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Oily water treatment using a new steady-state fiber-bed coalescer

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ABSTRACT

This study was concerned with the possibility of oil separation from two heavily polluted wastewater types: formation water and wastewater from hardening shop, using bed a newly developed coalescer. Experiments were carried out using original wastewaters and an artificial model wastewater. Results obtained for seven samples of formation water of very different quality showed that the water properties had no significant effect on bed coalescence efficiency. In contrast to this, crude oil properties strongly influenced steady-state bed coalescence. In the treatment of hardening oily wastewater in situ during a 4-month period oil concentration in the effluent was less than 20 mg/l in all experiments. It appeared that oil concentration and water quality had no effect on bed separation efficiency. Special design of the coalescer and use of two filter materials ensured its good performance. Namely, the pipe-in-pipe construction provided the water orientation change several times while passing through the unit, making inertia one of dominant separation mechanisms.

1. Introduction

Oily waters may contain lubricants, cutting liquids, heavy hydrocarbons such as tars, grease, crude oils, diesel oil, and light hydrocarbons such as kerosene, jet fuel and gasoline, as well as fats, vegetable oils or fatty acids [1]. Several separation setups have been used for oily water treatment: settlers, deep bed filters, bed coalescers, centrifuges, adsorbers, membranes, and others [2–5]. However, very often, the selected separation technique does not meet the desired requirements in real situations.

Selection of separation technique depends on several factors, the most important being oil solubility in water. Namely, part of the oil is always soluble while the other part is dispersed in water. Adsorption is an effective and economically reasonable solution only for soluble oil. In case of dispersed oil, it is important to know its pour point. When the working temperature is higher than oil pour point, the dispersion contains two immiscible liquids, so that we deal with a liquid–liquid system. In the case when this temperature is below the pour point there exists a liquid–solid dispersion. Settlers, deep bed filters, centrifuges and membranes are useful and effective for both types of oil dispersions [6], while bed coalescers are suitable only for liquid–liquid dispersions, emulsions.

For oil separation from wastewater the most important data are water quantity, phase ratio, and emulsion stability.

Steady-state bed coalescers are very comfortable solution for the separation of unstable emulsions, regardless of their quantity and phase ratio. The use of fiber-bed coalescers is getting increasingly attractive in the industry due to their high efficiency and simple construction. However, their design is still based on experimental data and experience [7–9].

In the present literature, it is still not clearly explained that bed coalescers can operate in two regimes: unsteady-state and steady state. In an unsteady-state regime, drops collect in the bed and pressure drop increases with time [10,11]. This operation is similar or equal to deep bed filtration, where operation is discontinuous and filter needs washing. During the washing step, a new quantity of oily water is generated.

In the steady-state regime, pressure drop is constant with time, and fluid velocity determines its value. In these circumstances, saturated oil exists inside the bed. Small inlet droplets coalesce on the surface of saturated liquid inside pores, and larger drops (globules) detach from the surface and settle behind the bed [10,11]. This operation could work continuously for a long time, especially if the content of suspended solid in the wastewater is not extremely high. One of the advantages of these units is the possibility to automatize the process.

Bed coalescers consist of two sections: bed and settling section [8,9,12–14]. Separated oil, with low concentration of water, collects on the top of the settling section and is discharged discontinuously.

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The objective of this work was to develop a new bed coalescer with high separation efficiency, which could treat heavily polluted oil wastewaters. The tests were carried out in the Central Laboratory of Oil Company of Serbia and the Kikinda Foundry. Some of commercial separators that have been used there appeared to be unsuitable for these applications.

2. Materials and methods

2.1. Experimental fiber-bed coalescer

The bed coalescer is schematically presented in Fig. 1. The coalescer body is a vertical pipe-in-pipe system. The coalescer pipes are filled in with different polymer materials: granular expanded polystyrene (EPS) (pipe 1), and polyurethane (PU) fibers (pipe 2). Wastewater enters at the bottom of Section 4, passes vertical up through the EPS bed, changes its orientation to vertical down on the top of the unit, and then is passing through the PU bed. The waste oil collects at the top of unit 5, and is discharged discontinuously through valve 3. The tested coalescer was of two sizes: a small laboratory setup with the capacity of 0.025 m^3/h, and a pilot unit with the capacity of 1 m^3/h.

