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# Application of rhamnolipid as a novel biodemulsifier for destabilizing waste crude oil

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## HIGHLIGHTS

- ▶ Rhamnolipid showed a high demulsification activity on waste crude oil.
- ▶ The demulsification activity of rhamnolipid was confirmed on model emulsions.
- ▶ The demulsification activity of rhamnolipid was confirmed at pilot sale treatment.
- ▶ The recovered crude oil can enter into refinery process.
- ▶ Rhamnolipid showed great prospects in industry as a biodemulsifier.

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## ABSTRACT

Waste crude oil emulsion was inevitably produced in the petroleum industrial process, causing harmful impact on the ecological and social environment. In this study, rhamnolipid was for the first time investigated for demulsification of waste crude oil. As found in this paper, rhamnolipid treatment could obtain over 90% of dewatering efficiency on refractory waste crude oil and such efficient demulsification was confirmed on model emulsions. As further demonstrated on the pilot scale (100 L), rhamnolipid treatment could recover over 98% of crude oil from the wastes. The recovered oil contained less than 0.3% of water and thus can directly re-enter into refinery process while the aqueous phase can be disposed into dischargeable water due to largely reduced soluble COD after subjected to 5 days of active sludge treatment. It seems that rhamnolipids as biodemulsifiers were of great prospects in the industrial demulsification of waste crude oil.

## 1. Introduction

Millions of tons of waste crude oil generated from crude oil transportation, storage and refinery process were highly stable due to the presence of indigenous surface active components (asphaltenes, resins, naphthenic acids, etc.), the proposed added chemical surfactants and the natural solid particles (clay and waxes) (Banat et al., 2000; Jiang et al., 2010; Rondón et al., 2007). Such waste crude oil was normally comprised of 30–90% of oil, 30–70% of water and 2–15% of solids by mass and presented as a complex water-in-oil (W/O) type emulsion (Yang et al., 2005; Zhang et al., 2012). They cannot be directly used due to a high content of water or released into environment due to their hazard to micro-organisms, natural biodegraders and even human health (Cambiella et al., 2006). Hence, demulsification is needed to separate this waste into oil phase and aqueous phase so that the recovered oil, if containing less than 0.5% of water, can re-enter into refinery process (Bhardwaj and Hartland, 1994) and the water at a low oil content can be subjected to conventional wastewater treatment (Xia et al., 2010).

So far, diverse strategies like electro-sedimentation, ultrasonic, centrifugation, chemicals, membrane separation and ionic liquids have been applied for breaking W/O type crude oil emulsions (Marchese et al., 2000), among which chemical demulsifier is most widely used (Feng et al., 2009). Three generations of chemical demulsifiers appeared since last century. The anionic surfactants

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*Abbreviations:* W/O, water-in-oil; O/W, oil-in-water; CMC, critical micellar concentration; MLSS, mixed liquor suspended solids; COD, chemical oxygen demand; Tween, polysorbate; SDS, sodium dodecyl sulfate; OP, poly oxy ethylene octyl phenol ether.

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including fatty acid and naphthenic acid appeared as the first generation around 1920–1930 (Staiss et al., 1991) followed by the second generation at 1940s composed of nonionic surfactants like polysorbate (Tween) and poly oxy ethylene octyl phenol ether (OP), etc. (Staiss et al., 1991). The third generation is polyether-type surfactant represented by alkoxylated vinyl polymer (Stephenson, 1990), etc. But these chemical demulsifiers, though being effective, are mostly refractory organic polymers and often made the ambient ecosystem subjected to more hazardous risk, greatly limiting their applications (Huang et al., 2010).

In opposite to chemical demulsifiers, biodemulsifier such as demulsifying bacterial cells or their extracellular metabolites (Huang et al., 2012) was more desired for use in demulsifying due to its higher interfacial activity, no secondary pollution, low toxicity and good performance under extreme conditions (Liu et al., 2010). Hence, the academic study of biodemulsifiers have been enthusiastically reported on their potential applications particularly in petroleum field (Van Hamme et al., 2003) and food processing (Ly et al., 2006). However, such biodemulsifiers are commonly cost-ineffectively produced due to the low yield at bioprocess and the high instability of product at transportation, preventing their practical applications (Liu et al., 2010).

Rhamnolipids possess unique high surface activity and thus have been widely gained interests in diverse industrial fields as emulsifier, detergent and antibiotics etc (Banat et al., 2000; Reis et al., 2011). So far, rhamnolipid is one of the most important biosurfactant due to its commercial availability (Lang and Wullbrandt, 1999) as well as its great application potentials. This paper will investigate the applicability of rhamnolipids in demulsifying waste crude oil.

