Column study of the leaching and degradation of anionic surfactants in oil-polluted soil

Aare Selberg[a,b*], Jana Budashova[a], and Toomas Tenno[a]

[a] Institute of Physical Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia
[b] Institute of Technology, University of Tartu, Nooruse 1, 50411 Tartu, Estonia

Abstract. The study was carried out with coarse-grained and fine sandy oil-polluted soils in column tests and the soil was treated with the bioremediation agent SR-100. The concentrations of the hydrocarbons and anionic surfactants were determined in the fractions of soil from the column. In the experiments with the coarse-grained soil the highest concentration of residual surfactants (up to 122 mg/kg) was found in the column with unpolluted soil. The distribution of the residual surfactants was even for the fine sandy soil samples and it was slightly higher for the mixture of polluted soil and $CaCO_3$. The results indicated degradation of surfactants in the polluted soil but the degradation did not completely remove the surfactants and leaching from soil was observed.

Key words: anionic surfactants, biodegradation, leaching, oil-polluted soil, sandy soil.

INTRODUCTION

Surfactants are amphiphilic molecules with a hydrophilic polar head group and a hydrophobic nonpolar tail group. The surfactants can be categorized by the kind of hydrophilic head as anionic, cationic, non-ionic, or amphoteric (zwitterionic). Surfactants are applied as emulsifiers or solubilizers; soluble in water, they affect the physical and chemical properties of the solution by decreasing the surface tension [1–4].

The main surfactants contaminating soil are the soap-based detergents and synthetic surfactants used in the household and industry. The largest amounts of surfactants are used in detergents and cleansing agents for domestic and commercial use. Surfactants are also used in fabric softeners, crop-protections, and ore flotation [5, 6]. The surfactants can be discharged from wastewater treatment

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* Corresponding author, aare.selberg@mail.ee

plants (WWTP) and from the sewage sludge used as a fertilizer in the agriculture, because anionic surfactants can accumulate in the sewage sludge [7–9].

The problem of secondary pollution has risen as a result of the use of surfactants for the surfactant-enhanced remediation of soil contaminated with hydrophobic organic compounds [4, 10–14]. Microorganisms (bacteria) produce a variety of surfactants (biosurfactants), which are produced mostly on microbial cell surface or excreted extracellularly. Biosurfactants help to disperse the hydrophobic compounds and therefore the surface area will be increased for the growth of microorganisms. There are many reviews of various aspects of bio-surfactants [15–18]: the low-molecular-mass biosurfactants lower surface tension, whereas the higher-molecular-mass ones are more effective at stabilizing oil-in-water emulsions [15, 16]. Biosurfactants have many advantages over their chemically synthesized counterparts: they are biodegradable and active under a variety of conditions [17, 18].

Surfactants, especially anionic surfactants, cause the pollution of ground and surface waters and accumulation of anionic surfactants can be toxic to biota [1, 4].

Elimination of surfactants added into soil is important for a successful use of the surfactant-based technologies. Numerous studies have been published about the biodegradability [19, 20] and biodegradation of surfactants in the environment [2, 19–23]. The presence of organic contaminants enhances surfactants bio-degradation, suggesting a probable synergistic effect of organic pollutants [21]. Surfactant molecules with aromatic rings or secondary carbon chain structures appear to have lower biodegradability [22]. Several studies show that some surfactants are easily biodegradable in aerobic conditions, but there are less or no surfactants degradable under anaerobic conditions [2, 4, 24]. The biodegradability of surfactants depends on the length of the alkyl chain, and total molecular weight and concentration of surfactants. The surfactants containing a branched alkyl chain are resistant to the bacterial biodegradation by the steric hindrance [1, 2, 22]. It would be interesting to use the self-formation of the thermodynamically stable microemulsions for the biodegradation of hydrocarbons through the large specific surface area of microemulsion. The biodegradation of hydrocarbons can be faster due to the large specific area of microemulsions [25, 26].

Besides biodegradation, the leaching of surfactants takes place. Therefore it is also important to study the leaching of pollutants and surfactants from soil. The behaviour of linear alkylbenzene sulphonates (LAS) in sandy soils was studied by Küchler & Schnaak in a field trial and lysimeter studies [27]. The in situ biodegradation of pollutants and surfactants usually requires a long time, and leaching occurs by rainwater. Due to leaching it is difficult to identify the reason for the reduction of the concentrations of pollutants in the soil: is it degradation or leaching (washing out) that occurs?