2.2. Operating conditions

In all experiments, the steady-state regime was achieved by pre-oiling the PU fibers. Therefore, a steady state was established from the very beginning of the experiment, which was confirmed by a constant pressure drop.

In all experiments fluid velocity was 7 m/h. Temperature was determined for each set of experiments. Oil concentration in water was determined by IR spectrometry using a carbon tetrachloride extract. Oily water samples were conserved by adding HCl to pH 2.0.

2.3. Formation water

Formation water treatment was carried out in the Central Laboratory of Oil Company of Serbia. Two sets of experiments were performed; one involving real formation water (samples marked from DA to DG) and the other involving model formation water (marked from DMA to DMG). Wastewater was mixed in the inlet tank to obtain oil drops of the mean drop size of 20 μm. Wastewater temperature was kept constant at 35 °C.

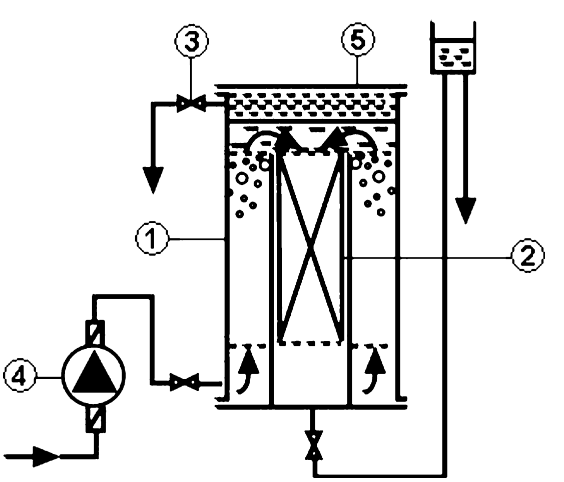

Fig. 1. Schematic of the coalescer.

Seven samples of formation water of very diverse composition were selected, special care being paid to those which have low separation efficiency by gravity. Main characteristics of the wastewaters and crude oils (A–G samples) are given in Tables 1 and 2.

Model formation water was treated under similar conditions. In this case, the continuous water phase was prepared by adding 13.5 g/l NaCl and 1.5 g/l $CaCl_2$ to tap water to obtain a salinity of 15 g/l. The discontinuous oil phase consisted of those crude oils that existed in the real formation water. The influent oil concentration was constant, 500 mg/l.

For each sample tests were run for 15 h in continuity. Oil concentration in the effluent was determined every 2 h in composite samples, collected at the outlet of the unit during the last 15 min at 5-min interval.

2.4. Hardening shop wastewater

In case of hardening shop wastewater, two discontinuous tests were performed in situ on real hardening wastewater and in laboratory on a model wastewater. The pilot coalescer was located in the hardening shop of the Kikinda Foundry after the equalization tank, and testing lasted 4 months. Oil concentration in the effluent was determined in the composite samples for every work shift, in 2 h interval.

Characteristics of the hardening wastewater determined during the test period are given in Table 3. Main properties of the hardening mineral oil at 20 °C were: density 885 kg/m^3, viscosity 147.60 mP s, and refraction index 1.49.

The model water, with constant inlet oil concentration of 130 mg/l was prepared by mixing tap water and waste hardening mineral oil. Oil concentration in the effluent was determined in composite samples for every work shift.

3. Results and discussion

3.1. Crude oil separation from formation water

Crude oil production is always accompanied by remarkable quantities of formation water, which represents a very complex dispersion, with high concentration of suspended solid, high salinity, crude oil, phenols, ammonium, inorganic ions (calcium, magnesium, sodium, lithium, barium, strontium, chlorides, sulfates, nitrates, etc.). This water represents a very big environmental problem. The best way to solve this problem is to inject formation water back into oil well. Before injection, some treatment of formation water has to be done. Crude oil separation is necessary because the big oil droplets could block pores inside earth layers. The separated crude oil is of economic value as a by-product, important for sustainable development.

