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Evaluation of calcium chloride for synergistic demulsification of super heavy oil wastewater

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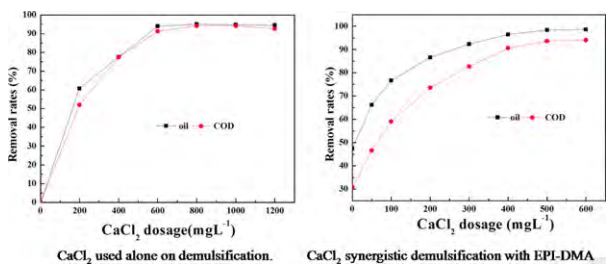
HIGHLIGHTS

- $CaCl_2$ has a good performance in synergistic demulsification of super heavy oil wastewater.
- A new demulsifier REB is combined with P-DcE,$CaCl_2$ and CPAM.
- REB can remove more mineral oil, COD and organic compounds than two traditional demulsifiers.
- The REB effluent has low BOD/COD and delivers good performance in anaerobic digestion.
- REB is an efficient, safe and economical demulsifier of super heavy oil wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium chloride ($CaCl_2$) is used together with cationic poly (dimethylamine-co-epichlorohydrin) (P-DcE) and cationic polyacrylamine (CPAM) to demulsify super heavy oil wastewater. A new reverse emulsion breaker (REB) with the optimal ratio of P-DcE to $CaCl_2$ to CPAM of 20:600:1.2 (m/m) can remove 98.04% mineral oil and 94.48% COD. Compared to P-DcE used alone and P-DcE supplemented with concentrated sulfuric acid to enhance demulsification, the advantages of the REB are high removal rates for mineral oil and COD, low cost, and environmental friendliness. GC–MS indicates that the REB can remove more organic compounds such as mineral oils than other agents and most of the residues are oilfield chemicals such as corrosion inhibitors, scale inhibitors, biocides, and demulsifiers. The REB, which exhibits good efficiency in anaerobic digestion and synergistic demulsification of SHOW arising from $CaCl_2$, is efficient, safe, and economical.

1. Introduction

Super heavy oil wastewater (SHOW) in the Liaohe oilfield in China is a complex one that comprises not only water produced from the oil extraction, but also steam-assisted gravity drainage wastewater (SAGD) [1], scum and filtered wastewater, as well as ion-exchanged wastewater. It is a complicated system containing high amounts of oil, SS (total suspended solid), reductive substances (such as sulfide, Fe and Mn) and saline materials [2]. It is enriched with dissolved recalcitrant organic compounds such as polymers, surfactants [3] or oilfield chemicals (OCs) [4], and the super heavy oil has a density of 0.95–1.20 g/cm^3 (20 °C) and viscosity larger than 10,000 mPaS (50 °C) [5]. The mineral oils in SHOW contain a number of asphaltenes, resins, and naphthenates, which are polar and surface-active species, and are natural emulsifiers [6]. Naphthenates, particularly sodium naphthenates,

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are highly hydrophilic compounds that lead to the formation oil-in-water emulsions [7]. Furthermore, some nonionic surfactants such as nonyl phenol ethoxylate are added to improve the transportability of heavy-viscous crude oils [8]. These organic compounds decrease the crude-oil-water interfacial tension and increase the emulsion stability [9]. Owing to the presence of a high concentration of mineral oil, high suspended solids (SS), high chemical oxygen demand (COD), high temperature, and high stability of the o/w emulsion, it is difficult to remove pollutants but it is important to recover oil [10] from the wastewater before discharging.

There are many methods to demulsify oily wastewater [11], for example, electrochemical techniques [12,13], coupling flocculation with electro-flotation [14], hybrid-modified resin and activated carbon systems [15], biochemical demulsification [16], gas flotation [17], chemical demulsification [18], as well as combined demulsification and reverse osmosis [19]. Addition of chemicals which is normally the easiest and most effective method to destabilize emulsified oil droplets can be implemented on an existing system using known settling and filtration processes to treat the produced water [20], although these methods may not be directly adaptable to other industrial devices for chemical demulsification.

