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Oil recovery from refinery oily sludge using a rhamnolipid biosurfactant-producing *Pseudomonas*

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ABSTRACT

In this study, a rhamnolipid biosurfactant-producing strain, *Pseudomonas aeruginosa* F-2, was used to recover oil from refinery oily sludge in laboratory and pilot-scale experiments. The optimum values of carbon to nitrogen ratio, temperature, sludge–water ratio and inoculum size for oil recovery were determined as 10, 35 °C, 1:4 and 4%, respectively. An oil recovery of up to 91.5% was obtained with the equipping of draft tubes during the field pilot-scale studies. The results showed that strain F-2 has the potential for industrial applications and may be used in oil recovery from oily sludge.

1. Introduction

Oily sludge is a complex mixture of petroleum hydrocarbons, sediments, heavy metals and water, generated during the exploration and development of oilfields and also in the petroleum refineries. The annual output of oil sludge by China's refinery industry was estimated to be about 1,000,000 tons, mainly derived from the cleaning process of oil storage tanks (Liu et al., 2011).

Oily sludge is listed as hazardous waste in Resource Conservation and Recovery Act (RCRA) (USEPA, 1989), and represents a major source of contamination for soil, air and ground water. Because of its large yield, treatment difficulties, and potential hazards to the environment, oily sludge has become as a major problem plaguing the petroleum and petrochemical industry (Chang et al., 2000).

Due to the numerous sources of oily sludge, there is no single method for oily sludge treatment. Typically, oil sludge can be handled via various physical and chemical processes such as dewatering and incineration, stabilization, solvent extraction, washing by hot water and surfactant, pyrolysis, and biodegradation (Jing et al., 2011). However, each method has its own advantages and disadvantages. In general, expensive reagents and complex equipments are needed during the oil recovery from oily sludge using physical and chemical methods, complicating the processes and increasing operating costs. In addition, secondary pollution may be caused when chemical approaches are applied. Microbial degradation of oily sludge typically saves energy, capital investment and operating costs. However, it would be inadvisable to decompose oil by microorganisms, since oily sludge is recognized as a valuable energy resource that can be recycled as fuel (Shie et al., 2000).

Synthetic surfactants that are used to enhance contaminant solubility are often toxic, representing an additional source of contamination (Banat et al., 2004). Recently, extensive studies have been conducted on the isolation and characterization of surfactant-producing microorganisms and their application in environment remediation (Lai et al., 2009; Saeki et al., 2009; Sarachat et al., 2010; Ferhat et al., 2011).

Biosurfactants can be used not only for bioremediation processes, but also for cleaning oil storage tanks, increasing flow though pipelines and enhancing oil recovery from oil reservoirs (Desai and Banat, 1997). However, studies on the application of biosurfactants for oil recovery from oily sludge are still very scarce. Pornsunthorntawee et al. (2008) reported obtaining higher oil recoveries using biosurfactants than that obtained using synthetic surfactants on a laboratory scale.

In this study, studies on oil recovery from oily sludge using the biosurfactant-producing microorganism, *Pseudomonas aeruginosa* F-2, were carried out in laboratory and pilot-scale experiments. The orthogonal experimental design was used to determine the optimum conditions for oil recovery from the oily sludge. The

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outcome of this work is expected to provide a basis for developing environmentally friendly and economically competitive approaches for oily sludge treatment.

2. Methods

2.1. Microorganism

In this present study, a biosurfactant-producing microorganism, identified as *P. aeruginosa* F-2, was used in the laboratory and field pilot tests. This strain was isolated from petroleum-contaminated soil and stored in our laboratory (unpublished results). Preliminary experiments revealed that the rhamnolipid biosurfactant produced by strain F-2 could effectively emulsify crude oil and possessed stable surface activity at variable ranges of pH and salinity.

2.2. Oil sludge

The oil sludge sample used in the study was derived from the bottom sludge of oil separating tank in Dalian Petrochemical Branch Company, PetroChina, Liaoning Province, north-east China. The oil sludge sample appeared to be black, viscous and in the form of semi-solid cake at ambient temperature (Supplementary Fig. S1).

The organics containing oil and grease were represented by total extractable organics (TEO). The characteristics of the oil sludge sample were: moisture, 14.46 wt.%; pH, 7.1; ash, 1.98 wt.%; volatile matter, 95.62 wt.%; TEO, 46.80 wt.%; net calorific value, 28.27 MJ/kg; bituminous, 5.18 wt.%; saturated hydrocarbon, 23.52 wt.%; aromatic hydrocarbon, 9.53 wt.%; non-hydrocarbon, 8.57 wt.%. The oil sludge had lower moisture, lower ash content, higher volatile matter and oil content.

