Research on the treatment of oily wastewater by coalescence technology

Chunbiao Li, Meng Li and Xiaoyan Zhang

ABSTRACT

Recently, oily wastewater treatment has become a hot research topic across the world. Among the common methods for oily wastewater treatment, coalescence is one of the most promising technologies because of its high efficiency, easy operation, smaller land coverage, and lower investment and operational costs. In this research, a new type of ceramic filter material was chosen to investigate the effects of some key factors including particle size of coarse-grained materials, temperature, inflow direction and inflow velocity of the reactor. The aim was to explore the optimum operating conditions for coarse-graining. Results of a series of tests showed that the optimum operating conditions were a combination of grain size 1–3 mm, water temperature 35 °C and up-flow velocity 8 m/h, which promised a maximum oil removal efficiency of 93%.

Key words | coarse-graining, influencing factors, oily wastewater treatment, optimum operating conditions

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INTRODUCTION

Usually, oily wastewater has complex compositions due to widespread sources such as oil and gas field development processes, oil leakages, and ship accidents. Discharge of oily wastewater not only destroys the environment posing a serious threat to people's safety but also causes great economic losses (Deepa *et al.* 2005). Hence, oily wastewater treatment has gradually become a hot research topic across the world recently (Chen *et al.* 2002; Gu *et al.* 2002; Mendonca *et al.* 2004; Vityaz *et al.* 2004). Traditional oily wastewater treatment technologies mainly include coagulation–sedimentation, biological treatment and gas flotation processes, among others (Zhong *et al.* 2003). Nevertheless, these processes have common disadvantages like high costs and instability of removal efficiency (Ahmadun *et al.* 2009). In order to overcome these disadvantages, a promising approach named coalescence technology was reported initially in the 1940s. And it has been used in oily wastewater treatment since the 1970s (John *et al.* 2001; Ji *et al.* 2009).

Generally speaking, coalescence technology refers to the processes of coarse-graining and subsequent settling aiming to remove the dispersed oil or the non-surfactant stable emulsified oil from the raw oily wastewater efficiently (Moazed & Viraraghavan 2002). Coarse-graining technology has some other merits such as smaller land coverage, easy operation, and lower investment and operational costs. Nevertheless, there are still some shortcomings showing up in practical projects. For instance, oil content in the effluent would surpass 10 mg/L under heavy influent burden of more than 100 mg/L (Zhang *et al.* 2004). That means the effluent quality cannot invariably meet desired treatment goals. Furthermore, coarse-graining materials are prone to clogging, which makes them difficult to use in large industrial operations under ideal conditions (Zhu *et al.* 2014). Thus, a new kind of chemical surface modification process is urgently needed to greatly reduce the load of the foregoing processes so as to ensure the content of oil in the treated effluent meets the A1 standard of *Water quality standard of oilfield injecting waters (SY/T5329–1994)*.

MATERIALS AND METHODS

Experimental materials

In this experiment, a new type of ceramic filter material (Liu *et al.* 2011), developed by Shandong Aluminium Industry Co. Ltd, Jinan, China, was chosen due to its attractive characteristics (i.e. large surface area, high hardness and strong resistance against corrosion/oxidation without toxicity). The special filter material was made from integrated sludge, coal gangue, fly ash and pore forming agent coal dust by the following procedures:

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Integrated sludge, coal gangue, fly ash and coal dust came from Wuhna Iron and Steel Company, Wuhan, China. Chemical compositions of each raw material are shown in Table 1. By mixing the raw materials according to the sintering conditions listed in Table 2, the new type of ceramic filter material is obtained.

The primitive ceramic ball was designed to be oleophobic. To further improve its oleophobicity, non-ecological benzene coating was chosen as a modifier to enhance its surface energy (Hua *et al.* 2007).

Table 1 | Chemical compositions of raw materials (wt %)

Compositions	Integrated sludge	Coal gangue	Fly ash	Coal dust
SiO_2	6.37	52.23	41.53	5.54
Al_2O_3	3.12	21.67	22.29	1.31
Fe_2O_3	5.71	3.81	5.46	0.92
CaO	40.00	2.15	1.97	0.91
MgO	1.05	1.42	0.54	0.42
K_2O	0.28	1.07	1.85	0.23
Na_2O	–	1.19	0.94	0.17
SO_3	0.72	0.36	0.91	0.5
P_2O_5	0.29	–	–	–
TiO_2	0.21	–	–	–
Cr_2O_3	0.05	–	–	–
MnO	0.24	–	–	–
ZnO	0.14	–	–	–
SrO	0.05	–	–	–
ZrO_2	0.01	–	–	–
BaO	0.04	–	–	–
Cl	0.06	–	–	–
Loss on ignition	41.66	–	–	–
Moisture	–	–	–	4.1
Ash content	–	83.9	75.49	10.0
Volatile	–	11.4	9.62	35.3
Free carbon	–	4.7	14.89	50.6

