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Heavy metal removal from sediments by biosurfactants

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Abstract

Batch washing experiments were used to evaluate the feasibility of using biosurfactants for the removal of heavy metals from sediments. Surfactin from *Bacillus subtilis*, rhamnolipids from *Pseudomonas aeruginosa* and sophorolipid from *Torulopsis bombicola* were evaluated using a metal-contaminated sediment (110 mg/kg copper and 3300 mg/kg zinc). A single washing with 0.5% rhamnolipid removed 65% of the copper and 18% of the zinc, whereas 4% sophorolipid removed 25% of the copper and 60% of the zinc. Surfactin was less effective, removing 15% of the copper and 6% of the zinc. The technique of ultrafiltration and zeta potential measurements were used to determine the mechanism of metal removal by the surfactants. It was then postulated that metal removal by the biosurfactants occurs through sorption of the surfactant on to the soil surface and complexation with the metal, detachment of the metal from the soil into the soil solution and hence association with surfactant micelles. Sequential extraction procedures were used on the sediment to determine the speciation of the heavy metals before and after surfactant washing. The carbonate and oxide fractions accounted for over 90% of the zinc present in the sediments. The organic fraction constituted over 70% of the copper. Sequential extraction of the sediments after washing with the various surfactants indicated that the biosurfactants, rhamnolipid and surfactin could remove the organically-bound copper and that the sophorolipid could remove the carbonate and oxide-bound zinc. Therefore, heavy metal removal from sediments is feasible and further research will be conducted. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sediments; Biosurfactants; Remediation; Heavy metals; Washing

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1. Introduction

Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous heavy metals and are included on the EPA's list of priority pollutants [1]. Recently, the EPA has announced that the decontamination of sediments will receive the highest priority. Sources of metals include domestic and industrial effluents, the atmosphere, runoff and lithosphere. Once heavy metals are allowed to pass through the municipal waste treatment facility, they return to the environment where they are persistent, cannot be biodegraded and can thus follow a number of different pathways. The metals can adsorb onto the soil, runoff into rivers or lakes or leach in the groundwater, an important source of drinking water. Exposure to the heavy metals through ingestion or uptake of drinking water (particularly where water is reused) and foods can lead to accumulation in both animals, plants and humans.

The term speciation is related to the distribution of an element among chemical forms or species. Heavy metals can occur in several forms in water and soils. Interest has increased in sequential extraction techniques to relate the degree of mobility with risk assessment (i.e. the more mobile the metal is, the more risk associated with it [2] and as a method of designing remediation techniques [3]). Not only is total metal concentration of interest, but it is now accepted that understanding the environmental behaviour by determining its speciation is of paramount importance. Based on the metal speciation in contaminated soil, the most appropriate method for soil remediation can be determined. Selective sequential extraction can potentially be used to determine if the heavy metals can be removed by remediation techniques such as soil washing or to predict removal efficiencies. It is believed that exchangeable, carbonate and reducible oxide fraction may be amenable to soil washing techniques [4]. Removal of organically and residually bound fractions may not be economical to recover or necessary due to lack of bioavailability. Gombert [5] used sequential extraction to determine if cesium, cobalt and chromium could be removed by soil washing. Since $<20\%$ was extracted after dissolving 20% of the soil mass, soil washing was abandoned as an option. Mulligan et al. [3] demonstrated that sequential extraction techniques could be used prior to soil washing to design and monitor the remediation process for a contaminated soil sample.

Since sediments contain large quantities of water, dewatering is frequently necessary after dredging to enable treatment. However, very few treatment techniques in comparison to soil treatment have been used commercially. Due to the different properties of sediments including higher clay and organic matter contents than soils, processes that are effective for soil may not be efficient for sediments. The main treatments for metal-contaminated sediments include solidification/stabilisation and washing. The latter is primarily useful for sands and gravels. Solidification/stabilisation techniques are successful but significant monitoring is required since the solidification process can be reversible. Vitrification is applicable for sediments but is expensive. Only if a useful glass product can be sold will this process be economically viable. Thermal processes are only applicable for removal of volatile metals such as mercury. Highly pure mercury can be obtained and could potentially provide economic benefits to the process. Biological processes are under development and have the potential to be low cost. Since few low cost metal treatment processes for sediments are available, there exists significant demand for further development.

Surfactants can be added to washing water to assist in the solubilisation, dispersal and desorption of contaminants from excavated soils or sediments in a washing unit for subsequent return of the cleaned soils to their original site. They can also be used during pump and treat procedures where the groundwater is recovered for ground level treatment after in situ flushing of the contaminated soil with a surfactant-containing solution. Several synthetic surfactants have been evaluated in soil decontamination tests [6–8]. It would, thus be preferable to employ agents that are less toxic, and biodegradable than synthetic ones. Biosurfactants, surface active agents produced by bacteria or yeast, are potentially useful, particularly due to their anionic nature, low toxicity, biodegradability and excellent surface active properties. The feasibility of using biodegradable biosurfactants to remove heavy metals from an oil-contaminated soil was recently demonstrated by batch washes with surfactin, a rhamnolipid and a sophorolipid [3].