The emulsion breakers presently used to treat SHOW in the Liaohe oilfield consist of the cationic poly (dimethylamine-co-epichlorohydrin) (P-DcE) supplemented with concentrated sulfuric acid to enhance demulsification. This method is efficient but not economical and safe. P-DcE is a good organic cationic polymer flocculant/coagulant agent in wastewater treatment [21]. It has high positive charge, water solubility, ability to handle molecular species, high efficiency, innocuity, and low cost [22] and has been applied to petroleum, paper making and dying wastewater treatment by charge neutralization and adsorption [23]. Cationic polyacrylamine (CPAM) which is widely used as coagulant aids [24] can remove organic pollutants by charging neutralization and "bridge" adsorption. Calcium chloride has been widely used in wastewater treatment such as removal of phosphates and fluorides [25,26], demulsification of diluted oil/water emulsions [27], destabilization of cutting oil emulsions [28], and coagulation/flocculation [29,30] by reducing the negative charges. Combining these three agents may constitute an ideal reverse emulsion breaker for the treatment of super heavy oil wastewater and the objective of this work is to investigate his feasibility experimentally.

2. Materials and methods

2.1. Materials

SHOW was obtained from a heavy oil wastewater treatment plant in Liaohe oilfield in northeast China. The wastewater was composed of the produced water (70%), steam assisted gravity drainage wastewater (15%), scum and filtered wastewater (10%), and ion-exchanged wastewater (5%).

$CaCl_2$ was obtained from Weifang Taize Chemical Industry Co., Ltd. with $CaCl_2$ > 94%, Alkali Chloride <5.0%, water insoluble matters <0.2%. The pH of 10% water was 9–10 and whiteness was 90. The P-DcE was synthesized by polycondensation of epichlorohydrin with dimethylamine using a polymerization process previously described (viscosity of 110 mPas and cationicity of 4.5 mmol/g) [22]. The CPAM had a molecular weight of 6–7 million and cation content of 25%. The concentration of concentrated sulfuric acid was more than 98%. All the chemicals except P-DcE were industrial grade and conformed to the Chinese National Standards.

2.2. Experimental methods

2.2.1. Determination of different type oil in SHOW

The filter columns were prepared according to the following procedures. The quartz sand was sifted through a sieve with a 0.15 mm aperture to remove dust and washed several times with distilled water to remove fine particles until the effluent was visually clear and colorless. The scum and light impurities were skimmed off and the quartz sand with diameters of >0.84 mm, 0.84–0.42 mm, 0.42–0.21 mm was homogenized at a ratio of 6.4:5.7:1 and put into glass tubes (ϕ 50 mm and 200 mm long) tightly.

SHOW was pre-treated by the following procedures. It was poured into a 2000 mL graduated container and let standing for 120 min. The floating oil was skimmed off and then filtered by the filter column at a flow velocity of 20 m/min. The effluents were used in the demulsification tests.

The total oil, floating oil, dispersed oil, emulsion oil, and dissolved oil were measured on an infrared spectrophotometer.

2.2.2. Demulsification tests

A jar apparatus (ZR4-6, Laboratory Stirrer, Shenzhen Zhongrun Water Industry Technology Development Co., Ltd., China) with six 1000 mL beakers was used. All the agents were prepared using tap water and the concentrations of P-DcE, CPAM, and $CaCl_2$ solution were 10, 1.2 and 100 mg/g, respectively. The sample volume in each beaker was 500 mL and heated to 70 °C to simulate the treatment plant wastewater before the test. The beakers were stirred at 250 rpm for 3 min after the agent was added and left standing for 30 min. The surface oil was skimmed and discarded. The wastewater was filtered by the filter column and the effluents in the middle 300 mL were used to determine the mineral oil concentration, COD, and light transmittance.

2.3. Analytical methods

The mineral oil concentration was determined on an infrared spectrophotometer (F2000, Jilin China). The light transmittance was measured by ultraviolet spectrophotometer (7230G, Shanghai) at 420 nm, and COD was determined using the dichromate method (Water quality-Determination of the chemical oxygen demand-Dichromate method GB11914–89). The oil value and light transmittance were measured three times to obtain average values.

Ion detection was by ion chromatography (Dionex Ionpac, USA) and Cl^- ions were detected as follows: AS11-HC 4 × 250 mm, 30 mmol/L NaOH, 30 °C, 1.5 mL/min, detector being ASRS-ULTRA, and injection volume being 10 mL. Similarly, Na+, K+, and Ca^{2+} ions were identified under the following conditions: CS12A 4 × 250 mm, 20 mmol methanesulfonic acid, 30 °C, 1.0 mL/min, detector being CSRS-ULTRA, and injection volume being 25 mL.

