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Biodegradation and Leaching of Surfactants During Surfactant-Amended Bioremediation of Oil-Polluted Soil

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1. Introduction

1.1. Theoretical overview

1.1.1. Bioremediation as green-tech solution for soil decontamination

Pollution of soil (and water) is quite hot problem in the different places in the world due to its generation through variety of sources (waste dumps, petrol stations, underground storage, and accidents by pipelines) [1] and soil acts as a permanent residence for pollutants and the dynamic movements of hydrological cycle transports them to groundwater aquifer [2]. The pollutants can be removed using different physical methods, among them mechanical recovery of oil by the sorbents is one of the most promising countermeasures [3]. Washing with surfactant solutions has been shown to be effective for the removal of hydrophobic organic contaminants (PAH, hydrocarbons, PCB, chlorinated solvents) from soil [4, 5] but the degradation of pollutants is not carried out through it. Generally, removal of pollutants from soil using physical and chemical processes is quite expensive [6]. The different chemicals used for the chemical treatment can induce the secondary pollution of soil and/or groundwater.

The using of indigenous microorganisms is the greener solution for soil (and water) decontamination. The enhancement of natural biological degradation processes can be a preferred cost-effective method of removing contaminants from the contaminated environments and the role of microorganisms has been shown to be essential in the remediation of organic pollution [7 - 9].

Bioremediation technologies exploit the natural ability of microorganisms to degrade organic chemical contamination in soil and ground water [7, 10] and the goal of active bioremediation of soil is to enhance the microbial systems to efficiently remediate contaminated area and to decrease the impact of natural heterogeneity of environmental conditions [11]. The most widely used bioremediation procedure is the biostimulation of indigenous microorganisms by the addition of nutrients because the input of large quantities of carbon sources (i.e. organic pollutants) tends to result in a rapid depletion of the available pools of major inorganic nutrients such as nitrogen and phosphorus [12]. The most reliable way to achieve the successful bioremediation is to ensure that appropriate microorganisms are present in adequate numbers and that the physicochemical environmental conditions are optimized through appropriate site engineering design, to enhance microbial growth and activities [13].

The activity of the indigenous microorganisms can be inhibited through the non optimal environmental conditions (content of oxygen, moisture and/or nutrients, pH) or insufficient availability (hydrophobic contaminants) or degradability (xenobiotics) of pollutants. Therefore it is necessary to optimize the conditions to activate the work of microorganisms [12, 14, 15]. Water activity is considered to be proportional to free water that is able to transport soluble nutrients to the biomass, in contrast with moisture which includes all water content (available and non-available) [14]. It is important to note that the contamination by hydrocarbons increased biochemical and microbial activities and improved soil structure [16].

It would be good to use commercial products of specified microorganisms to enhance the biodegradation of xenobiotic pollutants, but it needs monitoring for the influence of added microorganisms on the diversity of local (indigenous) organisms [17, 18]. During bioremediation, the rate of degradation of hydrocarbons in the field is largely controlled by the rate of supply of nutrients and oxygen [19], which makes it difficult to extrapolate directly the results from the laboratory to bioremediation in the field [20].

The mineralization of pollutants is the best solution for the decontamination of polluted soil, but the level of the residual amounts, which is degraded very slowly, is very important for the applicability of the bioremediation process [10]. However, with a global political shift towards sustainable and green bioremediation technologies, the use of plant-associated bacteria to degrade toxic synthetic organic compounds in environmental soil may provide an efficient, economic, and sustainable green remediation technology for future environment [21].

1.1.2. Environmentally friendly enhancement of bioremediation

The addition of surfactants can increase the bioavailability of hydrophobic pollutants [22-25] and the toxicity of organic compounds is strongly linked to their bioavailability in the soil [26], but it is necessary to monitor the leaching of surfactants. Temperature is a very critical factor in determining microbial activity, although the optimum temperature for biodegradation of petroleum products has generally been found to be in the range of 20-30°C, local environmental conditions may select for a population with a lower optimum temperature [27-29]. The decontaminations of contaminated soils achieved at 10°C showed that, even at low temperatures, abiotic processes and cold-adapted indigenous soil microorganisms contribute to a great extent to diesel oil contaminations in alpine soils [28, 30]. Cold-adapted indigenous hydrocar-

bon degraders also play an essential role in the in situ decontamination of deep soil horizons in temperate climates [12]. In the sub-arctic soil with the higher level of contaminants (8,100 mg/kg) low soil temperature was probably the primary factor limiting field biodegradation and the maximum microbial activity occurred at about 21°C [31]. The CO₂ production of tundra soils below 0°C is caused, at least partly, by a specialized ecological group of microorganisms adapted to extreme Arctic conditions and life at sub-zero temperatures [32]. The optimization of temperature could be good way to enhancement biodegradation of pollutants. For in situ remediation it is generally too expensive to increase the soil temperature, but for ex situ remediation, increasing temperature provides realistic option [33, 34, 35].