The main goal of this work was to study the behaviour of anionic surfactants in sandy soil. Determination of the concentrations of anionic surfactants and petroleum hydrocarbons at different depths of soil was the aim of our study. Sandy soil was chosen due to the fact that porous soils containing gravel and

sand are the most favourable for the application of bioremediation because of their good natural oxygen supply.

MATERIAL AND METHODS

Materials

The soil was treated with the bioremediation agent SR-100 (E-Tech, USA, 2000) offered on the market for bioremediation of oil-polluted soil [28]. It contains 9.18% anionic surfactants as the methylene blue active material (MBAS) and water soluble nutrients: 0.24% phosphorus and 0.49% nitrogen. Limestone powder ($CaCO_3$) was obtained from the Rakke Lime Factory (Estonia). The methylene blue (MB), sodium dodecylsulphate, *n*-hexane, and chloroform were of analytical grade.

Soil

The first series of the experiments was carried out with contaminated coarse-grained (diameter 2–8 mm) sandy soil from the Ämari airport (northwestern Estonia). The soil was contaminated with jet and diesel fuel and lubricating oil. The soil contained hydrocarbons up to 3800 mg hexane extractable material (HEM)/kg dry soil (DS). The experiments by respirometry [29] showed a low biological activity of the polluted soil by oxygen deficiency due to low porosity. To achieve a higher porosity in the test the polluted soil was mixed with unpolluted sand and the final concentration of the hydrocarbons was 500–600 mg HEM/kg DS.

Another series of experiments was carried out with fine (diameter 0.2–4 mm) natural sandy soil from Kloogaranna beach (northwestern Estonia). It was artificially contaminated with used diesel oil and the concentration of hydro-carbons was also about 500–600 mg HEM/kg DS. Limestone powder (10%) was added to the fine sandy soil in order to increase its pH. The columns with the unpolluted sand and the mixture of the contaminated sand and limestone powder were used to compare the leaching of hydrocarbons and surfactants from the different soils. Soil pH was determined by extracting the soil samples with 5 volumes of distilled water and measured with a glass electrode (Jenway 3320, UK). The determined values of the soil pH are presented in Table 1.

Table 1. The values of the soil pH used in the experiments

Soil	pH_{H2O}
Unpolluted coarse-grained soil	8.00
Polluted coarse-grained soil	8.08
Polluted coarse-grained soil + $CaCO_3$	8.26
Unpolluted fine soil	5.80
Polluted fine soil	6.17
Polluted fine soil + $CaCO_3$	7.91

Chemical analyses

Colorimetric methods are widely used for the determination of the concentration of surfactants [19, 22, 30, 31]. Anionic surfactants form ion pairs with MB and can be extracted with chloroform. The concentration of the anionic surfactants was determined by the spectrophotometric method using MB [30]. The soil samples (1 g) were mixed with 200 mL of distilled water, and the mixture was agitated for 30 min. A water phase sample of 10 mL was taken. It was placed in a separatory funnel and 5 mL of a 1 mM MB solution and 5 mL of chloroform were added. The mixture was agitated for 90 s, and the emulsion was allowed to demix. The chloroform phase with the dissolved coloured complex was separated. The absorbance of the chloroform solution was measured at 654 nm by the spectrophotometer KFK-3 (USSR) [30]. The concentration of the anionic surfactants was calculated by the calibration curve as the MBAS. The concentration of the surfactants in the leachate was determined in the same way. Each analysis was repeated at least three times.

The concentrations of the water soluble total nitrogen and phosphorus were determined by the standard methods (APHA 4500) [32]. The concentration of the hydrocarbons was determined gravimetrically as HEM by the USEPA methods 1664 [33].

Bioremediation experiments

The experiments in bioremediation were carried out in Plexiglas columns (length 50 cm, inner diameter 6 cm). Each column contained 1.4 L (2.2 kg) of soil. It was added into the columns by 200 mL and tightened by manual shaking. In the experiments the columns with soil were treated once with 80 cm^3 of the diluted solution of SR-100 (4% dry solids). Every week 30 mL of aerated distilled water was added to the column to moisten the soil and to supply the soil with oxygen to model the natural conditions (rain).