GC–MS was carried out on an Agilent 7890 A/5975C GC–MS system (Agilent Technologies Co. Ltd., USA). 1000 mL of the sample were extracted by 60 mL of CH_2Cl_2 and methanol (v/v = 2:1) three times at pH of 2, 7, and 11. The organic phase was merged, dehydrated by an anhydrous sodium sulfate capillary column, and concentrated to 1 mL by purging with nitrogen. The pretreated samples (1 μL) were analyzed by GC–MS. 99.999% pure He was used as the carrier gas (flow rate of 1.1 mL/min). A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, J&W Co. Ltd., USA) was adopted in the separation system. The temperature of the gasification compartment was maintained at 290 °C. The temperature control program for the column maintained the temperature at 50 °C for 5 min. The temperature was increased at an increment of 10 °C/min to 300 °C and maintained for 10 min. The electron energy and electron double

Table 1
Super heavy oil wastewater characterization.

Parameter	Concentration	Parameter	Concentration
Temperature(°C)	81.5	SiO_3^{2-} (mg/L)	184
pH	8.2	Mg^{2+} (mg/L)	31
Mineral oil (mg/L)	6650	Ca^{2+} (mg/L)	403
SS (mg/L)	2475	$Na^+ + K^+$ (mg/L)	3113
COD (mg/L)	23480	SO_4^{2-}(mg/L)	1086
Cl^- (mg/L)	2345	color	Brownish-black

voltage were set at 70 eV and 1365 V, respectively. The molecular weights were scanned from 50 to 550 amu.

2.4. Data analysis

The removal rate was calculated by the following formula:

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\%, \quad (1)$$

where η is removal rate, C_0 (mg/L)is the COD or mineral oil concentration in the influent, and C_e(mg/L) is the COD or mineral oil concentration in the effluent.

The biodegradability was calculated by the following formula:

$$R = \frac{BOD_5}{COD_{Cr}}, \quad (2)$$

where R is biodegradability, BOD_5 (mg/L)is the BOD_5 concentration in the influent, and COD_{Cr} (mg/L) is the COD concentration in the effluent.

3. Results and discussion

3.1. Properties of SHOW

As shown in Table 1, the SHOW has high concentrations of mineral oils and suspended solids (SS), high chemical oxygen demand (COD), high temperature, high stability of o/w emulsion, and a brownish-black color. The mineral oil recovered from SHOW has a high density close to that of water, high pouring point, large viscosity, and asphaltenes and resins contents of more than 30% (m/m) as shown in Table 2. Generally, it is difficult to demulsify the emulsion if the density difference between the oil and water is less than 0.05 g/cm^3. Since the density difference is only 0.01 g/cm^3, it is difficult to demulsify SHOW. The oil in the oilfield wastewater is mainly a stabilized oil-in-water emulsion with droplet size in the range 3–20 μm [17]. Table 3 shows about 44.93% and 2988 mg/L mineral oil in this range and so SHOW is a special oil wastewater that it is very hard to treat.

3.2. Optimal dose of agent used alone

The effects of the P-DcE dose on demulsification are shown in Fig. 1. The COD and mineral oil removal rates increase rapidly with increasing P-DcE doses from 10 to 60 mg/L and then slowly with the P-DcE dose increasing from 60 to 80 mg/L. The mineral oil and COD achieve largest removal rates (86.57% and 85.27%, respectively) when the P-DcE dose is 70 mg/L. Therefore, the suitable dose of P-DcE selected is 70 mg/L.

P-DcE is prepared by polycondensation of epichlorohydrin with dimethylamine [23]. As a cationic polyelectrolyte, it has both hydrophobic groups (methyl groups and backbone chain) and hydrophilic groups (positively charged quaternary amines), which can be used to remove suspended solids and colloidal particles from wastewater by charge neutralization and adsorption-bridging [21,23].