Biostimulation of the contaminated soil with air and mineral nutrients showed that both respiratory activity and the number of hydrocarbon-degrading bacteria sharply increased in the first two days of the treatment, in parallel with deep changes in the structure of the bacterial community as it was shown by population fingerprinting [36]. Biostimulation of microorganisms can be carried out through addition of different fertilizers, but chemical properties of used fertilizer have influence on the results: water-soluble fertilizers can be leached into the deeper layer if they are not consumed quite fast, but water insoluble fertilizers can be insufficiently available to consumers. For example, the experiment showed that combination of fast release and slow release phosphate sources may be the best for immediate treatment and long-term maintenance [37].

The addition of nutrients could be quite easy to activate bioremediation, but the real biodegradation of pollutants is carried out by microorganisms. The lack of microbial growth factors [28] can be the reason for the low ultimate degradation rate of contaminants. The results of analysis showed that the biodegradation of petroleum products is more related to the inherent biodegradability of the constituting compounds (a low bioavailability of the contaminants [38]) than to the specific enzymatic capabilities of the microbiota [39]. At the same time the sites with high percentage of total petroleum hydrocarbon removal were characterized by the presence of high levels of estimated biomass and consisted of a large diversity of microorganisms [40].

The analysis of different soil environments confirmed that vegetation has been enhanced the rate and extent of biodegradation in the rhizosphere as root exudates provide carbon and energy, which increases the diversity and number of microbial species [41, 42]. The carbon and energy sources supplied by plants help sustain the microbial population that is degrading the contaminants, for example root exudates associated with vegetation can provide sufficient carbon and energy to support $\approx 10^8$ - 10^9 vegetative microbes per gram of soil in the rhizosphere [41]. Through the exudation of a wide variety of compounds, roots may regulate the soil microbial community in their immediate vicinity, cope with herbivores, encourage beneficial symbioses, change the chemical and physical properties of the soil and inhibit the growth of competing plant species [43, 44, 45]. The efficient attachments of microorganisms to host plants as well as the improvement of the degradation activity of microorganisms are critical factors for the efficient bioremediation by plant-microbe systems [46].

The addition of simple organic carbon sources (the simpler fatty acids [47] or methyl derivatives of vegetable oils called as biodiesel [48, 49]) has been identified as a useful technique for

further stimulating the biodegradation of petroleum hydrocarbons by an indigenous microbial biomass. Even in the optimal conditions the biodegradation of pollutants takes place more readily when the target contaminants are dissolved in an aqueous solution and the improvement of the bioavailability of hydrocarbons is performed through the use of surfactants and both non ionic and anionic surfactants increase the solubility of hydrocarbons by forming micelles [22, 24, 25, 38].

More often the enhancing of solubility of organic hydrophobic contaminants in soil is carried out by using synthetic surfactants [50], but problems can be associated with reduced availability of compounds sequestered into micelles, their toxicity and ultimate resistance to biodegradation leading increased secondary pollution [23, 51-53]. The toxicity of the surfactant and its potential degradation products is one of the most important criteria for the selection of surfactant in soil clean-up [24, 25, 33]. There are many advantages of biosurfactants compared to their chemically synthesized counterparts and it is discussed by different authors [50, 52, 54 - 56].

The use of surfactants is widely studied to increase the bioavailability of PAH which solubility is very low [7, 57-59] and a significant PAH amount (>94%) was removed from the soil solid phase to surfactants solution of Tween 80 and approximately 0.8 mg of Tween 80 was needed per milligram of total PAH removal from the soil solid phase with five successive washing [58]. Soil organic matter (such as humic acids) is a very important adsorbent for cationic surfactants and the sorbed surfactant obviously enhanced the soil sorption of PAHs [60].

The experiments showed that the biosurfactants had similar PAH bioavailability-enhancing properties to synthetic surfactants but with the advantage of being biodegradable and non-toxic to PAH-degrading bacteria and additional advantages of some biosurfactants were the lack of a true micellar formation at high surfactant concentrations [52].

The main factor that works against the wide production of truly natural surfactants (biosurfactants) is the cost of their work-up (separation and purification) [54, 56]. Nowadays the approach to the use of renewable resources increases the interest in the ability of humic acids to sequester organic pollutants, because humic acids can be used as natural surfactants for technological purposes [23]. The effectiveness of surfactants in improving contaminant biodegradation is a combination of the solubilizing power of the surfactant and the bioavailability of micellar contaminant [33, 52].