The leachate was collected and the concentrations of the leached surfactants and hydrocarbons were determined. After the experiments the contents of the columns were divided into four equal fractions by volume and the concentrations of the surfactants and hydrocarbons were determined for each soil fraction.

RESULTS AND DISCUSSION
Behaviour of the surfactants in the soil columns

The concentrations of the anionic surfactants were measured regularly in the upper layer (0–5 cm) of soil in the columns. The determined concentrations of the anionic surfactants as MBAS in the experiments with coarse-grained polluted sandy soil are presented in Fig. 1.
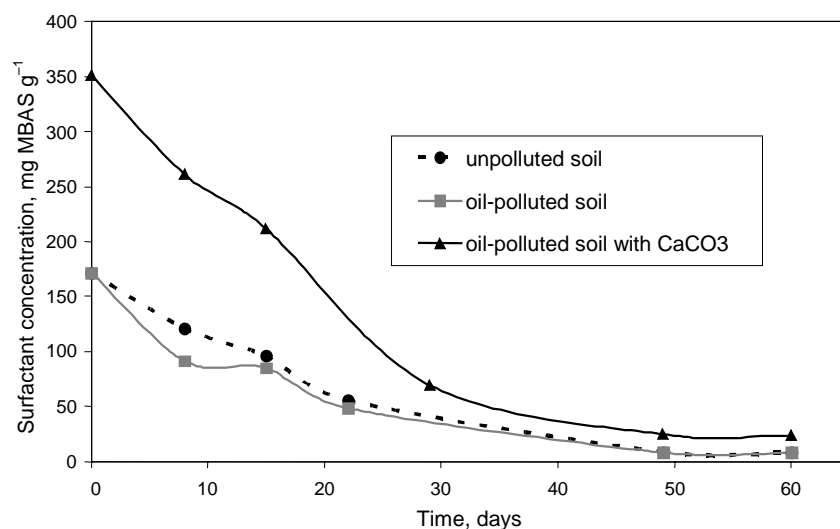
Fig. 1. Concentration of the anionic surfactants in the upper layer (0–5 cm) of columns with coarse-grained soil.

The columns with soil were treated once with the solution of SR-100 (total 816 mg MBAS). First time the concentration of the surfactants was determined next day after the treatment when the solution of surfactants had immersed completely into the soil in the columns. The results of analysis showed that the initial concentration of surfactants (Fig. 1) was half of the concentration of that for the unpolluted and oil-polluted coarse-grained soils in comparison with the mixture of coarse soil and limestone powder. The columns with unpolluted or polluted coarse-grained soil showed a negligible difference in the concentration of surfactants in the upper layer (0–5 cm) of soil during the experiment. The higher concentration of the surfactants in the upper layer of soil in the case of the mixture of soil and $CaCO_3$ can be explained by the higher specific surface of limestone powder, which adsorbed the anionic surfactants by soaking the solution of surfactants in soil [34].

The experiments lasted for 60 days. Then all four fractions of the soil samples were analysed. The calculated masses of the anionic surfactants are presented in Table 2. The masses of the surfactants in the soil fractions (Table 2) had no clear relationship with the type of soil. After the experiments the polluted soil contained generally the lowest amounts of surfactants but in the second fraction (12–24 cm) it was the highest in comparison with other soil columns due to the compacted layer of soil. The lowest layer (36–48 cm) of the unpolluted coarse soil contained a much larger amount of the surfactants than the other columns. The largest amount of anionic surfactants was determined in the leachate of the column of unpolluted soil (15.8% of added surfactants). This indicates a significant leaching of surfactants from the unpolluted soil, which had low microbial activity. The addition of $CaCO_3$ increased the leaching of anionic

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Table 2. Masses of the surfactants (mg MBAS) in the soil fractions and leachate of the columns with the coarse soil after the experiment

Fraction of the column	Unpolluted soil	Polluted soil	Polluted soil + CaCO$_3$
1 (0–12 cm)	22.7 (±2.7)	8.5 (±1.4)	23.5 (±2.8)
2 (12–24 cm)	52.6 (±7.5)	75.9 (±3.9)	35.3 (±1.4)
3 (24–36 cm)	64.3 (±2.2)	4.4 (±1.7)	30.9 (±2.5)
4 (36–48 cm)	270.6 (±5.7)	4.1 (±1.4)	14.1 (±1.2)
Leachate	124.8 (±16.8)	20.2 (±4.4)	36.8 (±4.5)
Total	535.0	113.1	140.6

surfactants (4.5% of added surfactants) in comparison with the polluted soil (2.5% of added surfactants). These results indicate the degradation of surfactants in the polluted soil, but 60 days was not enough to degrade completely the surfactants in soil, and therefore leaching from the coarse-grained soil was detected.