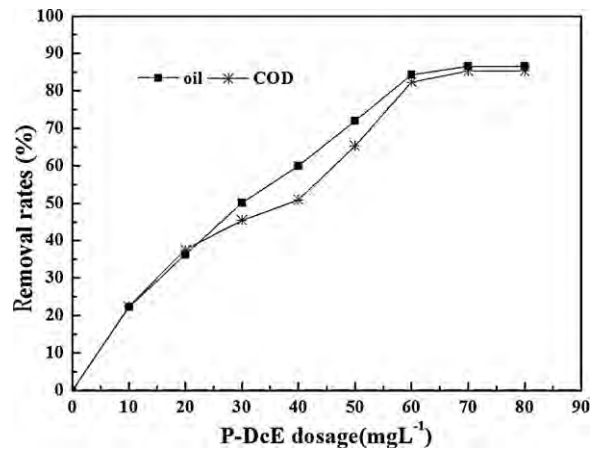
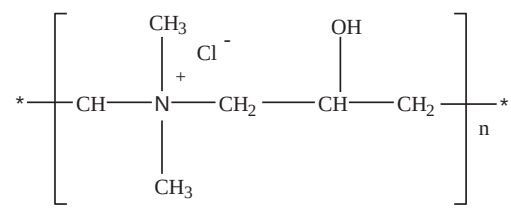


Fig. 1. Effect of P-DcE dosage on mineral oil and COD removal rates used alone.



P-DcE chemical structural formula

Kleimann [31] has found that the optimal flocculation occurs at polyelectrolyte doses of around that needed to just neutralize the particle charge or to give a zeta potential close to zero. More positive charges on the particle surface (a positive zeta potential) will re-disperse the particles and demulsification deteriorates.

The effects of the $CaCl_2$ dosage on demulsification are shown in Fig. 2. When $CaCl_2$ is added, floc appears and precipitates on the bottom and the wastewater turns clear and transparent at once. The COD and mineral oil removal rates increase rapidly as the $CaCl_2$ doses are increased from 100 to 600 mg/L and then increase slowly with the $CaCl_2$ doses are increased from 600 to 800 mg/L. The mineral oil and COD show the largest removal rates (94.98% and 94.15%, respectively) when the dose is 800 mg/L. $CaCl_2$ used alone in the treatment of SHOW can offer higher removal rates of pollutants, but it is not conducive to mineral oil recovery. Therefore, the dose of $CaCl_2$ selected is 600 mg/L.

$CaCl_2$ can reduce electrostatic repulsion, increase the zeta potential [32], and promote emulsion instability [33]. In addition,

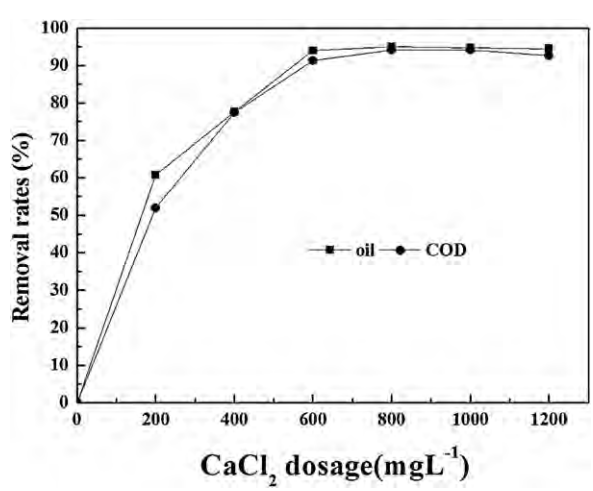


Fig. 2. Effect of $CaCl_2$ dosage on mineral oil and COD removal rates used alone.

Table 2
Physical properties and chemical components of the recovery mineral oil.

Density [a] ($g\,cm^{-3}$)	Pour point (°C)	Viscosity (mm^2/s)		Wax (%)	Resins (%)	Asphaltenes (%)
		80 °C	100 °C			
0.9897	45.9	5011.5	1208.8	<2.0	29.3	3.6

[a] 20 °C.

Table 3
Concentrations and contents of different type oil in SHOW.

Parameter	Total oil	Floating oil	Free droplets oil	Emulsification oil	Dissolved oil
Concentration (mg/L)	6650	2455	1183	2988	24.13
Diameter (μm)	/	≥100	10–100	0.1–10	≤0.1
Content (%)	100	36.92	17.79	44.93	0.36

$CaCl_2$ can hydrolyze hydroxide colloids and absorb oil drops, reduce the number of anionic surface active agent on the emulsion oil drops surface, and promote the emulsion break. When charges are balanced, adding more $CaCl_2$ will change the solution from negative to positive charges and the solution will be emulsified again. Consequently, the removal rates of COD and mineral oil decrease.