It is mentioned that a residual fraction of contaminants remained undegraded in the soil even when optimal biodegradation conditions are provided [61]. The influence of the nature of the soil and of the presence of specialized microorganisms on both the degradation rate and the residual concentration was tentatively singled out [62].

1.1.3. Dual application of surfactants

Surfactants are amphiphilic molecules that tend to partition preferentially at the interface between phases of different polarity and water bonding. Surfactants increase the aqueous solubility of non-aqueous-phase liquids (NAPLs) by reducing their surface/interfacial tension at air-water and water-oil interfaces [24, 63]. Many microbes are capable to synthesize different

types of biosurfactants and insoluble substrates (including hydrocarbons) induce the biosurfactant production [64].

Soil washing is a commonly utilized soil remediation technology which is performed on excavated soil and it can be adapted to fit different masses and different contaminant content by changing the composition of the soil washing fluid [65, 66, 67]. The ecotoxicological evaluation (by Microtox®) demonstrated that all soil washing treatments (chelating agent and non ionic surfactant) increased the toxicity of soil leachates, possibly due to increased availability of contaminants and toxicity of soil washing solutions to the test organism [66].

One of the main limitations for a wider application for surfactants in soil remediation is the lack of knowledge about environmental fate and toxicity of surfactant itself [22, 25, 68]. The application of surfactants to enhance soil remediation requires precise knowledge of soil microbial ecology as well as of the fate and transport of contaminants and surfactants in environmental systems [52] including the use of biodegradable surfactants [69]. Biosurfactants have been increasingly used in soil washing and oil removal from contaminated areas [70, 71] and in enhancing the biodegradation of oil by increasing the bioavailability of hydrophobic pollutants [55, 72].

In the absence of toxicity, the net effect of addition of surfactant to a contaminated soil depends on the benefits that result from enhanced solubility of target compounds versus the reduction in direct adhesion of bacteria to the NAPL [38] and several surfactants were toxic to the test bacteria [73].

Beside of concentration the influence of surfactants depends on the composition and properties of surfactants as well. The commercial linear alkylbenzene sulfonate (LAS) which is widely used anionic surfactant is primary the Na salt, but occurrence of Ca and Mg salts in the environment might cause precipitation of Ca and Mg salts, which have lower bioavailability and thereby influence the toxicity and biodegradation [74].

The growing use of non ionic surfactants is related to their good detergent performance, which is not affected by water hardness, and to their low toxicity and they can be mixed with ionic and amphoteric surfactants [22, 25, 75]. The experiments with endosulfan proved that *Pseudomonas aeruginosa* combined with non ionic surfactant Tween 80 was able to achieve 94% degradation of endosulfan in contaminated soil [76]. Tween 80 influenced the sorption of pyrene on the bacterial cell and thus enhanced the degradation of pyrene [77].

Surfactant biodegradability is a factor that can have negative and positive effects in the use of surfactants for bioremediation [22, 25]. The negative effects can be connected with depletion of minerals and/or oxygen, toxicity of surfactants or their intermediates and preferential degradation of the surfactant [24]. The most obvious positive effect of surfactant degradation is the removal of the surfactant from the polluted site. Another positive effect is fact that a degradable surfactant might be used as a primary substrate when the pollutant is degraded co-metabolically [33].

The study of biodegradation of petro-anionic sulfonate X-100 showed that the presence of organic contaminants apparently enhanced surfactant biodegradation, suggesting a probable

synergistic effect of organic contaminants [78]. Environmental risk assessment revealed that after 23 days in the case of LAS and 56 days in the case of nonylphenolic compounds (NPE) potential toxic effects could not be expected [79]. Cyclodextrins are natural, non-toxic compounds that are harmless to microorganisms and free enzymes, and their employment to form inclusion complexes with hydrophobic molecules gives opportunity to use cyclodextrins for the enhancement of biodegradation of aliphatic and polycyclic aromatic hydrocarbons [80].

The biosurfactant BS-UC produced by *Candida antarctica* from *n*-undecane had the capacity of changing the hydrophobicity and the zeta potential of the cell surface, but the biosurfactant enhanced the biodegradation of the organic compound whose structure was similar to that of the biosurfactant produced from [81].

In respirometric experiments, oxidation of all parts of the chemical will lead to oxygen consumption, which is the parameter used to quantify ultimate biodegradation [82].

Although the sorption of surfactants is very complex, especially for anionic surfactants, it is partly correlated with the organic carbon content in soil [83]. The adsorption of surfactants by soil components may lead to a significant reduction in their effectiveness to remove the contaminants from the soil and because it is important to consider surfactant tendency to be adsorbed by the soil or sediment to be decontaminated [84, 85].