Surfactin produced by *Bacillus subtilis* is one of the most effective biosurfactants known. It reduces the surface tension of water from 72 to 27 mN/m at a concentration as low as 0.005% [9]. The potential advantages of using the lipopeptide surfactin include the presence of two charges due to glutamic and aspartic amino acids as part of its peptide structure [10,11], its biodegradability, its effectiveness as a surfactant (low surface tension and critical micelle concentration (CMC) values) and its potential for in situ production.

Rhamnolipids from *Pseudomonas aeruginosa* have been studied extensively. They produce two types of rhamnolipids containing two rhamnoses attached to β-hydroxydecanoic acids or one rhamnose connected to the identical fatty acid from glucose and hydrocarbon substrates. They are currently produced commercially. Surface tensions of 29 mN/m are characteristic of these compounds [12]. These surfactants have been studied in various environmental applications. The most notable was that rhamnolipid surfactants have been tested and found to release three times as much oil as water alone from the beaches in Alaska after the Exxon Valdez tanker spill [13].

Sophorolipids are produced by the yeast *Torulopsis bombicola*. High yields of the sophorolipid can be obtained from soybean oil and glucose (0.35 g/g substrate) [14]. They can lower the surface tension to 33 mN/m. Although the sophorolipids have been used for the release of bitumen from tar sands [14], they have not previously been examined for remediation of contaminated soils or sediments.

In this paper, we evaluate the feasibility of using the biosurfactants, surfactin from *Bacillus subtilis*, rhamnolipids from *Pseudomonas aeruginosa* and sophorolipids from *Torulopsis bombicola*, to enhance the removal of metals from the sediments by washing, the mechanism of metal removal and the use of sequential extraction procedures as an aid in determining the most effective remediation process.

2. Materials and methods

2.1. Biosurfactants

Three types of biological surfactants were evaluated — surfactin from *Bacillus subtilis* ATCC 21332, rhamnolipids from *Pseudomonas aeruginosa* ATCC 9027 and sophorolipids

Table 1
Characterisation of biosurfactants

Surfactant	Surface tension (mN/m)	CMC (g/l)
Water	70	–
Sophorolipid	34	0.80
Surfactin	31	0.02
Rhamnolipid	26	0.03

from *Torulopsis bombicola* ATCC 22214. These biosurfactants were produced in our laboratory and isolation was performed using previously described techniques [3]. Their surface-active properties are shown in Table 1.

Surfactin from *Bacillus subtilis* ATCC 21332 and *Pseudomonas aeruginosa* ATCC 9027 was produced in a 1 l fermentor containing 4% glucose and mineral salts medium and isolated using previously described techniques [15]. The glucose–vegetable oil medium used for *Torulopsis bombicola* was described by Cooper and Paddock [14]. A temperature of 37°C, an aeration rate of 2.5 vvm and pH control at 6.7 were used as the growth conditions for all cultures. Surfactin and rhamnolipid were collected in the foam overflow and then purified by removing the bacterial cells by centrifugation (12,000 × g, 10 min), adding concentrated hydrochloric acid to adjust the pH to 2 and precipitating the surfactin. Sophorolipids were obtained from the fermentation medium as no foam was produced. Dichloromethane for surfactin and ethyl acetate for the rhamnolipid and sophorolipid were subsequently added three times and the top organic layer was collected each time, pooled and evaporated. The residue was then redissolved in basic water (pH 8) and filtered to remove impurities (Whatman no. 1 paper). It was stored as a powder at 4°C. All other chemicals were laboratory grade.

2.2. Sediment sample

The sediment sample used in this study was characterised using standard EPA or ASTM methods [16] and a modified procedure for cation exchange capacity [17]. Organic matter content (oil and grease plus natural organic matter) was determined by digesting air-dried soil with hydrogen peroxide. Aliquots of 30% hydrogen peroxide were added to 10 g of sediments until bubbling was not longer observed. Soil was then air-dried after removal of the supernatant. The difference in the soil weight × 100% and dividing by the initial soil weight gave the organic matter content. The sample was obtained from a canal area that had been contaminated with metals and some hydrocarbons by many years of industrial discharges into the canal. The organic matter content was 13.4%, the cation exchange capacity was 17.1 meq/100 g (pH 7) and the particle size distribution was 10% sand, 70% silt and 20% clay. These values are reproducible within 10%. This sediment with high organic content was chosen for study since the organic fraction is a very important component in metal retention for sediments and topsoils. The concentrations of copper, zinc, lead and cadmium were 110, 3300, 410 and 5 mg/kg, respectively. All analyses were performed in triplicate and did not vary more than 5%.

2.3. Procedure for batch sediment washing studies

All batch sediment washing studies were performed by varying surfactant concentrations and pH values in centrifuge tubes while maintaining a constant 10:1 w/w solution to soil ratios (15 g/1.5 g) [18]. Distilled water alone was used to account for removal of contaminants by physical mixing. Controls included the same additives (either hydrochloric acid or sodium hydroxide) as for the biosurfactant studies. Samples were taken after 24 h shaking on a reciprocating shaker (60 oscillations/min) and then centrifuged ($5000 \times g$, 10 min). The supernatant was then analysed for metal concentration by atomic absorption spectrometry. The percentage metal removal was determined based on the initial metal content in the sediment and all results are presented as percent metal removal. Single point K_d values were calculated by dividing the concentration of metal remaining on the solid (mg/g) by the concentration in the supernatants (mg/ml). All experiments were performed in triplicate and the average of the results is presented.