CPAM is a good flocculent aid in wastewater treatment [24], but it has no oil and water separation and flocculent characteristics when used alone.

3.3. Synergistic demulsification

The prior tests (Section 3.2) indicate that $CaCl_2$ and P-DcE are good agents for SHOW demulsification but they have different characteristics. For instance, $CaCl_2$ can produce high removal rates of mineral oil and COD, but is not good for mineral oil recovery. CPAM does not lead to obvious demulsification. Because each type of demulsifier has different mechanism, it is usually used together.

3.3.1. Effects of P-DcE dose on synergistic demulsification

The dose of $CaCl_2$ is fixed as 600 mg/L and the effects of the P-DcE dose on synergistic demulsification are shown in Fig. 3. When the P-DcE dose increases from 10 to 50 mg/L, the COD and mineral oil removal rates increase quickly at first then slowly attaining the highest value at 50 mg/L, but the economical dose is 20 mg/L. Hence, the best dose of P-DcE is 20 mg/L. The best dose of P-DcE in this study is less than that of P-DcE used alone, and the removal rates of mineral oil and COD are 98.69% and 92.74% higher than 86.57% and 85.27%. The mineral oil removal rate is also higher than that when using $CaCl_2$ alone (94.98%), and mineral oils aggregate quickly and recover easily.

3.3.2. Effects of $CaCl_2$ doses on enhancing synergistic demulsification

The dose of P-DcE is fixed as 20 mg/L and the effects of the $CaCl_2$ dose on synergistic demulsification are shown in Fig. 4. The removal rates of mineral oil and COD increase with $CaCl_2$ dose quickly from 100 to 400 mg/L, and then increase slowly as the $CaCl_2$ dose increases from 400 to 600 mg/L. The best removal rates of mineral oil and COD are 98.68% and 94.05%, respectively.

3.3.3. Effects of CPAM dose on synergistic demulsification

According to the experiments described in Section 3.3.1 and 3.3.2, the doses of P-DcE and $CaCl_2$ are fixed of 20 mg/L and 600 mg/L, respectively. The effects of the CPAM dose on demulsification are shown in Fig. 5. When the CPAM dose is increased from 0.3 to 1.2 mg/L, the removal rates of COD and mineral oil increase becoming highest at 1.2 mg/L and then decrease slowly when the CPAM dose is increased from 1.2 to 1.8 mg/L. The optimal dose of CPAM on synergistic demulsification is 1.2 mg/L. Based on mineral oil recovery, pollutants removal, and cost, the optimal dose of P-DcE: $CaCl_2$: CPAM is 20:600:1.2.

3.3.4. Apply orthogonal experiment for results verification

The famous orthogonal experiment [34] was applied for results of optimize the REB dosage to have synergistic demulsification of SHOW verification. The results obtained (Table 4) indicates this

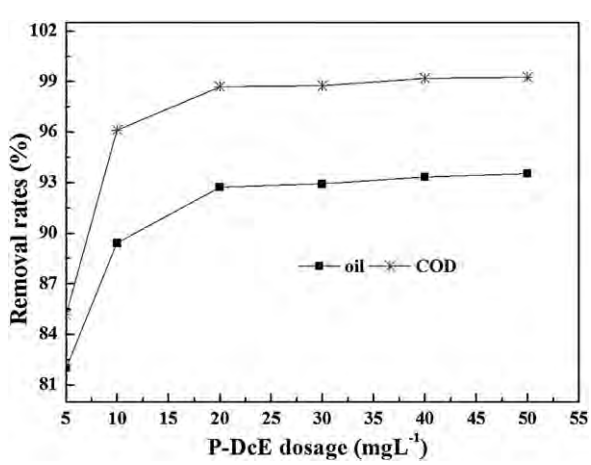


Fig. 3. Effect of P-DcE dosage on synergistic demulsification.