1.1.4. Polluted soil composting — The easiest technological approach

Composting is an aerobic process that relies on the actions of microorganisms to degrade organic materials, resulting in the thermogenesis and production of organic and inorganic compounds [6]. Whereas the primary benefit from composting of household waste is the reduction of volume, hygienization and stabilization for recycling or ultimate disposal, the objective of composting hazardous materials is solely to convert these substances into an innocuous end-product [86]. Microorganisms consume the supplied substrates as well as the contaminants, possibly by co-metabolisms and many hazardous wastes have been also converted into innocuous end-products in this manner [87].

There are variety of composting systems and most of them utilize bulking agents (such as bark chips, straw and chopped sugar beet), which increases the porosity and, therefore, aerobicity of medium under treatment and decrease the moisture levels [88]. Composting bioremediation strategy relies on mixing the primary ingredients of composting with the contaminated soil, wherein as the compost matures, the pollutants are degraded by the active microflora within mixture [6].

Soil composting pile is a promising approach of oil-contaminated soil and it was possible to degrade up to 60% of total petroleum hydrocarbon of heavy-contaminated soil during the first eight months [89].

Contaminated soil is often poor in organic matter and has a general low microbial activity, but usually the indigenous bacterial community is adapted to the presence of the contaminant. By adding an organic matrix to contaminated soil the general microbial activity is enhanced and also the activity of specific degraders, which may be found in the contaminated soil or

introduced along with the organic material [10]. The mixing of polluted soil with different organic material will be the better solution to enhance the biodegradation of xenobiotic pollutants and that technique is called cocomposting as it is the process of simultaneous stabilizing organic matter and degrading toxic compounds (pollutants) [14, 90, 91].

In contrast to composting, compost can be added to polluted soil after its maturation for remediation purposes as composts are capable of sustaining diverse populations of microorganisms (bacteria including bacilli, pseudomonads, mesophilic and thermophilic actinomycetes and lignin-degrading fungi), all with the potential to degrade a variety of aromatic pollutants, but the use of composts has not been widely applied as a method for bioremediation [6, 87]. The amount and nature of soil organic matter has been proposed by many workers as being one of the most significant factors dominating organic compound interactions within soil [92, 93].

Biodegradation pathways of organic pollutants may vary in accordance with the chemical structure of the pollutant and the particular degrading microbial species present and that pathways are described by Neilson and Allard [94].

Composting and the use of composted materials have both been successfully applied to the bioremediation of PCP-contaminated soil and the principal vector of PCP loss under both bioremediation regimes was mineralization and the changes in molecular weight distribution during the composting indicated that most of the removal of organic chlorine compounds occurred in the low molecular weight fractions [95, 96]. Whereas 90% losses of TNT from contaminated soil during composting was reported although no mineralization took place [97].

Nutrient provision is an important factor for the degradation of pollutants, but low C/N ratios should favor carbon utilization and thus enhance the total mineral oil and grease degradation as it was proved by substantially increased degradation of soil-derived mineral oil and grease as the C/N ratio was reduced from 49 to 17 [87]. Maintenance of thermophilic conditions in traditional composting is generally considered to be necessary, but more total mineral oil and grease was degraded when temperature profile was maintained at 23°C rather than imposing a 5-day plateau at 50°C [87]. The kinetic parameters of composting showed that the composting temperature (in concert with the microorganisms) accounted for 82.5% of the observed reduction in the composting treatment, while only 17.5% of this reduction could be attributed to additional composting-related factors (nutrients, organic matter, abundance of microorganisms) [90].

Rhizodegradation of pollutants in soil becomes promising for the areas where plants can grow because plant rhizospheres are the most biologically active microsites in soil [98, 99] and it can be used to remediate heavily oil-polluted soils where composting with optimal organic amendments amounts (2:1) and C/N ratio (15:1) effectively reduced total petroleum hydrocarbon concentration and allowed dominant plant species to grow in the remediated soil [100].

The experiments of diesel oil degradation during contaminated soil composting showed that volatilization loss of total petroleum hydrocarbons was only about 2% of initial hydrocarbons [91]. No significant effect of the bioaugmentation on the composting process of petroleum-contaminated soil was observed as well as none of the introduced organisms were re-isolated

by traditional plating techniques and because it is more important to create suitable conditions for the indigenous bacteria than to introduce new species [10]. The germination tests showed that no immediate phytotoxic properties could be attributed to the compost after 12 weeks of composting fresh biowaste together with the diesel-contaminated soil (10%) [90].