2.4. Surface tension and critical micelle concentration

Surfactant concentration by measuring the surface tension at various dilutions [15]. Surfactant concentrations were measured to determine the degree of surfactant adsorption onto the soil which must be minimised. A Fisher Tensiomat Model 21 was used to measure surface tension and interfacial tensions by the duNouy method. The CMC was determined by measuring the surface tension at various dilutions [19]. The CMC is the point at which the surface tension abruptly increases. The reciprocal of CMC is an indication of relative concentrations. Interfacial tensions were measured by the tensiomat by submerging the ring in the surfactant solution and then adding a 1-cm depth of oil extracted with hexane from the Toronto Harbour soil. The ring was then pulled through the oil/water interphase until the ring broke the surface (ASTM D971 method).

2.5. Zeta potential measurements

Zeta potential was measured with the aid of a Zeta-meter Model ZM-75 (Zeta-Meter Inc., New York, NY). Approximately 0.02 g (pre-sieved through a 200 mesh sieve) of sediment was added to 25 ml of solution prior to measurement. This ratio was used to enable tracking of the particles during measurement. Particle concentrations higher than this level causes interference between the particles and makes tracking of the particles impossible. The zeta potential (ζ) was calculated from the electrophoretic mobility, $Be = u_\mathrm{r}/E$, which is the ratio of the migration velocity of the particles to the field intensity applied, according to the equation: $\zeta = u_\mathrm{r}/E \times \eta/\epsilon_\mathrm{o}\epsilon_\mathrm{r}$, where ϵ_r is the absolute dielectric constant, ϵ_o the influence constant and η the viscosity. The dielectric constant and viscosity for water at 20°C were used for all measurements.

2.6. Ultrafiltration procedures

Ultrafiltration experiments were performed using a 50 ml Amicon magnetically stirred ultrafiltration cell containing an XM 50 membrane as described in Mulligan and Gibbs [15].

Copper (10 mg/l) and zinc (10 mg/l) were added in the form of $(CuSO_4)_2$ and $Zn(SO_4)_2$, to the various concentrations of surfactant, prior to the ultrafiltration procedure. Volumes of 25 or 50 ml of solution were added to the cell and pressurised to 60 psi. The retentates and permeates were collected, the volumes of each recorded and then subjected to metal analysis. Rejection ratio (R) is defined as

$$R = \frac{\ln(C_f/C_o)}{\ln(V_o/V_f)} \times 100\%$$

where C_f is the final metal concentration in the retentate, C_o the initial metal concentration, V_o the initial sample volume and V_f the final retentate volume (Amicon Laboratory Separation Guide, 1988).

2.7. Sequential extraction procedures

The selective sequential extraction procedure to determine the speciation of the metal contaminants was similar to that of Yong et al. [20]. Soil samples (1.5 g) were washed with the surfactants solutions and controls and then subsequently dried prior to sequential extraction. Each of the fractions were collected and the concentrations of heavy metals were determined in each of the fractions by atomic absorption spectrometry. The amounts of metals extracted from each of the extractants were then calculated.

3. Results and discussion

3.1. Sediment washing experiments

Sediment washing experiments were performed at two surfactin concentrations with and without NaOH for the sediment (Fig. 1). Significant zinc removal was obtained at 2% surfactin (pH 8.0) while 2% surfactin with NaOH (pH 10.0) and 0.25% surfactin with NaOH (pH 10.0) removed equal amounts of copper.

Sediments were then washed with 0.5% rhamnolipid (pH 6.5) with and without NaOH (Fig. 2). Clearly, the presence of NaOH with rhamnolipid (pH 10.0) significantly enhanced the removal of copper and zinc. Over four times more zinc and six times more copper were removed by the combination of rhamnolipid and NaOH compared to the NaOH alone (pH 10.0). Compared to water alone (pH 6.5), 38 times more copper and four times more zinc was removed by the rhamnolipid. Therefore, the rhamnolipid can enhance metal removal from the sediment as well as an oil-contaminated soil as previously shown by Mulligan et al. [3].

A 4% sophorolipid solution with 0.7% HCl (pH 5.4) was added to the sediments to determine the capability of this biosurfactant in removing metals from this matrix in comparison to the acid alone. A 100% of the copper and zinc was removed with and without the sophorolipid since the pH dropped to 2 for both cases after washing. Therefore, another experiment was run using a lower acid concentration (0.3% HCl) with and without 4% sophorolipid to evaluate the biosurfactant. The results (Fig. 3) show that both copper and

