Baghdad).

Items	Inlet Water	Outlet Water	Units
pH	7.9	7.6	
Temperature	24	22.6	C^0
Cond./µs	1457	747	µs
Total dissolved Salt (T.D.S)	826	436	ppm
Turbidity	65.5	4.3	NTU
Dissolved (O_2)	3.6	4.2	ppm
Phenol	2.6	0.039	ppm
Sulphate (SO_4)	363	369	ppm
Sulphide (S^{-2})	0.166	0.054	ppm
Suspended Solid	250	32	ppm
Biological Oxygen Demand (BOD)	69	6	ppm
Oil	68.57	1.3	ppm
Chemical Oxygen Demand (COD)	341	50	ppm
Phosphates (PO_4)	0.64	0.21	ppm
Chloride Ions	525	506	ppm

The background spectrum before using the wastewater samples is shown in Fig. 5. Figs. (6 and

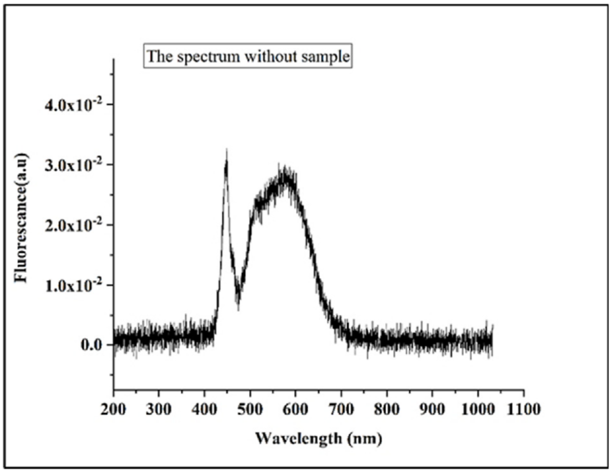
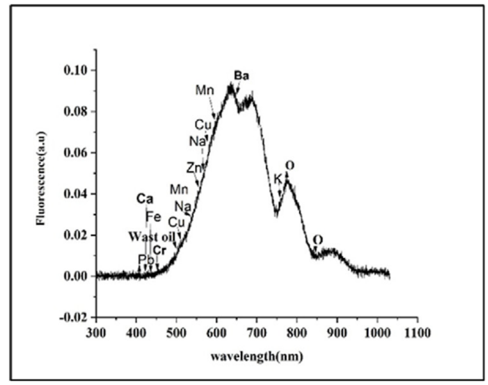


Fig. 5. The reference spectrum for the light source without a sample.

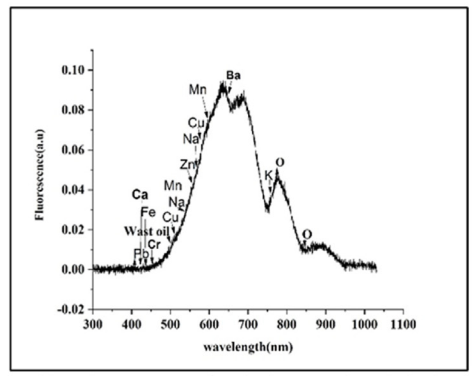
7) show the fluorescent emission spectrum of the water samples from the inlet water from Al-Dura and Baji Refinery, respectively. The measurements are done in laboratory conditions and at different distances from 1 m to 7 m. From Figs. (6 and 7), one can note that the spectrum received in the spectrometer is unaffected by the various distances used in the experiments and holds all the information about the minerals in the west water inter to the cooling units in the refineries.

From Figs. (5) and (6), we see that the fluorescence emission spectrum is in the range of 400–900 nm. The intensity of the fluorescence emission spectrum is higher for the Baiji refinery (0.18 a.u.) than for the Al-Dora refinery (0.1 a.u.), which is because of the nature of the crude oil used in each refinery system. The fluorescence wavelengths of the oil compositions are shown in Table 3, and the fluorescence wavelength emission spectrum is shown in Table 4. These fluorescence wavelength emissions are collected from Refs. [9,20] respectively. All the elements in the spectrum can be recognized in these tables, as shown in Figs. 6 and 7. This suggests that shorter wavelengths are more effective, but the entire range is suitable for fluorescence measurements.

