Biosurfactants as demulsifying agents for oil recovery from oily sludge – performance evaluation
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ABSTRACT
The oil producing and petroleum refining industries dispose of a significant amount of oily sludge annually. The sludge typically contains a mixture of oil, water and solid particles in the form of complex slurry. The oil in the waste sludge is inextractible due to the complex composition and complex interactions in the sludge matrix. The sludge is disposed of on land or into surface water bodies thereby creating toxic conditions or depleting oxygen required by aquatic animals. In this study, a fumed silica mixture with hydrocarbons was used to facilitate stable emulsion (‘Pickering’ emulsion) of the oily sludge. The second step of controlled demulsification and separation of oil and sludge into layers was achieved using either a commercial surfactant (sodium dodecyl sulphate (SDS)) or a cost-effective biosurfactant from living organisms. The demulsification and separation of the oil layer using the commercial surfactant SDS was achieved within 4 hours after stopping mixing, which was much faster than the 10 days required to destabilise the emulsion using crude biosurfactants produced by a consortium of petrochemical tolerant bacteria. The recovery rate with bacteria could be improved by using a more purified biosurfactant without the cells.

Key words | biosurfactant, demulsification, oily sludge simulation, Pickering emulsion, sodium dodecyl sulphate

INTRODUCTION
Oily sludge from petroleum and petrochemical processing plants can be found in oil storage tanks, product tanks, slop oil emulsions, wastewater treatment plants and other areas (Elektorowicz & Habibi 2005; Taiwo & Otolorin 2009). The sludge typically contains a mixture of oil, water and solid particles in the form of a complex slurry matrix (Kam 2001). This mixture, due to its heterogeneous nature, is difficult to treat using simplified physical–chemical processes.

Disposal of oily sludge at landfills is no longer a viable option since the oily sludge contains hazardous compounds such as polycyclic aromatic hydrocarbons (PAHs) and traces of heavy metals (Chunjie et al. 2009; API 2010). Toxic leachate from landfills receiving untreated oily sludge can pollute groundwater or surface water bodies eventually. Due to the oil content, the oily sludge is classified as semi-liquid flammable waste, and disposal of the oily sludge into landfills is prohibited (USEPA 1995). Thus such wastes should be treated or stabilised prior to disposal. Currently, the sludge is partially treated using chemicals before disposal to landfills. However, rising energy costs and increasing environmental concerns have inspired the need to utilise this potential energy resource while minimising impact to the environment.

In order to recover the oil from the heterogeneous sludge complex, it is normally suggested to suspend the sludge into a stable emulsion that introduces structure of the oil slurry matrix into stable droplets of oil stabilised by hydrophobic particles. The mechanism responsible for the emulsion formation and stability is the adsorption of the solid particles at the oil and water interface (Kriipsalu et al. 2008). This creates a barrier between the oil droplets, thus hindering droplet coalescence (Sztukowski & Yarranton 2005). Any material with good adsorption properties can be integrated into the sludge before beginning the oil separation process from sludge. Many adsorptive materials such as zeolite, kaolinite clay, and silicate based adsorbents can be envisaged for this process. However, the effectiveness of the above adsorptive materials in facilitating emulsion formation of oily sludge has not been tested.

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The oil recovered from the sludge can be utilised in the production process, or can be used as a source of energy (as combustion fuel) (Elektorowicz & Habibi 2005). Different methods of recovering oil from sludge have been proposed in the literature with varying degrees of efficiency. Some of these methods work by complete destruction of the waste (Yokoyama et al. 1987), whilst others allow for recycling of the valuable hydrocarbons (Abouelnasr & Zubaidy 2008; Pinheiro & Holanda 2013).

The objective of this study is to develop a method to recover hydrocarbons petroleum (oil) fractions from oily sludge using a low cost and energy-efficient process. Biosurfactants are chosen for the process since they can be produced at a low cost in a self-replenishing process. The oil recovery by the use of chemically synthesised surfactants was used as the baseline for comparison with the performance biosurfactants from a mixed culture of petrochemical metabolising bacteria.

MATERIALS AND METHODS

Chemicals and reagents

The chemicals used to simulate the organic fraction of the sludge were toluene, dichloromethane, benzene, heptane and ethyl acetate all obtained from Sigma-Aldrich Pty Ltd, Johannesburg, South Africa. Silica particles with an average particle size of 14 μm and kaolinite clay (Sigma-Aldrich) modified with Sasol bitumen were dispersed in distilled water, and the organics were then added to this to complete the sludge model. This mixture was then homogenised with a WiseStir® overhead stirrer Model HS-30D (witeg Labor-technik GmbH, Germany). The surfactant used as the demulsifying agent was sodium lauryl (or dodecyl) sulphate (Merck, Johannesburg, SA).