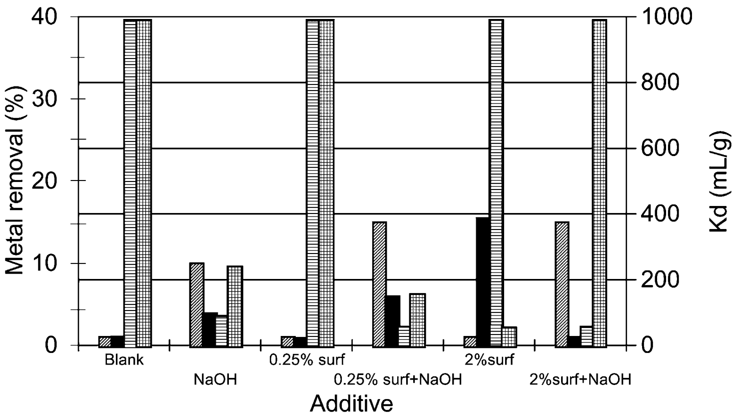

Fig. 1. Percent removal of copper (▨) and zinc (■) from the sediments by surfactin at concentrations of 0.25 and 2.0% surfactin with (pH 10.0) and without 1% NaOH (pH 8.0). K_d values for copper (⊟) and zinc (⊞) are also represented.

zinc removal improved in the presence of the surfactant compared to the acid alone. Copper removal decreased when the acid was added to the surfactant compared to the biosurfactant alone.

In Figs. 1–3, the values of the distribution coefficient K_d are shown as determined from single points. Normally, these values are determined from sorption isotherms [21]. The importance of this approach is that lower K_d values indicate more metal desorption by the washing solution. These values although obtained from soil suspension tests, could be used as a parameter in contaminant transport equations. There is, however, considerable controversy about whether these values should be applied to compact soil samples [21]. In

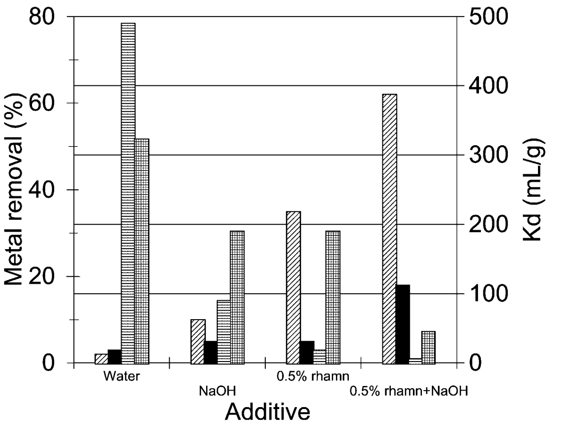

Fig. 2. Copper (▨) and zinc (■) removal from sediments by rhamnolipid (0.5% rhamn with and without 1% NaOH) K_d values for copper (⊟) and zinc (⊞) are also represented.

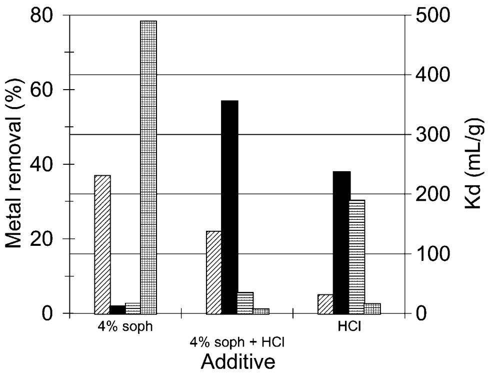

Fig. 3. Removal of copper (▨) and zinc (■) from the sediments using 4% sophorolipid (soph) in combination with and without 0.3% HCl. 0.3% HCl was also tested alone. K_d values for copper (⊟) and zinc (▦) are also represented.

the future, experiments should be performed in leaching columns to give better estimates of K_d values for use in contaminant transport equations.

3.2. Zeta potential

The zeta potential was measured on the sediment samples in the absence of surfactants at pH 6.5 and 9. Sediment samples with 0.1% rhamnolipid or 0.25% surfactin were also measured. Sophorolipid was not studied since it is not very soluble in water and forms an oily layer. The results are shown in Table 2. It can be seen that the sediment is negatively charged at both pH values. The values are close to those reported by Raatz and Hartel [22] for the clay minerals, kaolinite (−32 mV) and illite (−20 mV).

Measurements were also made in the presence of the two biosurfactants, surfactin and rhamnolipid. In both cases, the zeta potential decreased significantly. This would indicate that adsorption of the anionic surfactin and the rhamnolipid is occurring onto the sediment. Ko et al. [23] observed a similar decrease in zeta potential when the hydrophobic tails of the surfactant sodium dodecyl sulfate (SDS) adsorbed on to the hydrophobic kaolinite surface. Therefore, it seems likely that the surfactin and the rhamnolipid are behaving in a similar manner. In addition, others such as Raatz and Hartel [22] have postulated that surfactant adsorption is essential for removal of soil contaminants since surfactants that

Table 2
Zeta potential measurements of sediments in the presence of various solutions

Suspending liquid	Zeta potential of sediment (mV)
Distilled water (pH 6.5)	−28.4
Distilled water (pH 9, adjusted with NaOH)	−32.1
0.1% Rhamnolipid (pH 6.5)	−62.5
0.25% Surfactin (pH 9, adjusted with NaOH)	−48.1

adsorb at the solid–water or soil–water interphases are better detergents. Popov et al. [24] showed that chelating agents such as ethylene diaminetetraacetic acid (EDTA) can also decrease the zeta potential of soil since they form negatively charged complex compounds with the cation contaminants which adsorb onto the surface and influence the electrokinetic potential. Sorption of the biosurfactants onto the soil interphase followed by metal desorption by complexation with the biosurfactants would be the first step in the metal removal mechanism.