Formation waters from Vojvodina oil fields contain very different crude oils, their main characteristics being given in Tables 1 and 2. The range of suspended solids in the investigated samples was from 31 to 335 mg/l; ammonia was from 5 to 125 mg/l, and salinity from 2 to 27 g/l. The density of crude oils was from 850 to 920 kg/m^3; viscosity was from 7 to 1132 mP s; pour point was from −30 to 30 °C, and mean molecular weight was from 200 to 500 kg/kmol.

It is well known from the literature that emulsion characteristics are determined by the nature of both constitutive liquids. Interdependences between them are specified by their properties such as double layer, zeta potential, van der Waals forces, interfacial tension, etc.

The coalescer showed high separation efficiency for these complex oil–water dispersions. Effluent oil concentrations during 15-h

Table 1
Some characteristics of formation water

Sample	Suspended solid (mg/l)	Ammonia, NH_4^+ (mg/l)	Na^+ (mg/l)	Ca^{2+} (mg/l)	Sr^{2+} (mg/l)
WA	43.50	22.75	4003	9.70	1.60
WB	55.00	5.50	2540	220.00	20.00
WC	42.50	29.00	6800	155.00	18.00
WD	164.10	86.50	8000	1460.00	89.60
WE	78.00	22.75	1625	42.00	1.80
WF	31.00	122.00	8288	1800.00	88.00
WG	334.30	19.00	4625	46.00	6.80
Interval	31–335	5–125	1600–8300	9–1800	1–90

Table 2
Some physical characteristics of crude oils

Crude oils	Density at 20 °C (kg/m^3)	Viscosity at 35 °C (mPa s)	Neutralization number (mg KOH/l)	Pour point (°C)	Mean molecular weight (kg/kmol)
A	912.80	56.31	0.979	−30	374
B	847.15	9.22	0.554	15	217
C	867.44	30.00	0.455	29	251
D	898.20	180.00	1.608	33	460
E	836.04	7.79	0.384	12	201
F	921.68	1132	1.466	29	500
G	866.74	17.48	0.491	24	250
Interval	840–920	7–1132	0.66–1.60	−30 to 33	200–500

Table 3
Some characteristics of heavily polluted wastewater from hardening shop

Parameter	pH	NO_2^- (mg/l)	CN^- (mg/l)	PAM (mg/l)	Mineral oil (mg/l)
Number of samples	20	20	20	20	20
Maximum	11.9	2898	151	5.20	30182.00
Minimum	11.1	88	0.02	0.29	132.00
Mean	11.54	900.55	15.80	1.23	7137.70
Standard deviation	0.228	686.78	36.125	1.204	9129.04

tests of investigated samples are presented in Figs. 2 and 3 (filled symbols). Five out of seven samples had the effluent oil concentration less than 15 mg/l during the whole experiment. The effluent concentration increased with time for only two samples (DD and DF), reaching highest values of 18.12 and 37.84 mg/l, respectively. The effluent crude oil concentrations of all of formation waters samples are given in Table 4.

The results show that the effluent oil concentration is independent of the influent oil concentration for investigated formation waters. For a maximum influent oil concentration of 1026 mg/l, the mean effluent oil concentration was 2.56 mg/l, and for the minimal oil concentration of 140 mg/l this value was 13.10 mg/l.

Because of the high salinity range of investigated formation waters, it was possible to correlate the effluent oil concentration with water salinity, as shown in Fig. 4. Evidently, the bed coalescence efficiency did not depend on water salinity when its value was below 25 g/l. The effluent oil concentration increased exponentially above this value with increasing salinity.

Considering all these facts, it is possible to explain the highest effluent oil concentration of samples DD and DF by their very high salinity (27.18 and 26.89 g/l, respectively). Crude oils in these two samples had also very high values of viscosity, neutralization number, pour point, and especially of molecular weight.

In order to exclude the effect of water quality and focus only on crude oil properties and their influence on bed coalescence it was necessary to introduce a model system.

Continuous phase in the model formation water was prepared using a tap water with 13.5 g/l NaCl and 1.5 g/l $CaCl_2$ to produce a constant salinity of 15 g/l. In this way, the effect of suspended solid and other inorganic and organic ions was excluded.