1.1.5. Objectives of experimental work

The main objective of the experimental work was to study the behavior of surfactants in oil-polluted soil and soil compost. The sub-objectives for achieving the main goal are the following:

- a. To study leaching and biodegradation of anionic surfactants and their influence on the behavior of petroleum hydrocarbons in oil-polluted sandy soil;
- b. To study leaching and biodegradation of non ionic surfactant Tween 80 and its influence on the properties of leachate and on the behavior of petroleum hydrocarbons in soil compost.

2. Experimental

2.1. Experimental setup and analyses

The leaching experiments were carried out in thermostated Plexiglas columns (length 50 cm, inner diameter 6 cm) at temperature $20.0 \pm 0.2^\circ\text{C}$ (Figure 1.) Each column contained 1.4 L (2.2 kg) of soil, which was added into the column and tightened by manual shaking. In the experiments the columns with soil were treated once with 80 cm³ of the diluted solution of bioremediation agent SR-100 (E-Tech, USA), which contained 9.18% of anionic surfactants as MBAS [101]. Every week, 30 cm³ of aerated distilled water was added to the column to moisten the soil and supply the soil with oxygen in order to model natural conditions (rain). After the experiments the content of the columns was divided into four equal fractions by volume (Figure 2A).

The experiments with soil compost were carried out in the same columns (Fig. 1), which contained 1.4 L (1.9 kg) of soil compost. In the experiments the columns with soil compost were treated twice per week with aerated distilled water or 0.02% solution of Tween 80 and the amount of added liquid was calculated by mean annual precipitation in Estonia. After the experiments the content of the columns was divided into three equal fractions by volume (Figure 2B). All experiments continued two months.

First series of the experiments were carried out with contaminated coarse-grained (diameter 2-8 mm) sandy soil from Ämari Airport (northwestern Estonia). The soil was contaminated with jet and diesel fuel as well as lubricating oil. To achieve a higher porosity in the test the polluted soil was mixed with unpolluted sand and the final concentration of the hydrocarbons was about 1000 mg HEM kg⁻¹ DS. Another series of experiments was carried out with fine (diameter 0.2-4 mm) natural sandy soil from Kloogaranna beach (northwestern of Estonia). It

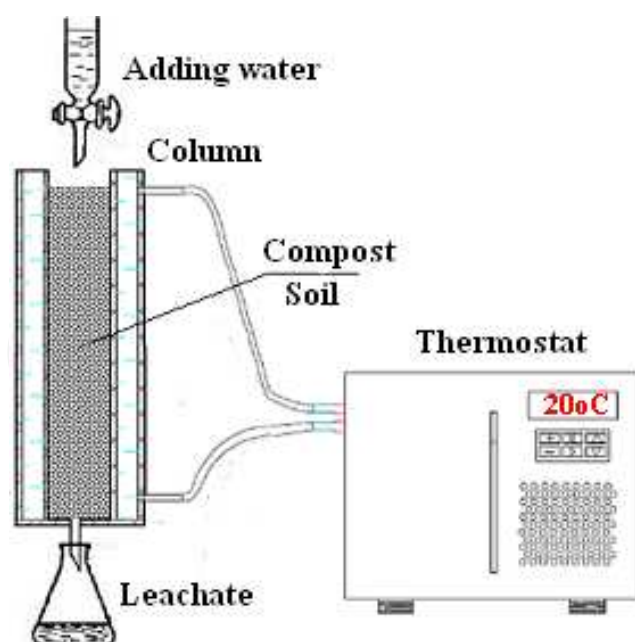


Figure 1. Experimental setup for leaching experiments

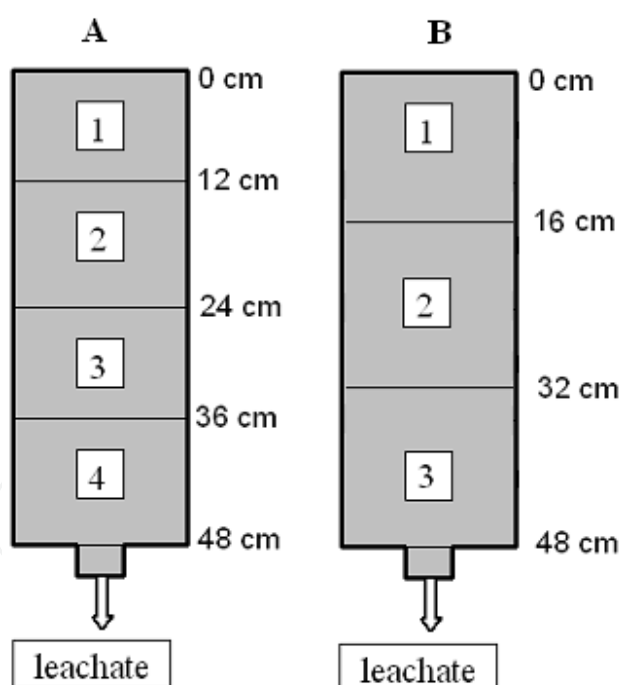


Figure 2. Fractions of soil (A) and soil compost (B)

was artificially contaminated with used diesel oil and the concentration of hydrocarbons was about 1400 mg HEM kg⁻¹ DS. The column with the unpolluted sand was used to compare the leaching of hydrocarbons and surfactants.