Table 2 | Percentage compositions and operating conditions for sintering process

Integrated sludge (wt%)	Coal gangue (wt%)	Fly ash (wt%)	Coal dust (wt%)	Sintering temperature (°C)	Sintering time (min)
32	30	18	20	1,130–1,160	120

Oily sewage samples

Oily sewage samples used in this experiment were derived from the production wastewater discharged by Sinopec Jianghan Oilfield Co. Ltd, Hubei, China. Oil concentration in raw samples varied from 203 to 230 mg/L. And the concentration of the samples used in the following experiments was diluted to 35.71 mg/L.

Experimental equipment

A coarse-graining column (2 m high and 50 mm diameter) was made of organic glass materials. The supporting layer was prepared with 150 mm cobble and a filter layer of 700 mm. A water pump, rotor flow meter and cut-off valve were used to control the quantity of influent/effluent. Flow rate for column backwashing flow was controlled at 4.0 L/s·m^2 for 20 minutes at a time.

RESULTS AND DISCUSSION

The key to disposing of oily sewage by coalescence technology is to ascertain suitable operation conditions, which are of vital importance to improve the oily wastewater pollutant removal efficiency and to extend the running period.

Effect of particle size

An up-flow mode with different particle sizes of 0.8–1.0 mm, 1–3 mm and 3–4 mm was tested under the following fixed conditions: filter layer thickness 700 mm, filtration velocity 8.0 m/h. Samples were analyzed every half an hour for a period of 3 h. Results are shown in Figure 1.

It could be seen that the grains padded with sizes of 1–3 mm and 3–4 mm had obviously higher oil removal efficiency than those padded with size of 0.8–1.0 mm (Figure 1). This could be explained by the fact that the coalescence bed would more easily be blocked with smaller

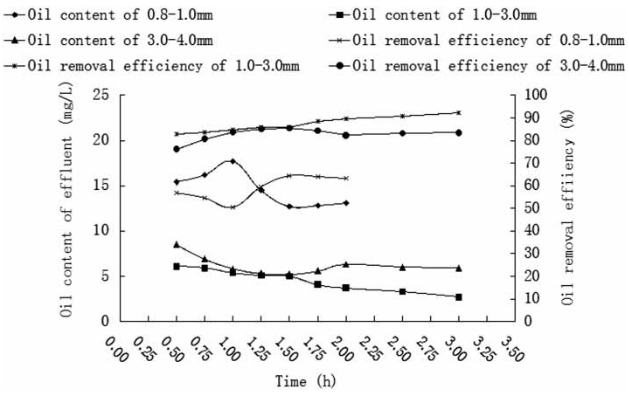

Figure 1 | Coarse-graining effects with different ceramic padding sizes.

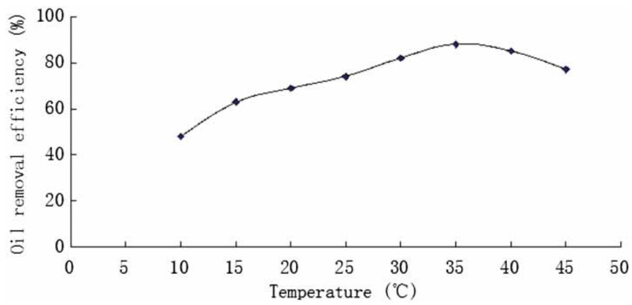

Figure 2 | The impact of temperature on treatment performance.

porosities, which finally affected the normal operation. Moreover, the formed oil bead flocs were more likely to be broken, leading to worsening removal efficiencies.

Further, there was no apparent difference between the medium size 3–4 mm and 1–3 mm for oil removal efficiency. Nevertheless, effluent oil content padded with 3–4 mm was higher than that padded with 1–3 mm during the whole operation and failed to meet the standard of <5 mg/L. Effluent oil content padded with 1–3 mm reached 5 mg/L at 1.5 h and corresponding oil removal efficiency was 86%, and it continued to increase with shorter sampling time (Figure 1). It could be inferred that with a larger filter size the probability of effective collisions might reduce, resulting in poorer treatment performance. According to the above results, an appropriate padding size of 1–3 mm might be proposed for the special ceramic filter.