3.3. Ultrafiltration experiments

To examine if the surfactant micelles were associated with the metals or if the surfactant monomers were attaching to the metals, experiments were performed with ultrafiltration membranes. The membranes (molecular weight cutoff of 50,000 amu for surfactin and 10,000 amu for the rhamnolipid) were chosen based on the previously determined molecular weight cutoff suitable for retention of the surfactin and rhamnolipid micelles [15]. Higher rejection ratios indicate higher levels of retention in the retentate and lower concentrations in the permeate. If the metals are associated with the micelles, they will be retained by the membranes. If they are attached to the surfactant monomer or unattached they will pass through the membrane since the molecular weights of the surfactants and metals are much lower than 10,000 amu. Since the sophorolipid forms an oily layer, it was not studied. Solutions of metals were mixed with the surfactant solutions at various concentrations near and above the CMC, which is the lowest concentration that micelles are formed (in the order of 0.001% for surfactin and 0.0025% for the rhamnolipid).

From Figs. 4 and 5, it can be seen from the rejection ratios that more metals were retained in the retentate and less in the permeate as the concentration for both surfactants is increased above the CMC. At concentrations of 0.01% surfactin and rhamnolipid, 99.8% of the surfactants are in the form of micelles and 0.2% are as monomers based on surface tension measurements. The micelles are retained and only the surfactant monomers passed

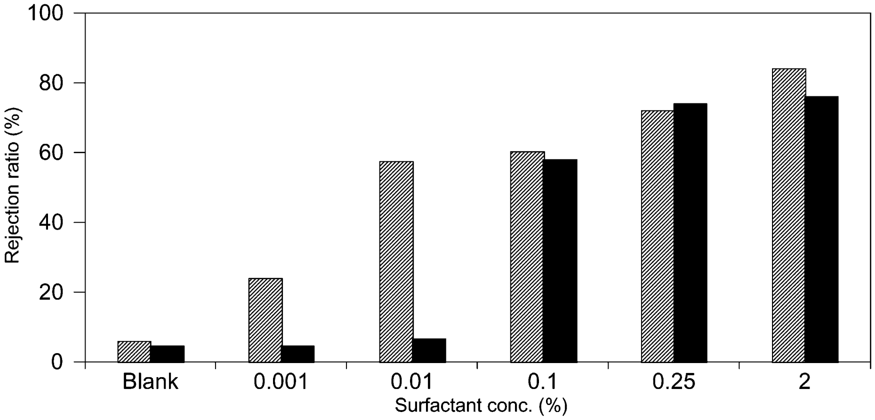

Fig. 4. Ultrafiltration of metal/surfactin solutions containing copper (▨) and zinc (■).

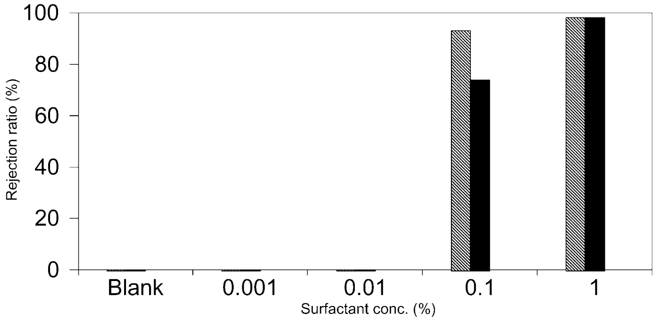

Fig. 5. Ultrafiltration of metal/rhamnolipid solutions containing copper (▨) and zinc (■).

through the membrane. The metals, thus, must be solubilised in the micelles since the metals remain in the retentate with the micelles.

One way to investigate further is to determine the amount of total moles of metal complexed per mole of surfactant. For surfactin, the ratio at 0.1% concentration (with 1% NaOH) is 1.22 mol of metal per mole of surfactin. This value is only slightly lower than the maximum theoretical value of 2 mol of metal per mole of surfactin due to the two charges on the surfactin molecule (aspartic and glutamic acids). For the rhamnolipid, (assuming an average molecular weight of 504 amu), the ratio of 0.33 mol metal per mole of surfactant was determined at a 0.1% rhamnolipid concentration. Since the rhamnolipid has one charge per mole, the theoretical ratio would be 1 mol of metal per mole of surfactant. On this basis, surfactin seems to have more affinity for the metals than the rhamnolipid.

In previous studies performed on rhamnolipids [25], the complexation ratio was 2 mol of rhamnolipid per mole of metal. Since the rhamnolipid is monovalent, it is reasonable that the divalent ions require the sites from two monomers of rhamnolipid. In our studies, we determined that 3 mol of rhamnolipids are required per mole of metal.

The metals therefore, must be complexed with the surfactant micelles since the metals remain with the micelles. This step prevents the metal from readsorbing onto the soil. The partitioning of the heavy metals can then be determined based on the results of these ultrafiltration experiments.

An additional consideration is that the retention of a substantial amount of the surfactant by the ultrafiltration membranes would enable the surfactant to be recovered for further reuse. The metals and surfactants can be separated by pH adjustments. The surfactants precipitate below pH 5 and the metals at higher pH values. Reuse of the surfactant will enhance process economics substantially.