In the latter experiments the coarse-grained soil was mixed with the hydrophobic porous adsorbent (10% v/v) prepared by modifying of the urea-formaldehyde resins. The leachate was collected and the concentrations of the leached surfactants and hydrocarbons were determined.

Soil compost was sampled from the composting windrows (composting facility of Ragn-Sells Ltd, Estonia) and for composting the polluted soil, which consist different petroleum hydrocarbons was mixed with gravel (to enhance the porosity), horse manure (as source of microorganisms), wood and bark chips and peat (as bulking agents). The concentration of hydrocarbons was about 77 g HEM kg⁻¹ DS.

2.2. Chemical analysis

The pH of the leachate and water extracts was measured by a pH-meter (SensION1, Hach, USA and Model 3320, Jenway, UK). Soil pH was determined by extracting the soil samples with 5 volumes of distilled water and measured with a glass electrode. The conductivity (EC) of water extracts was measured by a conductivity meter (Model 4320, Jenway, UK) and the values have been corrected to a constant temperature of 25 °C [102].

Colorimetric methods are quite widely used for the determination of the concentrations of surfactants [103 - 106]. Anionic surfactants form ion pairs with Methylene Blue (MB) and extracted with chloroform. The concentration of anionic surfactants in the soil and leachate was determined by the spectrophotometric method using MB [105]. The chloroform phase with the dissolved colored complex was separated and its absorbance was measured at 654 nm by the spectrophotometer KFK-3 (USSR). The concentration of the anionic surfactants in the leachate was calculated by the calibration curve as methylene blue active substances (MBAS). The concentration of non ionic surfactants was determined as cobalt thiocyanate active substances (CTAS) by method 512C [102]. The surfactant-cobalt complex will partition into methylene chloride from excess aqueous cobalt thiocyanate by a single extraction and measurement of CTAS in the methylene chloride at 620 nm by spectrophotometer (Model 6300, Jenway, UK).

The concentration of total petroleum hydrocarbons (abbreviated as TPH) in the solids and leachate was determined gravimetrically as HEM by the USEPA method 1664 [107]. The microbial activity of soil compost samples was characterized through the oxygen uptake over a 7-days period determined by manometric OxiTop system (WTW, Germany) at temperature 20±0.2 °C [108-110].

2.3. Results of column studies

2.3.1. Sandy soil

Concentrations of anionic surfactants were measured regularly in the upper layer (0-5 cm) of the soil in the columns [101, 111]. The determined concentrations of anionic surfactants as MBAS in the experiments with polluted sandy soil are presented in Table 1.

Time, days	Unpolluted soil		Oil-polluted soil		Oil-polluted soil with adsorbent	
	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil
0	172	292	172	260	552	612
8	121	176	91.4	142	461	549
15	95.7	108	85.4	97.5	213	401
29	51.7	46.6	48.5	2.1	109	254
49	8.9	2.3	8.4	1.1	64.8	119
60	8.1	1.5	8.1	0.93	43.7	87

Table 1. Concentrations of anionic surfactants (mg MBAS g⁻¹) in the upper layer (0-5 cm) of the columns with soil during the leaching experiments.

The columns with unpolluted or polluted coarse-grained soil had a negligible difference in the concentration of surfactants in the upper soil layer (0-5 cm) during the experiment. The higher concentration of surfactants in the upper soil layer in case of a mixture of soil and adsorbent could be explained by the specific higher surface of adsorbent which adsorbed the anionic surfactants by the soaking of the solution of surfactants in the soil.

For fine soil, the initial concentration of surfactants and its reduction in the upper layer (Table 1) was similar in all soil samples. The surfactants were washed out of the upper layer in the columns of unpolluted and polluted soil during the first 30 days. The concentration of anionic surfactants decreased linearly during the last 40 days of the experiment with the mixture of polluted soil and adsorbent and the surfactants were not completely washed out of the upper layer during the 60 days in the column. The experiments continued for 60 days after which all four fractions of soil samples and leachate were analyzed and the calculated masses of anionic surfactants are presented in Table 2.