Effect of water temperature

Temperature effects were analyzed under the following experimental conditions: up-flow mode, filter padding size 1–3 mm, layer thickness 700 mm, filtration velocity 6.0 m/h and an interval of 5 °C for temperature increment from 10 °C to 45 °C. The results are as follows (Figure 2).

The oil removal efficiency could reach an optimal value (88%) when the temperature went up to 35 °C (Figure 2). This could be explained by the following reasons. First, it could be partially attributed to the reversible physical absorptions caused by exothermic reactions (Bryan *et al.* 2014). To a certain extent, higher temperatures might promote desorption with the fully use of oleophobic ceramic filters. Second, higher temperature could also enhance the strength of effective collisions among oily molecules, which might promote the formation of larger flocs. Third, temperature increment would also enhance the viscosities of the aqueous and oily phases in varying degrees, which would be beneficial for coalescence. Finally, water density showed little change while density of oil declined greatly with the temperature increase, which meant temperature increment within a certain limit was conducive to the separation of oil from water. However, it should be noted that, when the temperature went up higher than 35 °C, oil removal efficiency would further decrease slightly. This was possibly because the formed flocs might disintegrate due to intense collisions occurring under excessive high temperatures as suggested by Figure 2.

Effect of inflow direction

These tests were performed by choosing two organic glass columns filled with the same coarse-grained materials. The first column was operated under up-flow mode, while the second one was with down-flow mode. The experiments were conducted for 3–4 h, and water samples were taken every half an hour. Then, appropriate flow direction was determined by evaluating the oil removal efficiencies under different flow rates of 6, 8 and 10 m/h.

It could be seen that effluent oil concentrations under up-flow conditions were generally lower than those under down-flow mode, corresponding to higher oil removal efficiencies for the former mode than the latter (Figures 3–5 and Table 3). Moreover, oil concentrations under up-flow conditions were generally stable over time, while for down-flow mode, they showed strong variations. When up-flow mode was applied, appropriate flow velocities would make the packing layer slightly expand. This would guarantee that suspended solids would not adhere to the surface of padding particles, ensuring adequate filter interstices to form unique microporous channels so

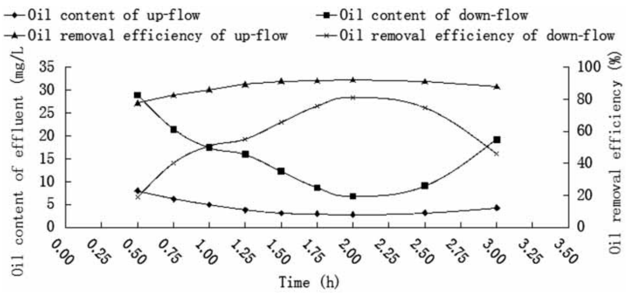

Figure 3 | Differences between up-flow and down-flow modes under a velocity of 6 m/h.

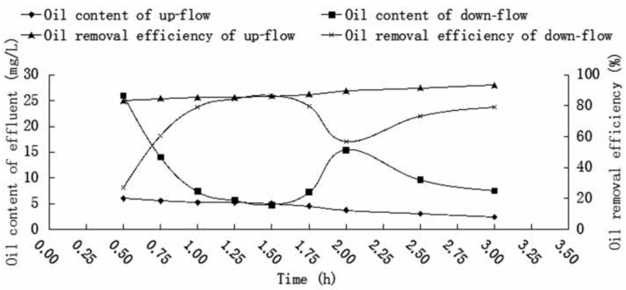

Figure 4 | Differences between up-flow and down-flow modes under a velocity of 8 m/h.

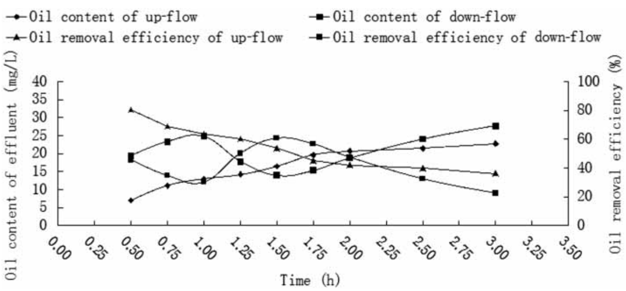

Figure 5 | Differences between up-flow and down-flow modes under a velocity of 10 m/h.

Table 3 | Comparison of treatment efficacy under different inflow directions

Direction	Velocity (m/h)	Maximum removal efficiency (%)	Minimum concentration of effluent (mg/L)
Up-flow	6	92.0	2.8
	8	93.0	2.4
	10	80.0	7.0
Down-flow	6	81.0	6.8
	8	87.0	4.7
	10	61.0	14.0

as to increase the probabilities of oily particle collisions. Regarding down-flow conditions, the filter interstices were easily blocked, due to high concentrations of impurities, in a short period of time and the probability of collisions decreased remarkably resulting in relatively low oil removal efficiencies.