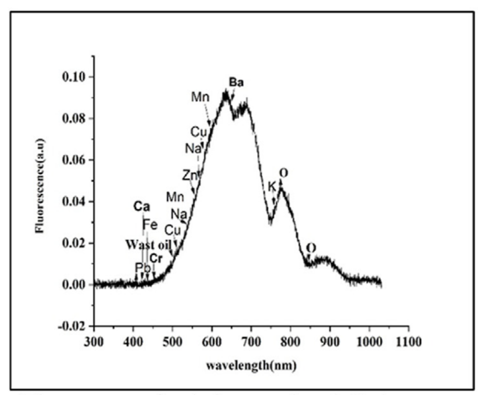
It has also been seen from Figs. 6 and 7 that the fluorescence intensity decreases with increasing excitation wavelengths beyond 680 nm. The results show that longer wavelengths are less effective in stimulating fluorescence, resulting in very weak fluorescence at the beginning of the infrared region. In achieving the maximum fluorescence intensity value in oil stains, excitation wavelengths of less than 400 nm should be focused on the range to obtain the best results.



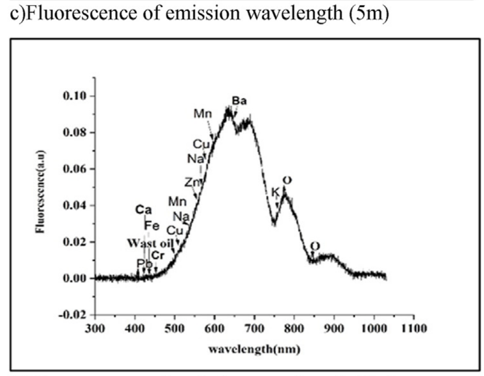
a) Fluorescence of emission wavelength (1m)



b) Fluorescence of emission wavelength (3m)

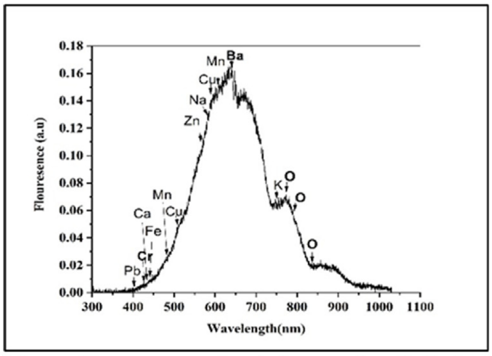


c)Fluorescence of emission wavelength (5m)

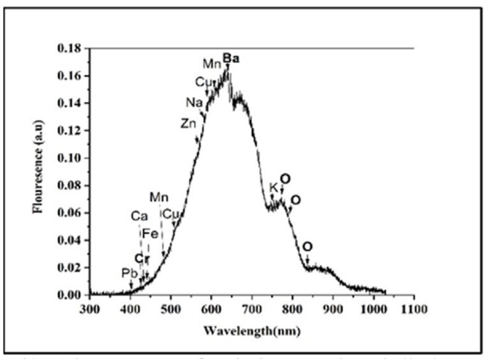


d) Fluorescence of emission wavelength (7m)

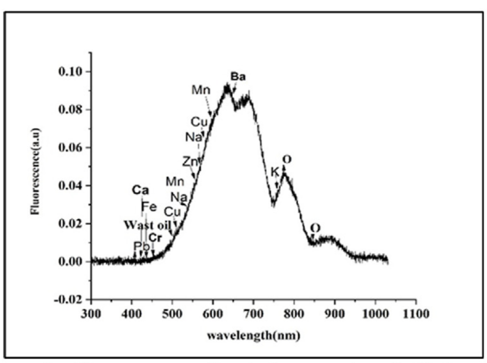
Fig. 6. Fluorescence spectra at different distances: (a)1 m, (b)3 m, (c)5 m, and (d)7 m, for wastewater treatment samples from the water-cooling system at Al Dura Refinery in Iraq.