Effluent oil concentrations for model formation waters are given in Table 5, while the data for the 15-h test given in Figs. 2 and 3 (empty symbols). No significant difference in coalescence efficiency between the real and model formation water were observed, except for samples DMA and DMF.

Table 4
Statistics of crude oil content in the formation water after separation

Oily water samples	Influent oil concentration (mg/l)	Effluent oil concentration (mg/l)			Standard deviation
		Maximum	Minimum	Mean	
DA	242	11.40	7.25	9.72	1.80
DB	172	5.40	1.94	2.74	1.27
DC	244	3.74	2.00	2.24	0.66
DD	140	18.12	7.36	13.10	4.80
DE	1026	3.40	1.40	2.56	0.68
DF	729	37.84	27.35	31.88	3.58
DG	875	14.32	4.05	6.72	3.96

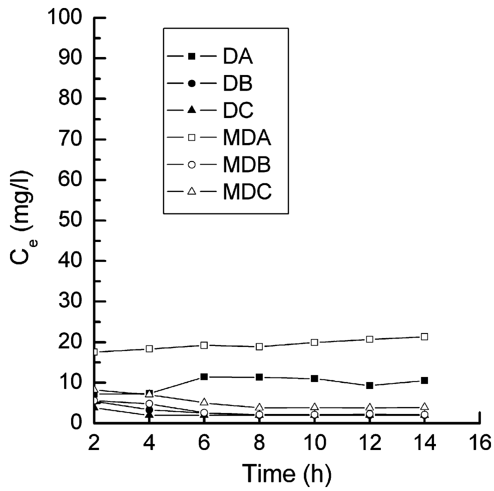

Fig. 2. Time dependence of the effluent oil concentration for formation water (full symbols) and model system (empty symbols) for samples with crude oils A–C.

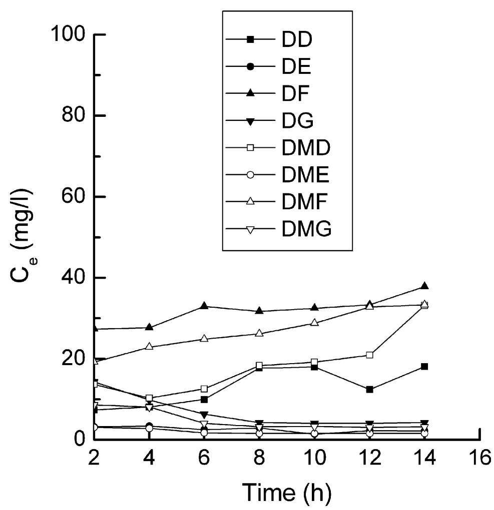

Fig. 3. Time dependence of the effluent oil concentration for formation water (full symbols) and model system (empty symbols).

Table 5
Statistics of oil content in effluent for model formation water

Samples	Effluent oil concentration (mg/l)			Standard deviation
	Maximum	Minimum	Mean	
DMA	21.3	17.6	19.4	1.32
DMB	5.6	2.1	3.1	1.46
DMC	8.2	3.8	5.1	1.81
DMD	33.2	10.3	18.3	7.61
DME	3.01	1.6	2.0	0.65
DMF	33.3	19.2	26.9	5.16
DMG	8.7	3.1	4.8	2.47

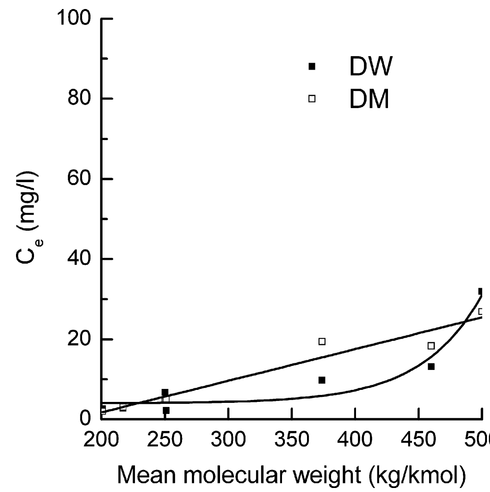

Fig. 5. Dependence of the effluent oil concentration on mean crude oil molecular weight.

