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Oil derivatives separating efficiency in treatment of water contaminated with diesel oil with bio-components

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ABSTRACT

Laboratory tests simulating the process of polluting stormwater with fuels and subsequent treating in a separator of oil derivative substances were conducted. Diesel oil (pure diesel oil abbreviated as DERV – diesel-engine road vehicle), diesel oil with bio-components, and pure biofuel – BIO100 were the subject of the tests. Depending on the kind of fuel, the differences in the concentration of oil derivatives in the treated samples were observed. The total reduction in contaminants after 2 min of separation amounted to 91% for BIO100, about 94% for DERV with bio-components, and almost 99% for DERV, however, after 10 s of separation, reduction of DERV was about 90%, whereas, reduction of BIO100 was only 2%. The basic parameters influencing the flotation process were also measured, being the interfacial tension and zeta potential. Depending on the type of fuel, the differences in zeta potential amounted to approximately 26% and differences in interfacial tension reached almost 40%. Such differences may indicate the different susceptibility of oily wastewater to gravity separation. It indicates the necessity for examination of whether the assumptions used for separator design will also be correct in the case of treating stormwater polluted with commercial fuels, including biofuels, available on the market.

Keywords: Stormwater; Biofuels; Zeta potential; Interfacial tension; Separators of oil derivative substances

1. Introduction

The contamination of natural environments with oil-related substances can take place during any stage of the petroleum life cycle such as during their extraction, processing, transportation, and appliance. Numerous applied techniques and methods which remove the oil-related substances from soil and water are used according to the kind and degree of contamination. These techniques and methods range from quite simple to highly advanced, for example, dissolved air flotation in combination with an advanced oxidation process [1], nanofiltration [2] or reverse osmosis (RO) [3] for sewage treatment, adsorption for areal spillage [4], gas stripping [5] and a combination of dissolved air flotation unit and activated sludge bioreactor [6] for water treatment as well as biostimulation and bioaugmentation for soil treatment [7,8].

Environmental contamination with oil derivatives can also be caused by stormwater draining away to both water and soil. From the ecological point of view, stormwater requires purification before it can be discharged into the sewer system or into surface waters. In particular, stormwater discharged from petrol stations may be polluted with petroleum derivatives [9,10] and, according to legal requirements, oils present in these wastewaters should be removed [10].

Many advanced treating methods have been used to purify the rainwater. Dissolved air flotation was applied in a stormwater treatment plant at the outlet of the Chelles River

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catchment area (Seine-et-Marne, France) [11]. The process was divided into two stages: coagulation/flocculation as the first stage and a flotation as the second. The tested processes were efficient in removal of suspended solids, chemical oxygen demand, and hydrocarbons. Other methods consist of a sorption filter in the flotation tank [12], a solution that was implemented at the Ust-Ilimskaya hydropower plant. Some processes combine air flotation, filtration and ultraviolet disinfection and have been tested at the pilot plant in the eastern suburbs of Paris [13]. These processes for the treatment of urban stormwater have been designed in order to obtain bathing water. For stormwater treatment, RO technologies are also used [14] whereby systems equipped with tailor-made open-channel membrane devices are used for treating water with a high suspended-matter content and for removal of synthetic surfactants and petroleum products.

Because of the need for simplicity or even maintenance-free service, such advanced stormwater treatment facilities are rarely used in practice and this is why one of the most commonly used and easy to operate devices is a lamella clarifier. In such separators, tiny oil droplets flowing through lamella sections, float and aggregate on the underside of lamella plates. Reaching specified sizes, aggregated oil droplets float along the underside of the plates towards the water surface, creating an oil film on it.

The possibility of stormwater treatment in such devices depends on the degree of dispersion of fuel in the water as well as the stability of the oil/water emulsion. From that point of view, the key properties of fuels are surface and interfacial tension, zeta potential, and droplet size distribution [15]. Also of importance is the velocity of flotation of fuel particles which depends on the difference in fuel and water density as well as the size of fuel droplets according to Stokes' law. This is due to the fact that the residence time of the wastewater in the unit is relatively short (less than 30 s) [16].

A properly selected and correctly used separator should guarantee the desirable treatment quality. Performance tests of separators, pursuant to EN 858-1 standard [17], are conducted by means of marine bunker fuel, whose properties responsible for separation processes differ significantly from DERV currently in use. The use of fuels with bio-components and pure biofuels causes that the nature of pollutions in stormwater can differ from those used for standard separator testing.