2.3. Laboratory batch experiments

To investigate factors impacting the recovery of oil using strain F-2, batch tests were carried out under varying conditions. The effects of four factors, i.e. C/N ratio, temperature, inoculum size and sludge/water ratio (v/v), on oil recovery were investigated using a L^9 (3^4) orthogonal experimental design (Table 1) (Taguchi, 1987). The results for all nine experiments were analyzed using the statistical software SPSS 13.0 (IBM, Chicago, IL, USA) for the analysis of variance (ANOVA).

The mineral medium (MM) consisted of (g/L): KCl, 1.1; NaCl, 1.1; KH_2PO_4, 3.4; K_2HPO_4, 4.4; plus 5 mL of a trace element solution containing (g/L): $ZnSO_4{\cdot}7H_2O$, 0.29; $CaCl_2{\cdot}4H_2O$, 0.24; $CuSO_4{\cdot}5H_2O$, 0.25; $MnSO_4{\cdot}7H_2O$, 0.17. Nitrogen was added as $(NH_4)_2SO_4$ in the proportions as shown in Table 1.

To obtain the inoculum, the bacterial colonies were transferred into a nutrient broth. Then the culture was incubated at 30 °C in a shaking incubator at 150 rpm for 48 h. The microbial growth was monitored as a function of cultivation time by measuring the absorbance of the culture medium every 2 h. From the graph plotting of microbial concentration and time, the best cultivation time was then determined. Then the culture medium was used as the inoculum for the tests.

Table 1
Factors and levels for the orthogonal test.

Design variable	Levels		
	1	2	3
(A) C/N ratio	5	10	20
(B) Temperature (°C)	20	35	45
(C) Sludge–water ratio (v/v)	1:2	1:4	1:6
(D) Inoculum size (%)	2	4	6

According to the levels listed in Table 1, oil sludge, MM, inoculum and water were added to a 250 mL Erlenmeyer flask to produce a total volume of 100 mL. The mixtures were then shaken on a rotator at 50 rpm. The extent of oil removal contributed by flushing with microorganism-free water was evaluated and considered as "blank effects" in comparison with that using inoculum to recover oil. To demulsify the mixture, after 72 h of incubation, dilute sulfuric acid was added to the flask at a concentration of 0.33% (w/v). Then the contents of the flask were allowed to settle for 2 h. The supernatant and oil layer were decanted from the flask after settling. The sludge was rinsed with distilled water and shaken for 3 min at 50 rpm, and the rinse water was decanted after settling. All the decanted solutions were pooled in a separating funnel, and the oil was extracted with dichloromethane. Oil recovery efficiency was calculated gravimetrically after evaporating the solvent under N_2.

2.4. Field pilot experiment

The pilot-scale experiment was carried out in the wastewater treatment plant of Dalian Petrochemical Branch Company. The schematic diagram and photos of the experimental system are shown in Figs. 1 and S2 (Supporting information) respectively. The system consisted of three identical stainless steel-made tanks (1.1 m long, 0.8 m wide, 1.1 m high), supported by a steel frame. They were laid side by side and the system has a total height of about 2.0 m. Three pipelines were placed on the side of each tank to introduce sludge, heating steam and tap water into the tanks, respectively. In addition, a level gauge was mounted on the side of each tank to control the addition of material and to monitor the separation of oil–water–sediment.

The tanks received oil sludge, inoculum solution, MM solution and water, based on the optimum conditions determined in the laboratory study. During the experiments, the local temperatures were relatively low (12–21 °C), thus the contents of the tanks were heated by the introduction of steam. The temperatures were controlled within the range of 30–40 °C by temperature controllers connected to the valves of the steam pipelines.

The treatment was terminated after 72 h of incubation by adding sulfuric acid to the tanks at a concentration of 0.33% (w/v). Then the treated sample was transferred into a centrifuge, and centrifuged at 5000*g* for 15 min. The oil and aqueous phase after centrifugation were separated, and the mass of oil layer separated was then measured and considered as the oil recovery.

The concentration of organic material in the aqueous phase separated from the oil was measured as chemical oxygen demand (COD). For this, samples were filtered through a 0.22 μm (pore diameter) membrane, and then were refluxed with a known excess of potassium dichromate for 2 h at about 150 °C. After digestion, the excess dichromate was titrated against ferrous ammonium sulfate.

2.5. Analysis of sludge properties

Sludge was analyzed for pH, ash and volatile matter using standard methods (Lu, 1999). Water contents were measured using the Dean and Stark method (ASTM D-95-05, 2005), which involves reflux distillation with toluene and separation of the water phase. The calorific value was determined using a PARR1281 calorimetric bomb. The sludge settling ratio (SSR) was measured as follows: Fresh sludge sample was mixed thoroughly, and then transferred into a 1 L graduated measuring cylinder for SER measurement. Sludge settling efficiency in each cylinder was monitored after 2 h of settlement and expressed as the volume ratio of settled sludge to mixed liquor.