In contrast to this, crude oil properties strongly influenced the steady-state bed coalescence efficiency. The effluent oil concentration increased with increase of molecular weight, especially for model water, Fig. 5. The difference between real and model water was due to high value of the effluent oil concentration in the model sample (DMA) with a molecular weight of 374 kg/kmol. It could be expected that the effluent concentration increased with increase in the oil density. The settling velocity was lower when the density difference between the two liquids decreased, Fig. 6. Bed coalescence efficiency was slightly influenced by oil viscosity too, Fig. 7.

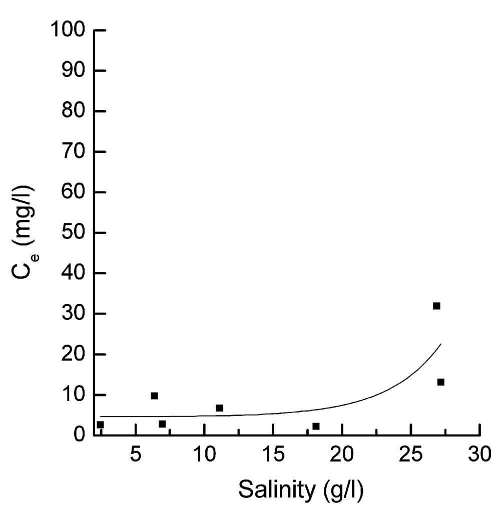

Fig. 4. Dependence of the effluent oil concentration on salinity of formation water.

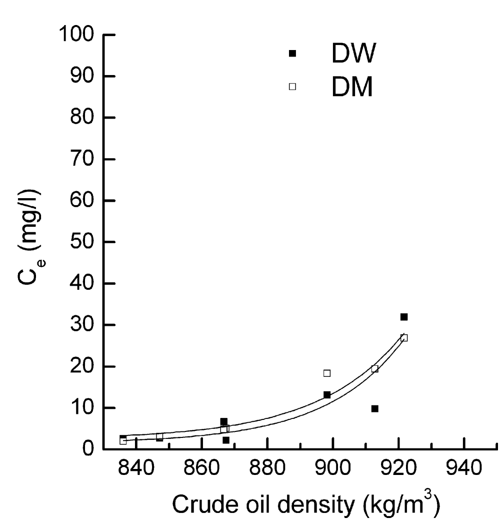

Fig. 6. Dependence of the effluent oil concentration on crude oil density.

Table 6
Statistics of oil content in effluent in situ test in hardening shop

Oily water samples	Number of samples	Effluent oil concentration (mg/l)			Standard deviation
		Maximum	Minimum	Mean	
Month 1	5	50	5.1	24.38	20.124
Month 2	5	16.6	4.5	10.8	5.873
Month 3	5	17.8	10.4	13.9	2.645
Month 4	5	16.5	3	7.94	5.098

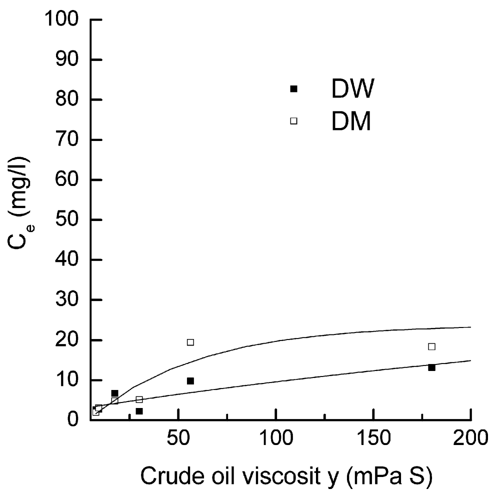

Fig. 7. Dependence of the effluent oil concentration on crude oil viscosity.