In accordance with Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels and other renewable fuels for transport, and Polish legal regulation, the current share of bio-components in diesel oil is 7% and will increase to 10% in 2020.

It is clear that the properties of fuels and biofuels are different and can, therefore, be susceptible in different ways to purification processes. For example, in the case of vegetable and lamp oils, significant differences in the efficiency of treating of oil-in-water mixtures by dissolved air flotation have been reported [18]. Different oils adsorption of diesel fuel and biofuel on mineral adsorbents has also been noticed [4]. There is also no doubt that even small additives of auxiliary components can change the properties of fuel [19,20].

In the literature, there are no reports regarding the impact of bio-components on fuel properties, especially the properties responsible for the separation processes such as interfacial tension and zeta potential. The question of the possibility of treating of stormwater polluted by diesel oil with bio-components and biofuels in existing separators is, therefore, still open. Nevertheless, there have been more and more discussions on biofuels within the European Union and the issues of treatment of stormwater polluted with biofuels have not been effectively tackled so far.

2. Experiment

The experiment conducted was aimed at testing the cleaning capabilities of the flotation process of water contaminated with diesel oils containing varying amounts of bio-components and with pure biofuel.

The process of the contamination of rainwater with various fuels and their subsequent purification in traditional gravity petroleum separators was simulated.

The basic values influencing the flotation process were measured: the interfacial tension and zeta potential.

2.1. Methods and sample preparation

Materials used for the tests:

- Market fuels – diesel fuel containing 7% of bio-components (DERV 7%) and pure biofuel (BIO100)
- diesel fuel with an increased amount of bio-components – 10% (DERV 10%)
- pure diesel fuel (DERV)

Pure diesel fuel without any additions of bio-components and biofuel BIO100 containing a minimum of 96.5% fatty acid methyl esters were made available by the PKN Orlen Company (Poland). Diesel fuels with the addition of bio-components were prepared by mixing DERV and BIO100 in appropriate volumetric proportions.

For the fuels being tested, the equilibrium interfacial tension in the water–fuel system was measured. The measurement was taken via a Du Noüy ring detachment method using a K12 Krüss tensiometer with an accuracy of up to 0.01 mN/m. The measurements were performed five times at a temperature of 21°C. Ultra-pure water with a conductivity of 0.0549 μS/cm at a temperature of 25°C was used in the measurements. The water was generated using the PURELAB water purification system (Elga company, UK). 10 mL of ultra-pure water was poured into the measuring vessel followed by 10 mL of fuel. After stabilizing the surface (10 min), the interfacial tension was measured via the "push" method, that is, the measuring ring was placed in the lighter phase (fuel) and then automatically pushed into the heavier phase (water).

Afterwards, four water–fuel mixtures were prepared from the tested fuels. They constituted a simulation of stormwater contaminated with different types of fuels. Table 1 shows the concentrations of the specific mixtures.

The prepared mixtures were shaken on an Elpin+ type 357 shaker (frequency 300/s, amplitude 4, time 120 s). This process simulated the process of fuel and water mixing during turbulent flow in sewer systems.

After this, the purification process of polluted water in the gravity petroleum separator was simulated, mixing stopped, and fuel flotation occurred. The concentration of contaminants in the mixtures was measured after 10, 30, 60, and 120 s from the moment the mixing ceased. For estimating the degree of contamination of the wastewater with organic matter found in the fuels, the COD value was measured using Lovibond cuvette tests with a COD measuring range of 0-1,500 mg O_2/L. The measurement was performed in an MD100 apparatus.

The same mixtures were used for the zeta potential measurements. The test was conducted with the use of a Zetasizer Nano ZS analyser (temperature 25°C; Malvern Instruments Ltd., UK). Before the measurement, the sample was thoroughly shaken and left to rest for a period of 1 min. 10 measurements were automatically taken for each of the mixtures, with intervals not exceeding 1 min.

