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Dewatering of floated oily sludge by treatment with rhamnolipid

Xuwei Long [a], Guoliang Zhang [b], Li Han [c], Qin Meng [a,*]

[a] Department of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou, Zhejiang 310027, PR China
[b] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou, PR China
[c] Shengli Refinery, Sinopec Qilu Petrochemical Corporation, Linzi, PR China

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ABSTRACT

Oily sludge dewatering is practically needed prior to sludge treatments. However, the conventional use of physical treatments with or without chemical conditionings presented poor feasibility in industrial applications due to either poor cost-efficiency or lacking environmental friendliness. In this paper, biosurfactant rhamnolipid was for the first time applied for dewatering of oily sludge. Rhamnolipid treatments under the concentration of 300–1000 mg/L, pH of 5–7 and temperature of 10–60 °C could directly separate 50–80% of water from the stable oily sludge. And both mono-rhamnolipid and di-rhamnolipid were identified to be of equivalent dewatering ability, which is closely related to their equivalent performance in breaking the emulsified oil droplets. Demulsification was found to be involved in settling water from oily sludge. Furthermore, the effectiveness of rhamnolipid was further demonstrated at pilot scale (1000 L) treatment of oily sludge. After pilot treatment, the settled water with residual oil of 10 mg/L and soluble COD of about 800 mg/L could be directly effluxed into the biotreatment system while the concentrated oil sludge with a reduced volume by 60–80% can be pumped into coking tower, achieving completely harmless treatment. It seems that rhamnolipid as dewatering agent was of great prospects in the industrial dewatering of oily sludge.

1. Introduction

The oily sludge, accumulated from dissolved air flotation (DAF) processes in petroleum refineries, has become a current problem due to its huge production as well as potential threat to the environment and human health. The semi-solid oily sludge from flotation process usually contains water of 90–99 w%, waste crude oil of 0.5–3 w%, and mineral particles of 0.2–7 w% (da Silva et al., 2012; Guo et al., 2011).

As clean-up strategies like incineration (Li et al., 1995; Liu et al., 2009) and bioremediation (Vasudevan and Rajaram, 2001) are energy/time-consuming for treatment of the oily sludge (Vasudevan and Rajaram, 2001), the dewatering by physical treatment is more efficient by separating the large amount of water from the oily sludge before clean-up treatment (Raynaud et al., 2012). Physical treatments including electro-kinetic dewatering (Yang et al., 2005) and pressure filtration (Jean and Lee, 1999) could remove 20–50% of water

Abbreviations: DAF, dissolved air flotation; TSS, total suspended solid; BOD, biochemical oxygen demand; COD, chemical oxygen demand; W/O, water-in-oil; O/W, oil-in-water; SDS, sodium dodecyl sulfate; SDBS, sodium dodecyl benzene sulfonate; Tween, polyoxyethylene.

* Corresponding author. Tel.: +86 571 87953193; fax: +86 571 87951227.
E-mail address: mengq@zju.edu (Q. Meng).

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from oily sludge. The further use of chemical conditioners like flocculants and coagulants prior to physical treatment could improve filterability of oily sludge by increasing cake porosity of sludge and reducing compressibility of sludge (Buyukkamaci and Kucukselek, 2007; Qi et al., 2011). Nevertheless, the physical treatments alone achieved much limited efficiency on dewatering and required high amounts of mechanical equipments and energy (Guo et al., 2011), resulting in poor applicability in industry. Moreover, the large use of chemical conditioners like lime (Hwa and Jeyaseelan, 1997) could significantly increase the final sludge volume, eliciting uneconomical properties in industrial applications. Hence, it seems that the dewatering by physical treatments with or without conditioning is inefficient in industrial dewatering of oily sludge.