3.4. Sequential extraction

The purpose of the sequential extraction studies was to determine the presence of metals in the sediments among the exchangeable, oxide, carbonate, organic and residual fractions. The harsher the chemicals required, the more difficult it is to remove the metals. The sediments were analysed to determine the speciation of copper and zinc before washing.

Table 3
Sequential extraction characterisation of metal contaminants in sediment samples

Metal	Fraction (% of total)				
	Exchangeable	Oxide	Carbonate	Organic	Residual
Copper	ND[a]	2	ND	88	10
Zinc	5	50	25	18	2

[a] ND: not detected.

Copper was found mainly in the organic fraction. For zinc, approximately 5% was exchangeable, 20% was carbonate, 20% organic and 5% residual with the largest amount being in the oxide fraction. The results are summarised in Table 3. Despite the fact that the sediment and the soil are quite different in composition and that the organic content of the hydrocarbon-contaminated soil [3] is in the form of oil whereas the sediment is decomposed organic matter, the affinities for the various fractions are very similar.

Limited studies have been performed on the sequential extraction of soils and sediments contaminated with copper, zinc, and lead. Cesium, cobalt and uranium fractions were examined by Gombert [5]. Other studies, such as the one by Yong et al. [20] have determined the distribution of zinc, lead and copper in kaolinite, illite, montmorillonite and clay soils which have organic contents of $<2\%$. Despite the high organic contents ($>10\%$) of the sediment used in this study comparisons can be made with illite and natural clay soil (pH 7) for zinc since the organic phase does not play a large role in the retention of this metal. For the sediment, the results for zinc, were similar, indicating preference for the oxide phase followed by the carbonate. The exchangeable fraction, however, was higher.

In a study by Ramos et al. [26], copper, lead, cadmium and zinc were sequentially extracted from soils with organic contents of approximately 15%. Similar to this research, they found that copper was associated with the organic matter or residual fractions, and zinc was primarily found in the oxide fraction.

3.5. Sequential extraction of samples after washing

Sequential extraction experiments were performed on the sediment residues following washing of selected samples to determine which fractions were removed by the surfactants and other additives. The pH of the sediment was not adjusted prior to sequential extraction. The fraction removed by the surfactant or control is designated as the soluble fraction. Sediment residues from several washing experiments that showed significant metal removal results were chosen for study.

Experiments were run to examine washing of the sediments with the three biosurfactants. For the experiments with 1% NaOH (Fig. 6), all showed a decrease in the copper in the organic fraction while the carbonate and oxide fractions were not significantly different. In Fig. 7, without the addition of NaOH, only 0.5% rhamnolipid showed significant removal which was from the organic phase.

For zinc, the experiments with 1% NaOH (Fig. 8) showed a decrease in the oxide phase after washing with 0.25% surfactin while there was little difference with the control for the 2% surfactin. The rhamnolipid (0.5%) soil residue showed lower oxide and carbonate

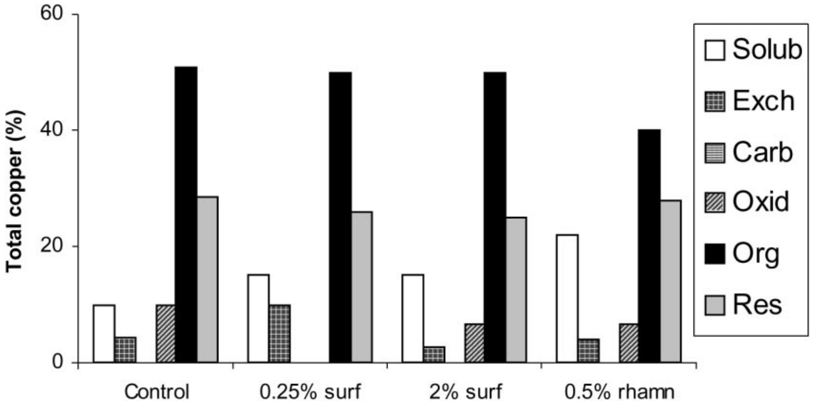

Fig. 6. Sequential extraction of copper after washing of sediments with surfactin (surf) and rhamnolipid (rhamn) and 1% NaOH. The following are represented — sol: soluble fraction; exch: exchangeable; carb: carbonate fraction; oxid: oxide fraction; org: organic fraction and res: residual fraction; 1% NaOH was the control.

contents. Using the surfactants with water (Fig. 9), decreases of zinc in the carbonate fraction were noted for the 0.5% rhamnolipid and 2% surfactin. The sophorolipid (4%) did not show significantly different results from the control.

The purpose of these sequential extraction studies was to determine from what fraction the surfactants removed the metals. This information can then be used to determine if surfactant use is potentially effective, what surfactants might be useful and under what conditions. For example, if the metals are retained mainly in the residual fraction, it may be very difficult, if not impossible, to use washing to remove the metals from the sediments.