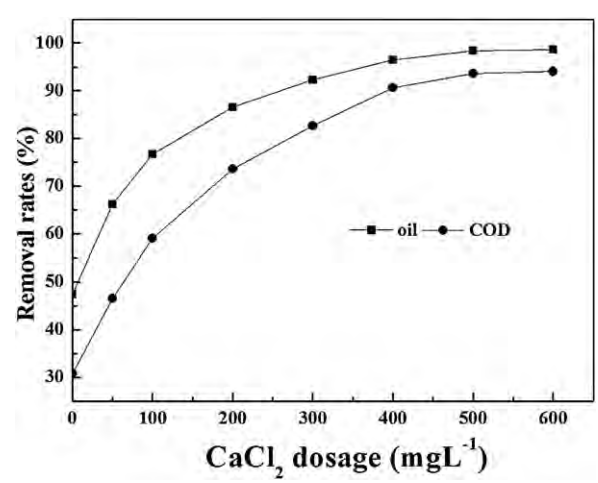


Fig. 4. Effect of $CaCl_2$ dosage on synergistic demulsification.

Table 4
Design dosages of three agents and contrasts.

No.	Dosage (mg/L)			COD removal rate (%)	Oil removal rate (%)
	P-DcE	CPAM	$CaCl_2$		
1	10	0.8	400	91.38	95.33
2	10	1.2	600	92.53	96.49
3	10	1.6	800	92.86	96.88
4	20	1.2	400	93.68	97.04
5	20	1.6	600	94.02	97.26
6	20	0.8	800	94.67	98.46
7	30	1.6	400	94.85	98.19
8	30	0.8	600	95.23	98.78
9	30	1.2	800	95.67	99.05

combinatorial optimal condition gives a comparatively optimal dose not only the COD and oil removal rates but also economic.

3.4. Contrast with two other demulsify methods

In order to evaluation this complex REB, the removal rates of mineral oil and COD, organic pollutant residues, degradability, and cost are compared to two other demulsify methods, P-DcE used alone and P-DcE supplemented with concentrated sulfuric acid.

3.4.1. Removal rate of COD and mineral oil

One demulsification method is to use P-DcE alone at the optimal dose of 60 mg/L and the other is P-DcE supplemented with concentrated sulfuric acid to strengthen demulsification. The process of the second demulsify method is described in the following. 540 mg/L of concentrated sulfuric acid is added to SHOW to adjust the pH to 5.5–6, followed by addition of 20 mg/L of P-DcE. The doses of concentrated sulfuric acid and P-DcE in this experiment are optimal. The REB is combined with P-DcE, $CaCl_2$, CPAM, and water at a ratio of 2: 60:0.12:940 and the best dose is 10 g/L. After the treatment, the removal rates of mineral oil and COD of P-DcE, H_2SO_4+ P-DcE, and REB are 97.26, 97.81, 98.04% and 93.54, 94.04, 94.48% respectively. Table 5 indicates that the highest removal rates of mineral oil and COD is achieved on REB, and it is also the most economical and safe.

3.4.2. Analysis by gas chromatography–mass spectrometry

The GC-MS results in Fig. 6 of the organic species extracted from the heavy oil wastewater after demulsification are quite complex. There are 66, 62, and 57 species belonging to 8 groups (Table 6) as shown in Fig. 6a–c. The seven groups are alkanes, ketones, alcohols, organic acids, benzenes, alkenes and esters or aldehydes. The other group consists of hexamethyl-cyclotrisiloxane, 2-ethylacridine, 2,4-dimethyl-benzo[h] quinoline, 1-(2-adamantylidene) semicarbazide, and so on. All the substances are large-molecular organic compounds and most of them are oilfield chemicals (corrosion inhibitors, scale inhibitors, biocides, and demulsifiers). As shown in Fig. 6a–c, the abundance and contents of the main substance in the effluent c (REB) are less than those of effluent a (P-DcE), b (P-DcE+H_2SO_4). The concentration of (2,3-diphenylcyclopropyl)methyl phenyl sulfoxide, trans- is largest in effluent a, but removed completely from effluents b and c. The concentrations of 23,28-bisnor-17.alpha.(H)-hopane and 23,28-bisnor-17.beta.(H)-hopane also decrease in effluents b and c, and they are the lowest in effluent c (Table 7). The chromatograms indicate that REB can remove much more organic substances than the other two methods, especially organic acids. Hence, it may be concluded that REB is the best demulsifier.