Effect of inflow velocities

The previous tests confirmed that oil removal efficiency under up-flow mode was higher than that under down-flow conditions. Thus, up-flow mode was adopted as the flow direction in the following tests to determine the optimal velocity of coarse-graining with filter layer thickness 700 mm. The tests were conducted under four different levels of velocities: 5, 6, 8 and 10 m/h. Results are shown as follows.

It was shown that effluent oil concentrations operating under the velocities of 5 m/h and 10 m/h were higher than the threshold of 5 mg/L during the whole sampling period (Figures 6 and 7; Table 4). Compared with 6 m/h, the oil removal efficiency under the velocity of 8 m/h was more stable. It almost reached its maturity in 0.5 h (corresponding to a removal efficiency value of 83%), and then increased gradually to 93% at the end of the testing period (3 h). Moreover, effluent oil concentrations under 8 m/h mode began to meet the requirement of the A1 standard of *SY/T5329–1994* after 1.5 h (Figure 6).

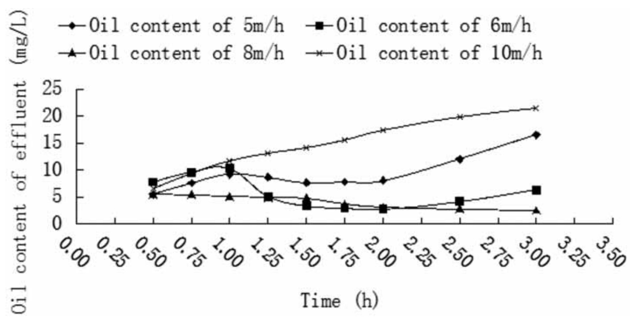

Figure 6 | Comparison of effluent oil contents under different flow velocities.

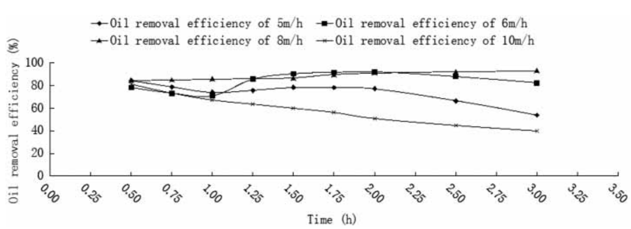

Figure 7 | Comparison of oil removal efficiency under different flow velocities.

Table 4 | Comparison of treatment efficacy under different flow velocities

Velocity (m/h)	Maximum removal efficiency (%)	Minimum concentration of effluent (mg/L)
5	85.0	5.5
6	92.0	2.8
8	93.0	2.5
10	82.0	6.6

From the above results, it could be deduced that unsuitable velocities were not beneficial to the oil removal. The higher the velocity the larger the number of oil particles that might enter the padding interstices. The extremely high velocity might allow the oil particles to pass through the padding layer quickly. But it would restrain most of the pass-through oil particles from colliding with the deposited oil particles effectively. Also, the coalesced oil particles might break down more easily under the stress of extremely high hydraulic loading, leading to the elevation of oil content in the effluent. In contrast, under too small velocity up-flow mode, oil particles collided with each other within the limited padding interstices and formed large oil flocs easily. As the oil particles became larger, their surface energy reduced gradually so that they could not adhere firmly to the surface of padding filters. Since oil particles in the inflow contacted completely with the established oil groups, forming larger flocs when passing through the channels, the padding filter could no longer capture coalesced oil particles. As a result, many tiny oil particles penetrated through the layer, leading to an increase of oil content in the effluent over time. This might be the partial reason for the poor oil removal efficiency under up-flow mode with extremely low velocities. Therefore, in practice, reasonable flow rates should be determined to ensure ideal effluent quality.

CONCLUSIONS

(a) Within a suitable range, increasing the size of ceramic filter particles would make a contribution to enhancing coarse-graining performance. Small porosities could decrease the cross-sectional areas for filtration, which would affect the treatment efficiency.
(b) Temperature controlled at 35 °C could achieve the optimal coarse-graining effect.
(c) Up-flow mode helped to increase the probability of oil droplet collisions, which was conducive to coarse-graining.
(d) At a velocity of 8 m/h, the capacity of the padding filter to adsorb oil droplets increased apparently, compared to other velocities, and the corresponding effect of wetting coalescence would be enhanced remarkably.

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