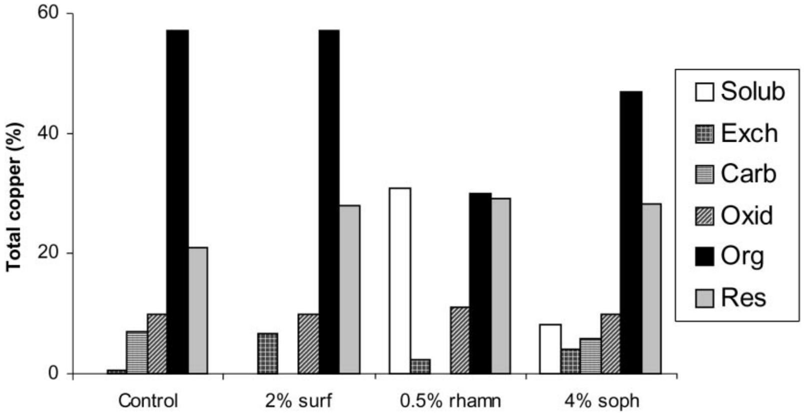

Fig. 7. Sequential extraction of copper after washing of the sediments with surfactin (surf), rhamnolipid (rhamn) and sophorolipid (soph). The following are represented — sol: soluble fraction; exch: exchangeable; carb: carbonate fraction; oxid: oxide fraction; org: organic fraction and res: residual fraction. Water was used as the control.

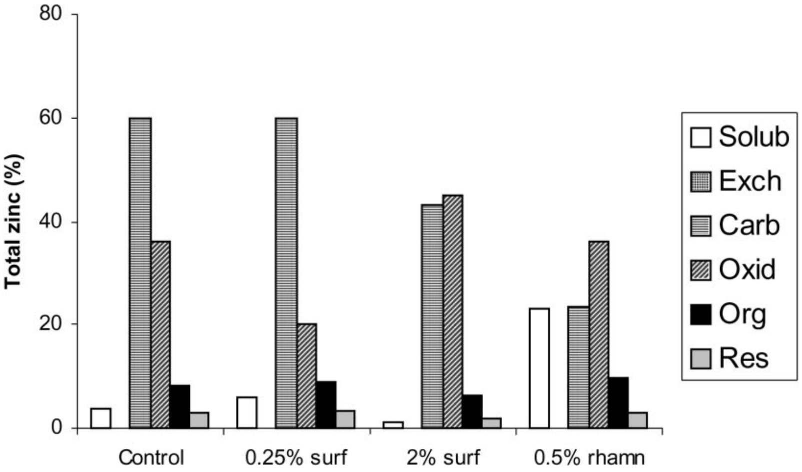

Fig. 8. Sequential extraction of zinc after washing of the sediments with surfactin (surf) and rhamnolipid (rhamn) with 1% NaOH. The following are represented — sol: soluble fraction; exch: exchangeable; carb: carbonate fraction; oxid: oxide fraction; org: organic fraction and res: residual fraction; 1% NaOH was the control.

Few attempts have been made to correlate sequential extraction results with soil washing results. Gombert [5] examined the sequential extraction of cesium, cobalt and chromium to determine if soil washing could be used to treat the soil. In this study, it was determined that any fraction other than the residual could be removed by chemically enhanced soil washing. Therefore, cesium could not be removed, since it occurred mainly in the residual phase (80%). However, no detail is given for what types of additives can be used for effective washing from the different phases.

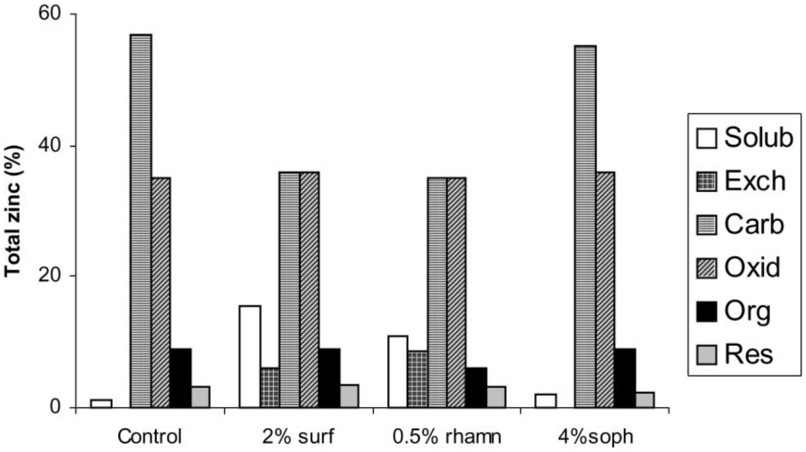

Fig. 9. Sequential extraction of zinc after washing of the sediments with surfactin (surf), rhamnolipid (rhamn) and sophorolipid (soph). The following are represented — sol: soluble fraction; exch: exchangeable; carb: carbonate fraction; oxid: oxide fraction; org: organic fraction and res: residual fraction. Water was used as the control.

In this research project, only the residual fraction was untouched during washing procedures. All other fractions under different conditions could be decreased with the exception of the residual. For example, under acidic conditions, the oxide phase containing the zinc would be released. Under basic conditions (co-addition of the surfactants with NaOH) copper could be released since it was found mainly in the organic phase.

Another study by Li et al. [4] examined the use of the sequential extraction procedure with EDTA extraction of metals. They concluded that the organic phase was very stable since metals in this phase could not be removed by the EDTA and should not be considered in washing processes, since it would be uneconomical to treat. As seen here however, the organic phase associated metals can be easily removed using the appropriate conditions.