Ca^{2+} can react with sodium naphthenate. Sodium asphaltene which stabilizes oil in the water emulsion becomes naphthenates, asphaltenes, or calcium naphthenates, and calcium asphaltenes make the emulsion break [35]. The electrolytes containing chlorides improve COD removal compared to that accomplished with sulphate ions [36]. After demulsification, the mineral oil separated from SHOW removed by charge neutralization and adsorption-bridging of P-DcE enhances charge neutralization, absorption-bridging, and absorption of CPAM.

$$2RCOONa + Ca^{2+} \Rightarrow Ca(RCOO)_2 \downarrow + 2Na^+$$

Here, *R* stands for naphthenates, asphaltenes, aliphatic acid, or aromatic acids.

3.4.3. Biodegradability analysis

In general, if the BOD/COD ratio of the untreated wastewater is 0.5 or greater, the wastewater is easily biodegradable. Below 0.3, the wastewater contains some toxic components, and special kinds of microorganisms are required for biodegradation [37]. In this study, the ratios of BOD_5 to COD of a, b and c are 0.12, 0.19 and 0.10, respectively, and so effluent c shows good performance in anaerobic digestion. Our results agree with those of Chipasa [38] and Ahn [39], and low biodegradation means that the residual organic compounds such as vyclotrisiloxane, hexamethyl-, 2-ethylacridine, and

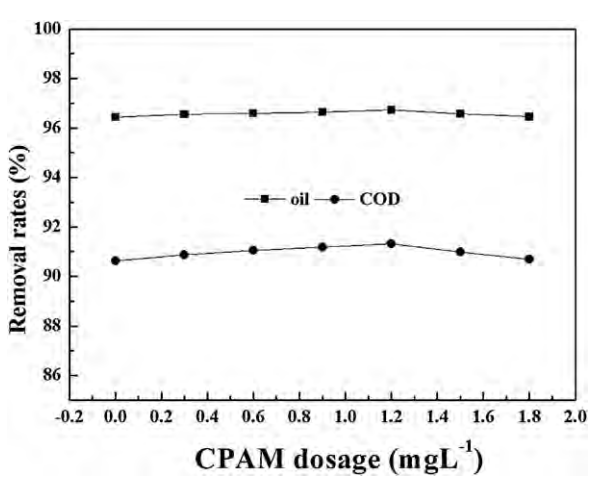


Fig. 5. Effect of CPAM dosage on synergistic demulsification.

Table 5
The treatment results and cost of three demulsifiers.

Parameter	a	b	c
Oil removal rate (%)	97.26	97.81	98.04
COD removal rate (%)	93.54	94.04	94.48
Light transmittance (%)	26.2	29.3	31.4
pH	8.29	6.06	7.76
Cost (CNY/m^3)	0.90	0.70	0.64

a: P-DcE, b:H_2SO_4+ P-DcE, c: REB.