The direct dewatering of oily sludge *via* acid conditioning was found to effectively reduce sludge volume and, more importantly, require no specific mechanical equipments and energy input (Guo et al., 2011; Rattanapan et al., 2011). By acid conditioning to an extremely low pH of 1–3, an acceptable dewatering efficiency of 50–80% could be achieved (Guo et al., 2011; Rattanapan et al., 2011). To be expected, acidification was also effective in dewatering of another more extensively existing activated sludge (Chen et al., 2001) which generally contains the similar compositions as oily sludge except for oil content and hereby shares the similar characteristics on dewatering (Guo et al., 2011). The combinational use of surfactants could further improve dewatering efficiency in acidification treatment of activated sludge (Chen et al., 2001).

However, so far, the treatment by surfactants alone, though enhancing filterability of sludge (Huang et al., 2002; Yuan et al., 2011), has never been reported to directly settle water from activated sludge or from oily sludge. Biosurfactant rhamnolipids were once evidenced of capability in dewatering of oily sludge in our lab. As well known, glycolipid rhamnolipids, composed of one or two rhamnose molecules and up to three molecules of hydroxyl fatty acids, have been widely applied in emulsifying, washing, solubilizing and dispersing etc. (Heyd et al., 2008). To our knowledge, rhamnolipids, superior in high surface/interfacial activity, high biodegradability as well as environmental-friendliness (Banat et al., 2000; Reis et al., 2011), have never been reported of dewaterability.

This paper will thoroughly examine the applicability of biosurfactants rhamnolipid in dewatering of oily sludge. The appropriate operation conditions will be firstly investigated on concentration, pH and temperature. Unlike common assay of sludge filterability including the specific resistance to filtration and capillary suction time after conditioning (Raynaud et al., 2012), this paper will detect a more applicable index of water separation ratio for characterizing the dewatering efficiency. Finally, the pilot treatment of oily sludge together with the possible mechanism will be also focused for addressing the feasibility on the industrial application.

2. Materials and methods

2.1. Oily sludge

The oily sludge was generated from flocculant coagulation and DAF processes in Shengli refinery, Sinopec Qilu Petrochemical Corporation (Zibo, China). The oily sludge was collected at different period for bench scale and pilot scale research. The oily sludge sample appeared black and possessed poor settleability. Table 1 presents the main characteristics of oily sludge.

2.2. Chemicals

Crude rhamnolipid solution (25 g/L, pH 7) consists of dirhamnolipid and monorhamnolipid (Fig. 1) at a mass ratio of 2.6 (Sha et al., 2012). Crude rhamnolipid solution and its two components of mono-rhamnolipid and di-rhamnolipid with purity over 99% (Jiang et al., 2013) were obtained from Huzhou Gemking Biotechnology Co., Ltd (Huzhou, China). Crude oil demulsifiers E23025 and E23171 for water-in-oil (W/O) type emulsion were obtained form Kurita Chemical (Dalian) Co., Ltd (Dalian, China). The remaining chemicals were supplied by a local supplier and all are of reagent grade.

2.3. Dewatering experiments

2.3.1. Bench scale dewatering

To carry out dewatering experiments, the desired concentration of rhamnolipid and other dewatering agents listed in Table 2 were respectively added to 500-mL beaker containing 200 mL of oily sludge. The pH of oily sludge was adjusted by adding concentrated sulfuric acid or 10 M NaOH solution. After stirred for 3 min, the mixture was then kept undisturbed in water bath at a certain temperature. A control treatment without addition of rhamnolipids was run as parallel. All experiments on the bench scale were carried out in triplicate. After settling for 2 h, the volume of separated water was recorded. And the dewatering efficiency on oily sludge was evaluated using the water separation ratio according to the following equation (Wen et al., 2010):

$$\text{water separation ratio}[\%] = \frac{\text{separated water volume}}{\text{added sample volume} + \text{original water in the sludge}} \times 100 \qquad (1)$$

2.3.2. Pilot scale dewatering

The dewatering experiment on pilot scale was carried out at the wastewater treatment section in Shengli refinery of Sinopec Qilu Petrochemical Corporation. As shown in Fig. 2, 1000 L of the oily sludge (30–40 °C) filled in a 1500-L tank (the left one) was subjected to the rhamnolipid treatment with pH adjustment, and a control tank (the middle one) was similarly treated as a