Microbial growth media

Organisms to be used as biosurfactants were grown in basal mineral medium (BMM) prepared from commercial salts. The medium contained 10 mM NH₄Cl, 30 mM Na₂HPO₄, 20 mM KH₂PO₄, 0.8 mM Na₂SO₄, 0.2 mM MgSO₄, 50 μM CaCl₂, 25 μM FeSO₄, 0.1 μM ZnCl₂, 0.2 μM CuCl₂, 0.1 μM NaBr, 0.05 μM Na₂MoO₄, 0.1 μM MnCl₂, 0.1 μM KI, 0.2 μM H₂BO₃, 0.1 μM CoCl₂ and 0.1 μM NiCl₂ distilled water (Roslev et al. 1998). Solid agar media were prepared following the instructions on the bottle. The right amount of media powder was dissolved in distilled water; the mixture was heated to dissolve and then sterilised by autoclaving at 121 °C for 15 minutes. The agar was cooled down and kept at 40 °C during use.

Sludge simulation

Sludge mixture was prepared from either kaolinite clay (Yan & Masliyah 1996) or fumed silica (Frelichowska et al. 2010) mixed with bituminous asphaltenes or hydrocarbons to simulate oily sludge. In this study, the sludge formed from fumed silica demonstrated properties most similar to the residue from refinery tanks and was used in the rest of the investigation. The fumed silica particles were first dispersed in distilled water using an overhead stirrer operating at 2,000 rpm. Different organic compounds were then added to the silica-distilled water suspension and the mixture was sheared at 1,800 rpm. Different amounts of silica (6, 11, 15 and 20 g) were added to a fixed amount of water and organics (350 and 95 g, respectively) per batch to determine the silica-mass fraction that could yield the most stable sludge.

Demulsification and oil recovery

Solutions containing 5, 10, 15, 20 and 25% (w/v) surfactant (sodium dodecyl sulphate (SDS)) in distilled water were prepared. Each was added in a beaker with the sludge at a volume ratio of 1:1. The contents were then homogenised for 2 minutes at 600 rpm using an overhead stirrer and then left to settle undisturbed to effect the phase separation. The amount of oil separated out of the solutions was measured gravimetrically and the separation efficiencies were calculated from these. The treatment solution that gave the highest separation efficiency was taken as the optimum and would be used in subsequent investigations. A control experiment was also conducted to investigate whether dilution alone would demulsify the sludge. The same volume of water as the sludge was added and the mixture was then homogenised and left to settle.

Biosurfactant activity

One litre of sterile BMM was inoculated with 100 mg of a hydrocarbon-contaminated soil sample collected from oil dump sites from service stations around Pretoria (South Africa). The inoculated medium was incubated for 5 days at 28 °C with continuous shaking at 120 rpm in a reciprocating horizontal shaker. Samples that showed bacterial growth were tested for biosurfactant production. This was done by adding a millimetre layer of the culture that showed
bacterial growth over a mixture of mineral medium with oils as carbon sources. The culture was then incubated at 28°C on a reciprocating horizontal shaker moving at 120 rpm for the required duration. After 24 hours, the medium was evaluated for emulsion formation. Batches showing emulsion formation were subcultured for use in the main experiment.

RESULTS AND DISCUSSION

Evaluation of emulsification stability

Stabilisation of emulsions into the aquatic phase was achieved by adding a solvent ethyl acetate to the sludge before adding water. Emulsification stability was tested with different amounts of sludge with 6–20 g fumed silica. Figure 1 shows results showing increased emulsification with increasing mass of sludge. The emulsions at lower sludge masses 6 and 11 g destabilised within 2–4 hours and the solvent (ethyl acetate) coalesced at the top of the mixture. These fractions could therefore not be used in an oil recovery process as most of the oil could still be on the sludge particles in the aquatic phase. The emulsion at the highest sludge mass (20 g) was the most stable; the emulsion did not destabilise after being left standing for 7 days.

The solution with 16 g fumed silica sludge also achieved a stable emulsion. However, this emulsion eventually broke down when the solution was left standing overnight. The results show that emulsion stability increases with increasing solid particle content.