2.2. Calculating the fuel concentration in the water

The degree of contamination of the sample with fuel was determined as COD. For determining fuel concentration in the water, a relationship between fuel concentration and the determined COD value was established. For this purpose, the tested mixtures (Table 1) were vigorously shaken and a sample was taken immediately for COD analysis. Known fuel concentration (FC) and determined COD value (COD) allowed for conversion factors (CF) to be calculated according to the formula:

$$\mathrm{CF} = \frac{\mathrm{FC}}{\mathrm{COD}} \tag{1}$$

Table 1
Fuel and water proportions in the tested mixtures

Mixture	H_2O	Fuel
H_2O – DERV, mL	999	1
H_2O – DERV 7%, mL	999	1
H_2O – DERV 10%, mL	999	1
H_2O – BIO100, mL	999	1

Table 2 lists the calculated conversion factors. Fuel concentration in the water was calculated for the indicated density values of the tested fuels:

ρ_{DERV} = 827 g/L

$\rho_{\mathrm{DERV\ 7\%}}$ = 831 g/L

$\rho_{\mathrm{DERV\ 10\%}}$ = 832 g/L

ρ_{BIO100} = 873 g/L

3. Results and discussion

3.1. Examining the flotation of fuels in water

In the first stage of the tests, the influence of separation time on the concentration of fuel in the mixture was determined. The COD value was converted into fuel concentration in the water according to the conversion factors specified in Table 2. The initial fuel concentration, the COD determination results for the tested mixtures, and the calculated fuel concentration in water are listed in Table 3.

On the basis of data in Table 3, the separation efficiency was calculated and is presented in Fig. 1.

As a result of mixing water and fuels, dispersed suspended solids formed, whereas part of the fuel did not disperse, creating a thin layer of fuel in the very first seconds after ending the shaking process. 10 s after the shaking process ended, DERV concentration dropped by almost 90%, whereas BIO100 concentration only dropped by 2%. The total reduction in contaminants after 2 min of separation amounted to 91% for BIO100, about 94% for DERV with bio-components, and almost 99% for DERV.

The efficiency of wastewater treatment (water contaminated with various oils) was compared with that presented in the literature. De Gisi et al. [3] used full-scale treatment of high COD wastewater (average COD higher than 40,000 mg/L) from a biodiesel fuel production plant and found that COD removal efficiency was greater than 90%. The treatment process consisted of the following phases: primary adsorption/coagulation/flocculation/sedimentation processes, biological treatment with a combination of trickling filter and activated sludge systems, secondary flocculation/sedimentation processes, and finally, a RO system with spiral membranes. Mozaffarikhah and Kargari [2] treating the biodiesel production wastewater, with a commercial nanofiltration system, achieved almost 80% of COD removal.

Table 2
Factors used for recalculation from COD into the corresponding fuel concentration

Parameter	Contaminated substance			
	DERV	DERV 7%	DERV 10%	BIO100
Fuel amount (FA), mL/L	1	1	1	1
Fuel concentration (FC), mg/L	827	831	832	873
COD measured (COD), mgO_2/L	1,060[a]	1,075[a]	1,198[a]	2,410[a]
Conversion factor (CF)	0.7802	0.7730	0.6945	0.3622

[a] Due to the relatively high COD values, the samples were diluted twice.

Table 3
COD value in wastewater based on separation time

Fuel		Unit	Separation time				
			0 s	10 s	30 s	60 s	120 s
DERV	COD	mg O_2/L		134	90	20	16
	FC	mg/L	827	105	70	16	12
DERV 7%	COD	mg O_2/L		822	330	256	70
	FC	mg/L	831	635	255	198	54
DERV 10%	COD	mg O_2/L		790	450	300	66
	FC	mg/L	832	549	313	208	46
BIO100	COD	mg O_2/L		2,366	1,134	340	220
	FC	mg/L	873	857	411	123	80

In this research, despite the fact that the concentration of oil was much smaller, the total treatment efficiency, for water contaminated with biodiesel, achieved a level of roughly 50% after a 30-s flotation time (period of time used for full-scale separator designing) and reached 90% only after a 2-min separation period. However, the treatment process was solely based on spontaneous coalescence and gravitational flotation. Additionally, the treatment process was much faster in water contaminated with pure diesel oil than in water contaminated with biofuel. The differences in the efficiency of treatment were also observed by Bandura et al. [4]; diesel oil was absorbed by zeolites faster than biodiesel although the sorption capacity was already higher for biodiesel (the differences ranged from 13% to 23% depending on the sorbent applied). The authors explained that the differences are due to density and dynamic viscosity ($0.36 \cdot 10^{-7}$ Pa s and $0.66 \cdot 10^{-7}$ Pa s for diesel and biodiesel, respectively).

It must be pointed out that in this research, the differences in flotation efficiency for the tested mixtures are much larger than would directly result from only the differences in used fuel density or viscosity. It would rather suggest, in accordance with Stokes' law, significant differences in the degree of dispersion (drop sizes) of the tested fuels.

3.2. *Factors influencing the flotation of fuels in water*

Two basic values that may affect the size of the fuel drops being formed in the mixtures and the stability of the fuel–water mixtures have been determined: interfacial tension for fuels and the zeta potential for fuel–water solutions.