In the case of fine soil the columns were also treated with 80 cm^3 of the diluted solution of SR-100 (total 816 mg MBAS). The concentration of the surfactants was determined next day after the treatment, when the solution of surfactants had immersed completely into the soil in the columns. The results of the surfactants analysis for the upper layer (0–5 cm) are presented in Fig. 2.
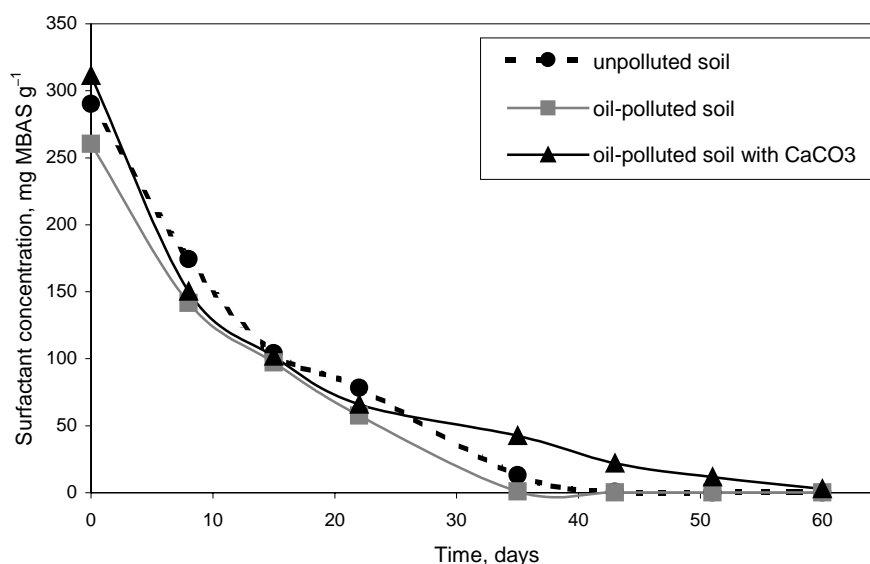

Fig. 2. Concentration of the anionic surfactants in the upper layer (0–5 cm) of columns with fine soil.

For the fine soil the initial concentration of the surfactants and its reduction in the upper layer (Fig. 2) were similar for all soil samples. The experiments lasted for 60 days, but the surfactants were washed out from the upper layer in the columns of the unpolluted and polluted soil during the first 35 days. The concentration of the anionic surfactants decreased linearly during the last 40 days of the experiment with the mixture of polluted soil and $CaCO_3$ and the surfactants were washed out from the upper layer during 60 days in the column.

The calculated amounts of the anionic surfactants in the four fractions and in the leachate of the columns with fine sandy soil are presented in Table 3.

The amounts of residual surfactants in the different fractions of the fine soil column (Table 3) had a clear trend: the lower fractions contained more surfactants. This trend indicated the leaching of the surfactants from the upper fractions into the lower ones. The highest amount of anionic surfactants was determined in the leachate of the column of polluted soil (6.2% of added surfactants). The addition of $CaCO_3$ decreased the leaching of anionic surfactants (3.3% of added surfactants).

Calculation of the mass balance of the anionic surfactants showed that the largest amount (86%) of anionic surfactants was degraded in the column of coarse-grained polluted soil. In the columns of coarse-grained unpolluted soil and the mixture of polluted soil and $CaCO_3$ the degraded amounts of the surfactants were 34% and 83%, respectively. The mass balance of the anionic surfactants showed the lowest degradation of the surfactants in the columns with fine sandy soil. In the experiments with fine sandy soil the highest degradation of anionic surfactants (28% of the added surfactants) was determined for the column with polluted soil. The degraded amount of anionic surfactants was 4.6% for the column with unpolluted fine soil and 8.1% for the mixture of polluted soil and $CaCO_3$. Because of the low porosity of fine soil not enough oxygen was diffused into the soil to achieve aerobic conditions, which are needed for the degradation of surfactants.