Effect of the surfactant (SDS) concentration on demulsification rate

The release of oil from sludge was achieved in a two-step process involving destabilisation of the emulsions formed in the emulsification phase (Figure 1) and separation of oils from a hydrated oil layer. During the destabilisation process, the emulsion is dewatered and an oil/water layer (without sludge particles) forms at the top of the mixture. This supernatant layer was observed to increase in height/volume over a period of time until it reached equilibrium. In the second step, the hydrocarbons separate out of the supernatant solution and build up at the top of the solution.

The height of the oily layer without sludge particles was used as a performance parameter. The height accumulated for different amounts of the surfactant added was measured for different standing periods to determine the rate of demulsification for varying amounts of surfactant. The results in Figure 2 show that the amount of oil accumulated decreased with increasing surfactant added. It shows that low amounts of surfactant are required to destabilise the emulsion. This led us to the hypothesis that small amounts of biosurfactants produced by certain petropollutant-tolerant bacteria could be sufficient to destabilise emulsions in such solutions.

After the initial separation process, the solvent used can be easily distilled away and the oils can be used in a range of applications depending on their composition (Abouelnasr & Zubaidy 2008). Uses of recovered oil have been documented in the literature including: (i) as fuel (Elektorowicz & Habibi 2005), (ii) re-integration into the feed stream (Pinheiro & Holanda 2013), and (iii) as platform chemicals in petrochemical manufacturing processes (Morgan et al. 2010).

Effect of SDS-sludge ratio on demulsification rate

The impact of specific surfactant loading per unit weight of solids was evaluated using different sludge:SDS ratios and measuring the amount of oil recovered at specific cut-off reaction times (Table 1). The 10% SDS w/v volume ratio was chosen as the baseline for the SDS mass/volume dose. The solids representing sludge were produced in solids:SDS ratios of 0.5:1, 0.6:1, 0.75:1 and 1:1 with the ratio 1:1 serving as the baseline control. The objective here was to see whether the performance of the surfactant

![Figure 1](https://iwaponline.com/wst/article-pdf/67/12/2875/440516/2875.pdf)

**Figure 1** Formation of emulsions from sludge simulation using (a) 6 g – 1.3% w/w – fumed silica, (b) 11 g – 2.4% w/w – fumed silica, (c) 16 g – 3.5% w/w – fumed silica, and (d) 20 g – 4.4% w/w – fumed silica.
is affected by solids loading. The results in Table 1 show that lower solids content reduces the efficiency of oil collection. At the short reaction times, an optimum oil recovery can be reached with the 0.75:1 solids:SDS ratio, whereas the maximum possible oil recovery by volume is obtained at the highest tested solids:SDS ratio of 1:1 for long-term reaction times (>150 min).

**Effect of temperature on the rate of demulsification**

The emulsification process is a function of the adsorptive capacity of the sludge particles. Stability of the oil molecules in water is known to depend on the formation of a stable microcapsule-like structure around microscopic oil droplets that separate the oil from the aquatic phase. This type of emulsion is also referred to as a ‘Pickering emulsion’ (Whitby et al. 2012). The whole particle will have partial hydrophilicity that will allow it to remain stable in the aquatic phase. Properties that hold the covered droplet structure together, i.e. adsorption and surface tension, are highly dependent on the temperature of the solution. For example, heating up the water will tend to weaken the surface tension of the water, thus affecting the destabilisation of hydrophilic particles around the oil droplet. The surfactant changes the chemical nature of the molecules surrounding the solid particles thereby facilitating disruption of the whole stable structure. It is therefore not surprising that quicker demulsification rates were associated with higher temperatures of the solutions in this study (Figure 3).

The shortest demulsification times were observed at the lowest surfactant dose (5% w/v), which is consistent with the demulsification results shown earlier in Figure 2. Increasing the surfactant dose slowed down the demulsification process at all the temperatures tested.

The boiling point of ethyl acetate is 77°C. The process temperature was limited by this low boiling point. Even though the highest demulsification rate was observed at 60°C (1 hour holding time), the demulsification rate levels off at about 50°C (5 hours holding time). The optimum temperature from the above system is still too high for application under natural conditions.

