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

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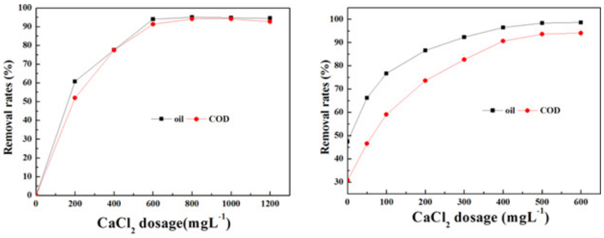
HIGHLIGHTS

- ▶ $CaCl_2$ 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



$CaCl_2$ dosage(mgL^{-1}) $CaCl_2$ dosage (mgL^{-1})

$CaCl_2$ used alone on demulsification. $CaCl_2$ synergistic demulsification with EPI-DMA

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ABSTRACT

Calcium chloride ($CaCl_2$) is used together with cationic poly (dimethylamine-co-epichlorohydrin) (P-DcE) and cationic polyacrylamide (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