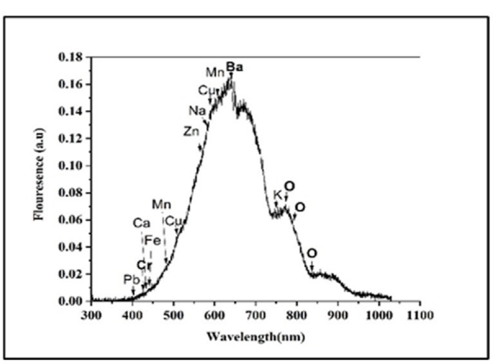
(a) Fluorescence of emission wavelength (1m)



b) Fluorescence of emission wavelength (3m)



c) Fluorescence of emission wavelength (5m)



d) Fluorescence of emission wavelength (7m)

Fig. 7. Fluorescence spectra at different distances: (a)1 m, (b)3 m, (c)5 m, and (d) 7 m, for wastewater treatment samples from the cooling system at Baiji refinery in Iraq.

Table 3. The fluorescence wavelength emission and Rayleigh scattering of the oil hydrocarbon (HC) compositions [9].

HC Sample	Rayleigh Scattering (nm)	Fluorescence Emission (nm)
Waste oil	450, 470	515
Diesel fuel	450, 465	585
Gasoline	450, 505	_
Lube oil	450	_

Table 4. Quantitative elemental determination (Fluorescence Emission Wavelength) [20].

Elements	Fluorescence Emission Wavelength (nm)
Pb	405.87
Si	288.16
Ca	393.37
Na	589.0
Zn	334.5
Sn	284.0
Cu	324.75
Ni	341.48
Al	396.15, 309.27
Fe	372.0, 373.49
Mg	285.21, 279.55
Cr	425.43, 283.57

Fig. 7 shows the fluorescence spectra at different distances: (a)1 m, (b)3 m, (c)5 m, and (d)7 m, for wastewater treatment samples from the water-cooling system at Baiji Refinery in Iraq.

Tables 5 and 6 and Fig. 8 show the relationship between slick oil thickness measurement and reflectance intensity for wastewater before treatment for the Al-Dora and Baji refining sectors, respectively. The results from the two tables are nearly similar for the samples from two different areas in Iraq, and the distance between them is more than 180 km. From these two tables, we note that when the thickness of the oil slick exceeds 180 μm, this technique is not affected, and one needs to use other analytical methods. These results confirm that this

Table 5. The relation of slick oil thickness measurement versus reflectance intensity for wastewater before treatment. Al-Dora refining sector.

Reflectance (R)	Slick oil thickness (μm) $d = \frac{ln\,(R)}{(0.13 \times (ln\,10))}$
108	156.4172
162	169.9627
200	177.0023
210	178.6323
215	179.4183
218	179.8813
220	180.1864
222	180.4887
223	180.6388

Table 6. The relation of slick oil thickness measurement versus reflectance intensity for wastewater before treatment in the Baiji refining sector.

Reflectance (R)	Slick oil thickness d(μm)
115	158.5152185
145	166.2590771
164	170.3726037
182	173.8516452
200	177.0023074
212	178.9489124
219	180.0341627
223	180.6388356
225	180.9371168

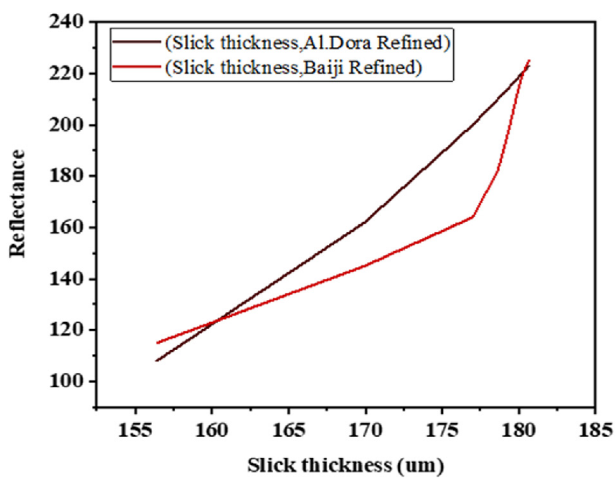


Fig. 8. Oil slick thickness for wastewater in the Al-Dora and Baiji refining sectors.

technique is correct and dependable in measuring the thickness of the oil layer floating on the river if the thickness is less than 200 μm.