Fraction of the column	Unpolluted soil		Oil-polluted soil		Oil-polluted soil with adsorbent	
	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil
1 (0-12 cm)	22.7	10.4	8.5	19.6	61.1	74.4
2 (12-24 cm)	52.6	17.1	75.9	75.5	70.7	81.3
3 (24-36 cm)	64.3	93.8	4.4	88.4	79.9	84.8
4 (36-48 cm)	271	617	4.1	351	71.3	97.5
leachate	125	40.4	20.2	50.4	0	0
total	535	779	113	584	283	338
Reduction (%)	34.4	4.5	86.2	28.4	65.3	58.6

Table 2. The cumulative masses of anionic surfactants (mg MBAS) in soil fractions and leachate of the columns after the experiments.

In the case of unpolluted soil the anionic surfactants were washed mainly deeper than 36 cm and the higher cumulative masses of surfactants indicated the higher level of degradation in the more porous coarse soil. Due to the low porosity of fine soil the amount of oxygen that diffused into the soil was not enough to achieve the aerobic conditions needed for the surfactants degradation [25].

Fraction of the column	Oil-polluted soil		Oil-polluted soil with adsorbent	
	Coarse soil	Fine soil	Coarse soil	Fine soil
Initial soil	1039	1463	882	1245
Soil + H ₂ O				
1 (0-12 cm)	216	318	154	246
2 (12-24 cm)	220	326	160	251
3 (24-36 cm)	229	340	175	259
4 (36-48 cm)	218	333	169	248
leachate	42	20	18	10
total	925	1337	676	1014
Reduction (%)	11.0	8.6	23.4	18.6
Soil + SR-100				
1 (0-12 cm)	107	186	60	152
2 (12-24 cm)	69	193	53	164
3 (24-36 cm)	82	258	63	144
4 (36-48 cm)	128	183	61	139
leachate	30	59	10	18
total	416	879	247	617
Reduction (%)	60.0	39.9	72.0	50.4

Table 3. The cumulative masses of TPH (mg HEM) in soil fractions and leachate of the columns after the experiments.

Addition of porous urea-formaldehyde adsorbent increased the mass of generated leachate (up to 25%) due to the higher porosity of soil but anionic surfactants were no leached out. The residual content of anionic surfactants was about 35-40% from the added surfactants independently on the soil properties and fractions. The analysis of soil fractions indicated no significant accumulation of anionic surfactants in the upper layer of mixture of soil and adsorbent.

The analysis of residual TPH (Table 3) showed that porosity was quite important factor for the biodegradation of hydrocarbons as coarse soil contained less hydrocarbon in comparison with fine soil. Added anionic surfactants accelerated the degradation of petroleum hydrocarbons,

but porosity of soil was important factor, too. Analysis of leachate showed very low content of hydrocarbons (less than 1% from dry residual) indicating quite active biodegradation of petroleum hydrocarbons in the soil columns.

2.3.2. Polluted soil compost

The profile of leachate generation is presented in Figure 3 and the generation of leachate had no significant difference by adding of non ionic surfactants Tween 80. The leaching experiments in the columns with the oil-polluted soil compost continued for 60 days. The measurements of leachate masses showed that 64% of added water and solution of Tween 80 leached out during the experiments and therefore the non ionic surfactant did not increase the amount of leachate during 2 months [112]. The results of leachate analysis are presented in Table 4.