Table 3. Masses of the residual surfactants (mg MBAS) in the soil fractions and leachate of the columns with fine soil

Fraction of the column	Unpolluted soil	Polluted soil	Polluted soil + $CaCO_3$
1 (0–12 cm)	10.4 (±1.1)	19.6 (±1.4)	24.6 (±2.1)
2 (12–24 cm)	17.1 (±1.2)	75.5 (±2.2)	32.9 (±1.9)
3 (24–36 cm)	93.8 (±4.3)	88.4 (±2.7)	93.2 (±2.5)
4 (36–48 cm)	616.9 (±15.7)	350.5 (±6.6)	572.8 (±8.5)
Leachate	40.4 (±2.5)	50.4 (±2.9)	26.4 (±1.8)
Total	778.6	584.4	749.9

Behaviour of the hydrocarbons

Our previous experiments with oil-polluted soil [35] showed a negligible leaching and degradation of hydrocarbons from the soil columns when the soil was treated with water only. The concentrations of the residual hydrocarbons in the different soil fractions were very close to the initial concentration of petroleum hydrocarbons [35].

In the current experiments the concentrations of the petroleum hydrocarbons (as HEM) in the soil fractions were also determined. The analysis of hydrocarbons showed that the concentration of residual hydrocarbons in the coarse-grained soil was about 30–40% of the initial concentration. After the experiment the samples of fine sandy soil contained 50–60% of the initially added petroleum hydrocarbons. The lower concentrations of the hydrocarbons in the columns of coarse-grained soil were connected with the better supply of oxygen into soil due to the higher porosity of coarse-grained sandy soil. The dry residual of the leachate from the columns contained about 5% of hydrocarbons.

CONCLUSIONS

The behaviour of anionic surfactants in oil-polluted sandy soil at different depths of soil columns was studied. The concentrations of residual surfactants in the different fractions of the coarse-grained soil column had no clear trend with the depth of soil fractions. The highest amount of surfactants in the leachate was determined for the unpolluted coarse soil (15% of added surfactants), while the leachate from polluted soil and the mixture of soil and $CaCO_3$ contained less than 5% of the added surfactants.

The concentrations of residual surfactants in the different fractions of the fine soil column had a clear trend: the lower fractions contained more surfactants, indicating the leaching of surfactants from the upper fractions. The amount of the leached anionic surfactants in the leachate from the fine soil column was below 6% of the added surfactants regardless of column properties.

The lower concentrations of the anionic surfactants in the columns of coarse-grained soil were connected with the better supply of oxygen into soil due to better conditions of diffusion of oxygen by the higher porosity of coarse sandy soil to achieve aerobic conditions needed for the degradation of surfactants.

The time of the experiments was not long enough for complete biodegradation of petroleum hydrocarbons and the reduction of the hydrocarbon concentrations was about 50–70%. The use of the bioremediation agent SR-100 indicated the leaching of surfactants from the soil, which can be a source of soil and ground-water pollution.

ACKNOWLEDGEMENTS

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Anioonsete pindaktiivsete ainete leostumise ja lagunemise uurimine reostunud pinnase kolonnides

Aare Selberg, Jana Budashova ja Toomas Tenno

On uuritud jämedateralist ja peeneteralist liivast naftasaadustega reostunud pinnast kolonnkatsetes. Pinnaseproove on töödeldud preparaadiga SR-100 ja määratud naftasaaduste ning anioonsete pindaktiivsete ainete kontsentratsioonid

pinnase erinevates fraktsioonides. Jämedateralise reostumata pinnase kolonnis on pindaktiivsete ainete jääkkontsentratsioon (kuni 122 mg/kg) katse lõpul, võrreldes reostunud pinnasega, kõrgeim. Peeneteralise pinnase korral on pindaktiivsete ainete jääkkontsentratsioonid lähedased ja veidi kõrgemad on need $CaCO_3$ ning reostunud pinnase segu korral. Katsete tulemused näitavad pindaktiivsete ainete osalist lagunemist reostunud pinnases, kuid see ei ole piisav, et ära hoida pindaktiivsete ainete väljaleostumist.