4. Conclusion

In conclusion, these results show that the organic phase-associated metals can be removed from sediments by either surfactin or rhamnolipid with sodium hydroxide. Acidic conditions with sophorolipid addition were effective for removing the zinc in the oxide and carbonate phases. Multiple washings may be effective since they can remove the easier to remove phases first such as the exchange and then the more difficult (such as the oxide and then carbonate). The mechanism for metal removal by the biosurfactants occurs through sorption of the surfactant on to the soil surface and complexation with the metal, detachment of the metal from the soil into the soil solution and hence association with surfactant micelles. Residual fractions, the most difficult ones to remove, were not affected during the surfactant washing studies. This information is important in designing the appropriate conditions for sediment washing.

Few technologies currently exist for heavy metal sediment remediation. The economics of this process will need to be determined to compare with existing technologies. However, with more development, the use of biosurfactants could be an effective, non-toxic means of remediating dredged sediments contaminated with heavy metals.

References

[1] R.E. Cameron, Guide to Site and Soil Description for Hazardous Waste Site Characterisation. Vol. 1: Metals, Environmental Protection Agency, 1992, EPA/600/4-91/029.

[2] A.C.M. Bourg, in: Heavy Metals, Springer, Berlin, 1995, p. 19.

[3] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Environ. Prog. 18 (1999) 50.

[4] W. Li, R.W. Peters, M.D. Brewster, G.A. Miller, Sequential extraction evaluation of heavy-metal contaminated soil: how clean is clean? in: Proceedings of the Air and Waste Management Association, 88th Annual Meeting and Exhibition, San Antonio, TX, 18–23 June 1995.

[5] D. Gombert II, Nucl. Technol. 108 (1994) 90.

[6] W.D. Ellis, J.R. Payne, G.D. McNabb, Treatment of contaminated soils with aqueous surfactants, US EPA No. EPA/600/2-85/129, 1985.

[7] J.C. Fountain, D. Hodges, Project Summary: Extraction of Organic Pollutant Using Enhanced Surfactant Flushing — Initial Field Test (Part 1), NY State Centre for Hazardous Waste Management, February 1992.

[8] L.M. Abriola, K.D. Panel, T.J. Decker, W.J. Weber Jr., in: Proceedings of the 19th Annual Risk Reduction Engineering Laboratory Hazardous Waste Research Symposium, Cincinnati, OH, 13–15 April 1993, p. 173.

[9] K. Arima, A. Kakinuma, G. Tamura, Biochem. Biophys. Res. Commun. 31 (1968) 488.

[10] A. Kakinuma, A. Oachida, T. Shima, H. Sugino, M. Isono, G. Tamura, K. Arima, Agric. Biol. Chem. 33 (1969) 1669.
[11] M.R. de Roubin, C.N. Mulligan, B.F. Gibbs, Can. J. Microbiol. 35 (1989) 854.
[12] L. Guerra-Santos, O. Kappeli, A. Fiechter, Appl. Environ. Microbiol. 48 (1984) 301.
[13] S. Harvey, I. Elashi, J.J. Valdes, D. Kamely, A.M. Chakrabarty, Biotechnology 8 (1990) 228.
[14] D.G. Cooper, D.A. Paddock, Appl. Environ. Microbiol. 47 (1984) 173.
[15] C.N. Mulligan, B.F. Gibbs, J. Chem. Tech. Biotechnol. 47 (1990) 23.
[16] American Public Health Association (APHA), American Water Work Association (AWWA), Water Pollution Control Federation (WPCF), Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1995.
[17] R. Chhabra, J. Pleysier. A. Cremers, The measurement of the cation exchange capacity and exchangeable cations in soil: a new method, in: Proceedings of the International Clay Conference, Applied Publishing Ltd., IL, USA, 1975, pp. 439–448.
[18] B.G. Ellis, in: W.E. Sopper, L.T. Kardos (Ed.), Recycling Treated Municipal Wastewater and Sludge through Forest and Cropland, Penn State Press, University Park, PA, 1973, p. 46.
[19] D.G. Cooper, J.E. Zajic, D.F. Gerson, Adv. Appl. Microbiol. 26 (1979) 229.
[20] R.N. Yong, R. Galvez-Cloutier, Y. Phadingchewit, Can. J. Geotechnol. 30 (1993) 834.
[21] R.N. Yong, Geoenvironmental Engineering, CRC Press, Boca Raton, 2001.
[22] S. Raatz, G. Hartel, Aufbereitungs Technik 37 (1996) 57.
[23] S.-O. Ko, M.A. Schlautman, E.R. Carraway, Environ. Sci. Technol. 32 (1998) 3543.
[24] K.I. Popov, N.A. Shabanova, A.A. Artem'eva, E.M. Urinovich, Y.V. Tulaeva, Colloid J. 59 (1997) 233.
[25] D.C. Herman, J.F. Artiola, R.M. Miller, Environ. Sci. Technol. 29 (1995) 2280.
[26] L. Ramos, L.M. Hernandez, M.J. Gonzalez, J. Environ. Qual. 23 (1994) 50.