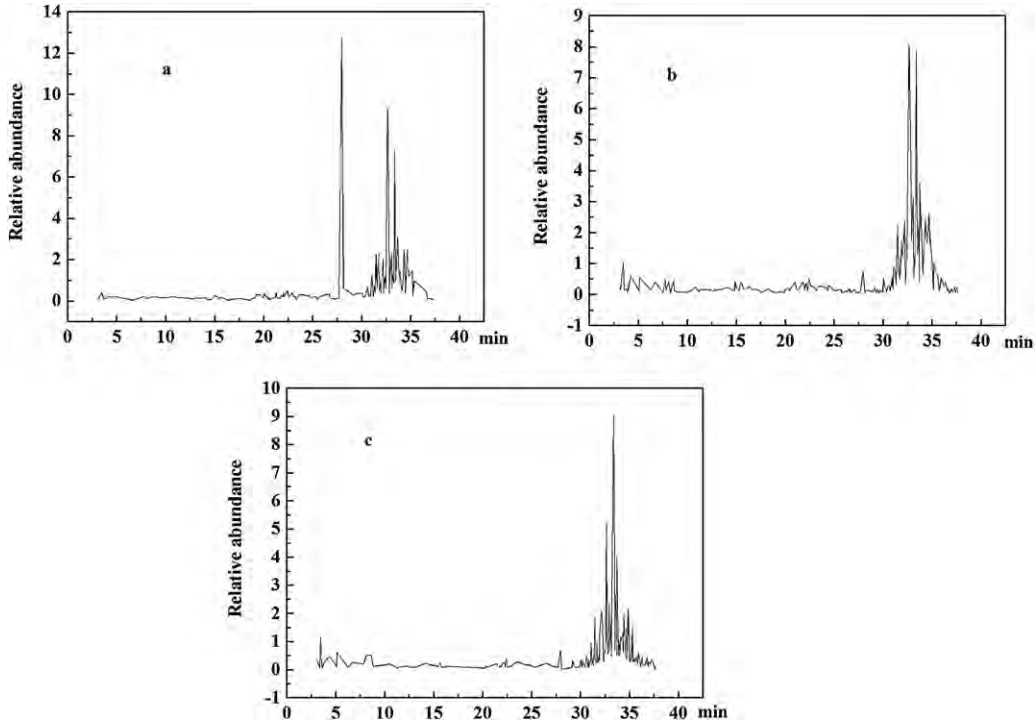


Fig. 6. Gas chromatography–mass spectrometry results: (a) P-DcE, (b) P-DcE + H_2SO_4, (c) REB.

Table 6
Organic species and contents in GC–MS chromatogram.

Group	a		b		c	
	species	Content (%)	species	Content (%)	species	Content (%)
alkanes	2	16.55	4	16.73	4	14.53
ketones	6	3.078	7	3.796	4	1.673
alcohols	3	2.094	3	2.713	2	0.990
organic acids	5	0.830	4	1.210	2	0.253
benzenes	4	0.714	9	3.350	4	1.583
esters	1	0.394	0	–	2	1.280
alkenes	1	0.202	3	0.817	3	0.426
aldehydes	0	–	1	0.266	0	–
others	44	76.14	30	71.12	36	79.26
total	66	100.0%	62	100.0%	57	100.0%

a: P-DcE; b:H_2SO_4+ P-DcE; c: REB; "–" Not detected.

Table 7
Main organic compounds and abundances in three effluents.

	Compound	Molecular formula	Content (%)			Abundance		
			a	b	c	a	b	c
1	2-Ethylacridine	$C_{15}H_{13}N$	17.50	18.09	13.59			
2	Cyclotrisiloxane, hexamethyl-	$C_6H_{18}O_3Si_3$	16.95	36.36	43.79			
3	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	$C_{22}H_{22}OS$	12.74	–	–			
4	Benzo[h]quinoline, 2,4-dimethyl-	$C_{15}H_{13}N$	9.887	–	4.039			
5	23,28-Bisnor-17.alpha.(H)-hopane	$C_{30}H_{52}$	9.261	8.026	9.049	150,000	75,000	61,000
6	23,28-Bisnor-17.β.(H)-hopane	$C_{30}H_{52}$	7.291	7.880	5.189	175,000	95,000	81,000
7	Indolizine, 2-(4-methylphenyl)-	$C_{15}H_{13}N$	2.485	–	–			
8	1-(2-Adamantylidene)semicarbazide	$C_9H_{10}NOS$	–	4.228	2.636			
9	Tetrasiloxane, decamethyl-	$C_{10}H_{30}O_3Si_4$	–	2.354	2.664			
10	Silicic acid, diethyl bis(trimethylsilyl) ester	$C_{10}H_{28}O_4Si_3$	–	–	2.640			

Note: a, P-DcE; b,H_2SO_4+P-DcE; c, REB; "–" Not detected.

so on are recalcitrant chemicals that cannot be removed by a single biological treatment [40].

4. Conclusion

A reverse emulsion breaker combined by P-DcE, $CaCl_2$, and CPAM with an optimal ratio of 20:600:1.2 offers good removal rates for mineral oil (98.04%) and COD (94.48%). GC–MS indicates that the REB can remove more organic compounds such as mineral oil than the others and most of the residues are oilfield chemicals including corrosion inhibitors, scale inhibitors, biocides, and demulsifiers. Compared to P-DcE and P-DcE coupled with concentrated sulfuric acid, the REB has high removal rates for mineral oil and COD, low cost, and environmental friendliness. The

REB effluent has low BOD/COD and delivers good performance in anaerobic digestion. $CaCl_2$ is also good for synergistic demulsification of super heavy oil wastewater. Some oilfield chemicals such as cyclotrisiloxane, hexamethyl- and 2-ethylacridine which are refractory organic compounds with high concentrations in SHOW may be replaced by other chemicals with easy degradation or recovery to reduce harm to the environment and save resources.

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