## 2. Methods

### 2.1. Materials

The waste crude oil was obtained from Shengli refinery (Zibo, China) at two bathes. The waste crude oil was very sticky and of great stability, its characteristics are listed in Table 1. Crude rhamnolipid solution (25 g/L, pH 7) was obtained from Huzhou Gemking Biotechnology Co., Ltd. (Huzhou, China). Its major components are di-rhamnolipid ($C_{32}H_{58}O_{13}$) and mono-rhamnolipid ($C_{26}H_{48}O_9$) at a mass ratio of 2.6 (Sha et al., 2012a). Kerosene was obtained from local gas station of Sinopec (Hangzhou, China). The surfactant Span 80 and Tween 60 were purchased form Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The remaining chemicals were supplied by a local supplier and all are of reagent grade.

### 2.2. Kerosene–water model emulsion preparation

To prepare model O/W emulsion, 200 mL of kerosene contain 0.8 g/L Span 80 and 300 mL of deionized water containing 1 g/L of Tween 80 were mixed at 10000 rpm for 3 min with the aid of high speed emulsifying machine (Nadarajah et al., 2002). Model W/O emulsion was obtained by mixing 300 mL kerosene contains 16.7 g/L Span 80 with 200 mL of deionized water at 10000 rpm for 1 min (Huang et al., 2009). The emulsion type was identified by electrical conductivity test (Brooks and Richmond, 1991) and Oil Red O test (Lee and Lee, 2000). Both W/O and O/W emulsions were stable and showed less than 5% of demulsification ratio at room temperature within 24 h.

**Table 1**
The composition of four types of emulsions.

| Emulsions | Fractions | | |
|---|---|---|---|
| | Water (%(v/v)) | Oil (%(v/v)) | Solid (%(v/v)) |
| Waste crude oil (W/O) for bench scale | 41.8 ± 0.6 | 54.1 ± 0.9 | 4.1 ± 0.4 |
| Waste crude oil (W/O) for pilot scale | 34.3 ± 2.7 | 61.2 ± 1.1 | 4.5 ± 1.7 |
| Model O/W emulsion | 60.0 | 40.0 | 0 |
| Model W/O emulsion | 40.0 | 60.0 | 0 |

Data are given as mean ± SD, *n* = 3.

### 2.3. Bench scale demulsification experiments

For waste crude oil, the demulsifying activity of rhamnolipid was tested under a concentration of rhamnolipid at 500, 1000, 1500 and 2000 mg/L, respectively. For model emulsions, the demulsifying activity of rhamnolipid was tested under a concentration range of 100–800 mg/L. To investigate the influence of pH on the demulsification activity of rhamnolipid, both waste crude oil and model emulsions were, respectively regulated to pH 3–10 using 1 N HCl or 1 N NaOH. After rhamnolipid addition and pH adjustment, the glass test tube filled by 5 mL crude oil or model emulsion was then vortexed at a maximum speed to achieve a complete mixing and then settled in water bath at 55 °C for 16 h. A parallel control was simultaneously run in each experiment. All experiments were carried out in triplicate. At the end of demulsification, the volume of separated water (bottom layer) and residual emulsion (middle layer) were recorded. And the demulsification performance on waste crude oil and model emulsions was evaluated by calculating water separation ratio (or named dewatering efficiency) and demulsification ratio, respectively, using the following equations:

$$\text{water separation ratio } (\%) = \frac{\text{separated water volume}}{\text{added sample volume} + \text{Original water in the emulsion}} \times 100$$

$$\text{Demulsification } (\%) = \left(1 - \frac{\text{remaining emulsion volume}}{\text{total emulsion volume} + \text{added sample volume}}\right) \times 100$$

### 2.4. Pilot scale demulsification experiment

To confirm the demulsification activity of rhamnolipids, two batches of pilot scale demulsification were conducted. One hundred litres of waste crude oil in a 150-L stirring reactor was subjected to the rhamnolipid treatment at 1000 mg/L (pH 10). After a mild stirring mixture for 10 min, the waste crude oil was maintained under a temperature of 55 °C. After settled for 48 h, the aqueous phase on the bottom was discharged, and its volume as well as oil content was measured. Then, the sticky oil phase in black was collected every 500 mL and its water content was immediately measured. Until the water content is detected to be less than 1%, all the residual oil was collected as the recovered oil while the collected fractions before that were merged as middle emulsion phase. The water content and volume in both the recovered oil and the middle emulsion phase were respectively measured. The oil recovery ratio was calculated using the following equation:

$$\text{Oil recovery } (\%) = \frac{\text{obtained oil phase volume} \times \text{oil content}}{\text{total oil volume in the emulsion}} \times 100 \qquad (3)$$

### 2.5. Analyses of residual water and oil content

The water content in oil phase or middle emulsion phase was measured using Karl Fischer titrator (WA-1A, Jiangfen electroana-