A control experiment was conducted at 60°C without addition of SDS. The emulsion formed showed signs of inverting after a period of only 3 hours. An aqueous layer

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**Table 1** Oil recovery efficiency under different solids:SDS ratios indicate the effect of reducing solids content on the oil recovery potential

<table>
<thead>
<tr>
<th>Reaction cut-off time (min)</th>
<th>Solids:SDS ⇒ 0.5:1</th>
<th>0.6:1</th>
<th>0.75:1</th>
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containing most of the fumed silica formed at the top of the mixture and a layer containing a combination of water, ethyl acetate and some of the fumed silica formed at the bottom. Even when the sludge was left to rest in the oven for over 24 hours, it was never possible to separate out the ethyl acetate from the sludge. This gives an indication that Pickering emulsions are resistant to heat treatment.

**Demulsification by microbial cultures**

Three hydrocarbons namely diesel, mineral oil and a petroleum sludge were tested as carbon sources for the bacterial growth in the mineral medium. After an incubation period of 3 days, the turbidity in the batch grown on diesel was highest, showing that bacteria preferred diesel as the carbon source. The medium with mineral oil and petroleum sludge remained clear indicating slow or no growth of bacteria. Thus diesel was chosen as a suitable carbon source needed for culturing the bacteria.

Organisms that degrade oily products are targeted as candidates for biosurfactant-producing activity due to their ability to reduce surface tension and emulsify the substrate as one of their adaptations to survive and utilise carbon sources in the petrochemical/petroleum-contaminated soil environments (Nast et al. 2009). Several soil-dwelling Bacilli and Pseudomonads have been shown to produce biosurfactants and allow them to metabolise a wide range of hydrophilic compounds in oil-polluted environments (Bodour et al. 2005; Batista et al. 2006).

The purified colonies grown from the bacterial culture grown on diesel were streaked on nutrient agar followed by incubating at 30 °C for 18 hours in preparation for 16S rRNA gene sequence analysis. The Blast search of 16S rRNA DNA gene segments from the purified colonies showed predominance of Chryseobacterium hominis, Staphylococcus hominis, Raultella planticola, and Acinetobacter baumannii with 99% confidence.

Further experiments were conducted using bacteria grown with diesel as the carbon source in 0.5 L batches. The bacteria culture was used as a whole with no purification, therefore both live cells and dead cells and the biosurfactant were expected to be present during the demulsification experiments. 0.5 L of the bacterial culture that was grown was harvested by centrifugation at the indicated times and the pellet was added to 0.5 L of the sludge, stirred and left to settle whilst continually being observed for signs of demulsification. Figure 4 shows the rate at which the ethyl acetate and oil were recovered from the sludge using the bacterial cultures as biosurfactant.

The sludge showed signs of destabilisation after 24 hours, as two layers developed, but there was no coalescing of the ethyl acetate oil at the top of the mixture. When the
mixture was left to settle for 3 days, the ethyl acetate was seen to separate out, but at very low separation efficiencies. After 5 days, 25% of the ethyl acetate had separated out. This indicated that as the bacteria grew, it produced a biosurfactant that altered the stability of the sludge. The fastest rate of demulsification was observed in batches inoculated with the cells harvested during early log phase (2 day culture) (Figure 4). These results suggest that biosurfactant-producing species were outcompeted by other species during longer times of incubation before harvesting.

It is possible to achieve quicker results with the biosurfactant-producing bacteria by either (1) concentrating further the culture harvested at the right moment, i.e. 2 day incubation so as to increase the amount of catalyst for the demulsification stage, or (2) purifying the actual biosurfactant from the culture in order to work directly with a purified reactant. The latter could be costly and as such could defeat the original objective of developing a cost-effective recovery process.

**CONCLUSION**

The stabilisation of an oily sludge emulsion using particulate matter with known adsorptive capability was shown to be important if oils are to be successfully extracted from petroleum oily sludge. In this study, a fumed silica dispersion of particle size 14 μm assisted by a solvent (ethyl acetate) formed stable emulsions that trapped oil inside an organised layer of interacting particles. A biosurfactant produced by petrochemical acclimated bacteria successfully demulsified the emulsion, which facilitated recovery of the oil in the supernatant. Surfactant loading per unit mass of sludge directly correlated with demulsification efficiency. The results from the biosurfactant experiments showed a slower recovery than the chemical surfactant (SDS) mainly because the biosurfactant was applied in its crude form with a lot of bacteria cells and non-essential organic component in the mixture. The effective concentration of the biosurfactant used in the experiments was therefore much lower than the applied SDS concentration. The results show a strong feasibility of utilising biosurfactants produced by living organisms for removal and recovery of oil from waste sludge for beneficial use.

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