The value of the interfacial fuel–water tension is presented in Fig. 2. The reduction in interfacial tension in relation to the increase of bio-components content in the diesel fuel is visible. The differences in interfacial tension between DERV and BIO100 reached almost 40%.

When measuring the zeta potential, a certain spread of results was observed, resulting most probably from the instability of the systems being tested. In Fig. 3, averaged zeta potential results for all the fuel–water mixtures tested together with calculated standard deviations are presented.

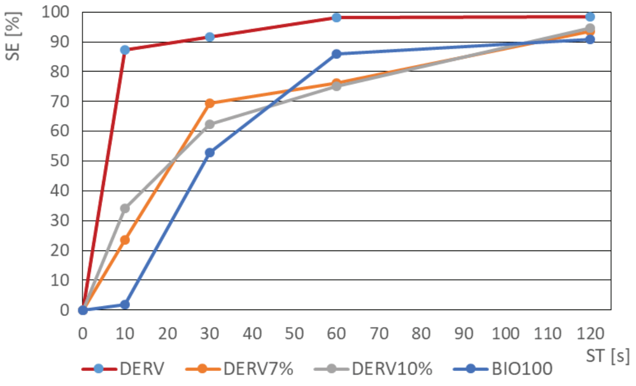

Fig. 1. Separation efficiency (SE) vs. separation time (ST).

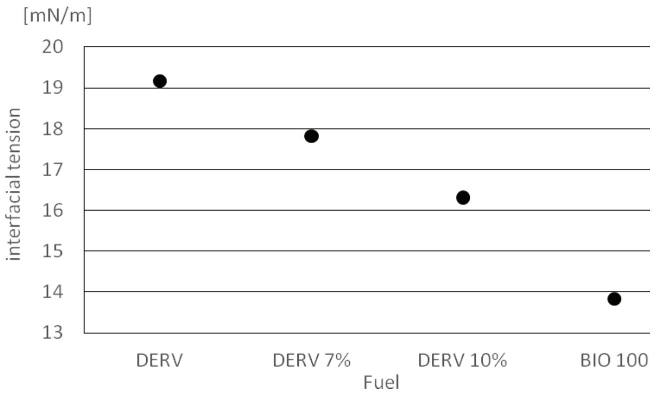

Fig. 2. Interfacial fuel–water tension for fuels with different concentrations of bio-components and BIO100.

A significant increase in the zeta potential value in relation to the increase of the bio-components content in the diesel fuel was observed. The differences in zeta potential between DERV and BIO100 amounted to approximately 26%.

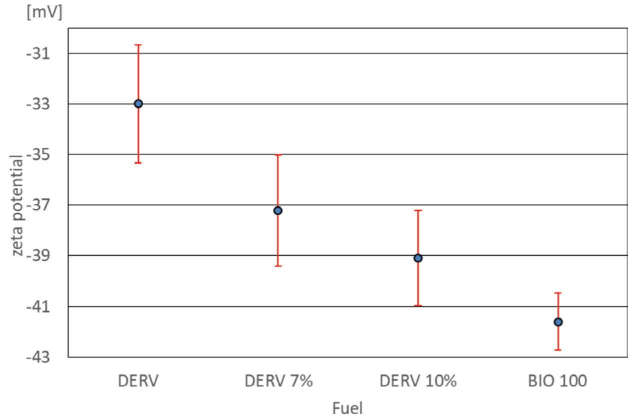

Fig. 3. Zeta potential for fuels with different concentrations of bio-components and BIO100.

4. Conclusion

The processes of stormwater contaminating and its subsequent purification in a gravity petroleum separator were simulated. With the same initial concentrations of the tested fuels as well as with the same conditions of mixing and separation times, even a 7% addition of bio-components in the fuels drastically reduced the efficiency of flotation. The fuel concentration in samples with pure biofuel was 5.8 to 8.2 times higher than in samples with pure diesel fuel. It was found that, together with the increase of bio-components content in the fuels, the fuel–water interfacial tension in the tested mixtures decreased and the zeta potential increased, indicating a change of factors responsible for particle dispersion during mixing as well as for the coalescence process during flotation.

Under real conditions, stormwater contaminated with diesel fuel with bio-components and biofuels may not be effectively treated in currently used gravity petroleum separators. The revising of the guidelines for designing of the standard gravity petroleum derivatives separators for stormwater contaminated by market fuels is, therefore, suggested.

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