As a summary of our results, we expressed pollution levels at different concentrations equivalent to distinct standards depending on absorption intensity [16,17] and fluorescence at the wavelengths used in evaluating different oil pollutants that have high fluorescence intensity when excited with wavelengths. Certain metals appear to have a higher fluorescence intensity when excited at a wavelength (400−900 nm). This characteristic of the fluorescent response distinguishes between the polluting components of the water. It is essential to assess water quality with an exact description of the fluorescence spectral behaviours to find the type of minerals and measure the thickness of oil stains in the water.

Wavelength directly affects excitation, as fluorescence intensity decreases with increasing wavelength beyond 700 nm, indicating that shorter wavelengths are more influential in fluorescence in these emulsions. This behaviour reflects the importance of choosing excitation wavelengths that are suitable for correct measurements. The paper shows specific excitation wavelengths that significantly enhance the fluorescence intensity of petroleum oil-in-water emulsions. Additionally, our results show that fluorescence and reflectance techniques can be used at different distances up to 7 m, limited by the laboratory's capabilities. These results can be generalised to a longer distance in real-world fields, such as rivers or other polluted regions, to detect oil slicks. The best excitation wavelength (highest absorption peak) affects the absorption and intensity, producing strong fluorescence responses in the emulsions. The study shows that the most effective fluorescence region occurs in the spectral region (400−900) nanometres, with a fluorescence peak seen in this range, and the maximum thickness that can be measured using the reflectance method is 180 μm.

There are several limitations to the fluorescence and reflectance spectral approach, despite its promising potential for examining minerals damaged by oil in Iraqi waters. First, there are issues with on-site deployment, such as noise and optical interference, which need to be fixed for reliable real-world use. Second, using just one wavelength might overlook important fluorescent data, suggesting that multi-wavelength analysis could enhance precision. Lastly, logistical challenges (such as the portability of field equipment and operational conditions) and environmental variables (like cross-contamination) may limit the practical application. These constraints suggest opportunities for further modification to enhance the method's dependability and applicability.

4. Conclusion

The identification of pollutants from the Al-Dora and Baiji refinery water cooling systems which have pollutants the Iraqi Tigris River by fluorescence technology. Our detection tool has excellent accuracy and efficiency, is responsive at a large distance and has sensitive capability. Remarkably, it could find slick thickness and detect mineral oil contamination during laboratory experiments at a range of up to 7 m. This study is important as it is the first time that fluorescence methods have been used for detecting oil pollution and slicks in the Tigris River. To reasonably estimate water quality, obvious spectrum-fluorescence properties and reflectance characteristics must be analyzed and found since they are useful to find minerals and floral thickness of oil spill on water. A decrease of the fluorescence intensity at longer wavelengths above 700 nm had been seen, showing the relevance of shorter wavelengths for absorption and emission in emulsions. We also discovered the peak excitation wavelengths which can increase fluorescence intensity of petroleum oil-in-water emulsions. Based on laboratory experiments, the fluorescence and reflectance techniques detect oil slicks as thick as 7 m and we assume that these results apply to larger distances (rivers and other contaminated areas). The best fluorescent region is in the spectral range 400−900 nm (the maximum measurable thickness by the reflectance method of the slicks of the oil is 180 μm). In general, the proposed method provides a promising means to measure mineral oil from a distance as well as to estimate the thickness for slick, even in the presence of a contaminated environment.

Ethics information

There are no animal experiments or human subjects in this study that need ethical approval. The authors understand that the corresponding author is the sole contact for the editorial process.

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Conflicts of interest

The author(s) declare(s) that they have no competing interests.

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