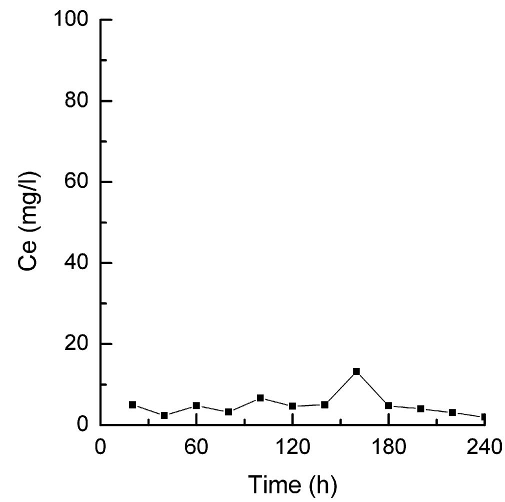

Fig. 9. Effluent oil concentration in the laboratory test of the model hardening wastewater treatment.

3.2. Oil separation from hardening shop wastewater

Hardening operations are heating processes aimed at obtaining better mechanical properties of metal pieces. Small metal products are heated in hot oil and/or melting cyanides salts, and quenched in cold water. Hardening shop wastewater is a complex dispersed system, with very large variation of oil concentration in the influent, from 20 to 30,000 mg/l, and high content of suspended matter. It also has a pH close to 12, and high content of nitrites and cyanides, Table 3. Other characteristics of wastewater also varied significantly with time. Temperature of the investigated water was from 18 to 25 °C.

During a period of 4 months the coalescer was located in situ on the equalization tank inside a new big hardening shop of the Kikinda Foundry. Depending on wastewater quantity, the coalescer operated discontinuously. Total working time of the unit was 372 h, and total quantity of separated oil was 115 kg. Statistics of the experimental data are given in Table 6.

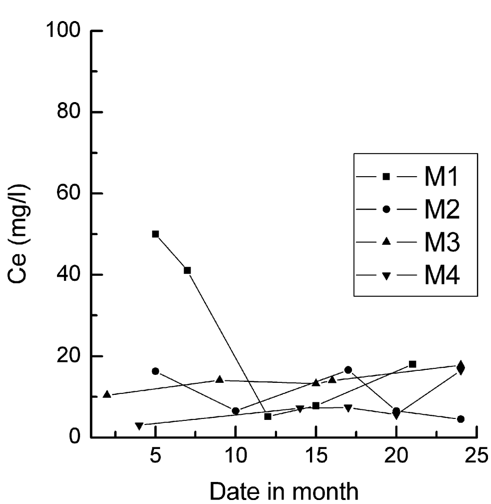

Fig. 8. Effluent oil concentration during the 4-month period of the in situ treatment of hardening wastewater.

As can be concluded from Fig. 8, the coalescer was very successful in the treatment of hardening shop wastewater, the achieved effluent oil concentration being less than 20 mg/l. The effluent oil concentration was independent on the inlet oil concentration and inlet wastewater quality. Only in the beginning, the effluent concentration was higher because of clean bed materials. In the steady-state regime, saturated oil in the coalescer bed had to be collected from the inside of the bed.

It is very important to point out that the oil dispersibility in water in the equalization tank was low and floating oil was dominant. That was the main reason for using model water in the experiments.

Laboratory tests included the effect of oil dispersibility by introducing stirring of the model wastewater to obtain mean drop size of 20 μm. At the same time, these experiments excluded the effect of variation in value of some parameters, like temperature, and inlet water quality, which was ensured by using tap water for the preparation of model water. Test period of these experiments was 240 h in total, 8 h per working day. The effluent oil concentration, as can be seen in Fig. 9, was less than 10 mg/l during the whole experiment.

4. Conclusions

The designed bed coalescer appeared to be a very effective setup for oil removal from heavily polluted wastewaters. The oil separation efficiency was independent on the influent oil concentration and oil drop size, wastewater quality, including high concentration of different mineral ions. High performance of the coalescer was achieved by its special design and application of two filter materials. Namely, the pipe-in-pipe design provides the water orientation changes several times while passing through the unit, making inertia one of dominant separation mechanisms. In addition, the treated wastewater passes through two beds of very different properties. After the first one, part of coalesced drops settles at the top of the unit, while the other bed captures the rest of the oil drops.

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