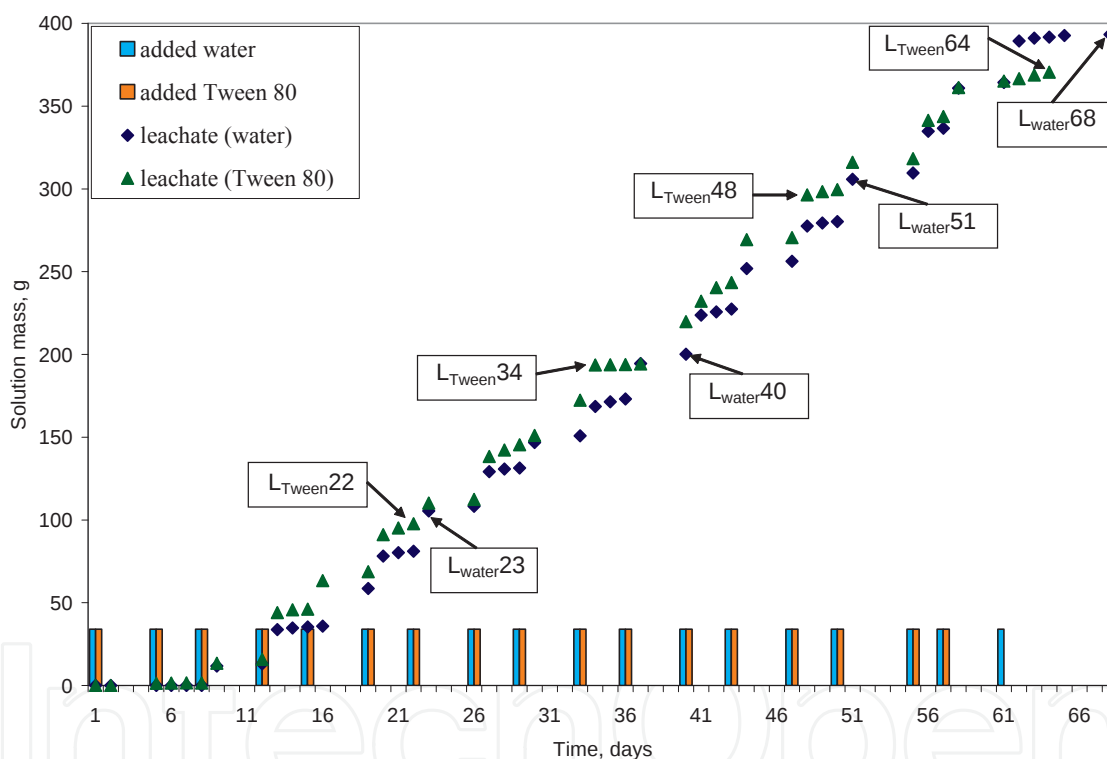


Figure 3. Profile of generation of leachate from the column of soil compost. The sampling of leachate is also presented.

In general, the leachate had quite low (below 15 mg HEM L⁻¹) content of TPH, but it was increased significantly (up to 70 mg HEM L⁻¹) for the last period through the added Tween 80 (Table 4). It means that the added non ionic surfactant can generate the leaching of petroleum hydrocarbon during longer period of treatment.

Similar trend was observed for the non ionic surfactant as well and leachate had more than 3 times higher concentration of non ionic surfactant as CTAS. The solution can be the turning of

H ₂ O				Tween 80				
Time, days	Added water, g	Leachate, g	TPH, mg HEM L ⁻¹	Time, days	Added water, g	Leachate, g	TPH, mg HEM L ⁻¹	Surfactant, mg CTAS L ⁻¹
1-23	238	105.4	15	1-22	238	97.7	10	2.9
24-40	136	94.8	11	23-34	102	96.0	10	20.9
41-51	136	105.6	10	35-48	136	102.7	10	25.1
52-68	102	87.4	13	49-64	102	74.1	70	85.1
1-68	612	393.2	12	1-64	578	370.5	22	30.2

Table 4. Leachate from the column of composted soil

soil compost which was impossible in the columns. The compost windrows were turned at least once per month in the composting facility and therefore the leaching of petroleum hydrocarbons and non ionic surfactant would not occur. After the experiments the fractions of soil compost were analyzed and the results are presented in Table 5.

Compost fraction, cm	Solid soil compost			Water extract of soil compost	
	Rate of oxygen demand, mg O ₂ kg ⁻¹ h ⁻¹	TPH, g HEM kg ⁻¹	Surfactant, mg CTAS kg ⁻¹	pH	EC, mS cm ⁻¹
Initial	462±3	77.3±2.1	0	6.92	0.27
Compost + H₂O					
0-16	358±11	61.6±5.2	0	7.13	0.46
16-32	307±8	55.4±4.2	0	7.12	0.33
32-48	375±14	64.2±4.2	0	7.47	0.48
Compost + Tween 80					
0-16	213±48	61.6±5.7	8.7±0.8	8.30	0.33
16-32	239±16	61.1±5.2	26.1±2.5	8.01	0.32
32-48	299±25	55.9±5.3	52.3±4.2	7.87	0.30

Table 5. Characteristics of fraction of soil compost after leaching experiments in the columns

The analysis of compost fractions showed that both water and solution of Tween 80 reduced the content of petroleum products in the compost mixture about 20%. The reduction of hydrocarbon content was generated through biodegradation as less than 0.01% of hydrocarbons were leached out from the soil columns. It is important to note that addition of surfactant did not increase the leaching of petroleum products [112]. In the column of soil compost which was treated with water the lowest TPH content as well as rate oxygen demand and conductivity were determined for the centre fraction (16-32 cm). In the case of treatment with Tween 80 the rate of oxygen demand was the highest for the lower fraction, but content of TPH was lightly higher for the upper layer. The analyses of soil compost fractions showed that non ionic surfactant was leached into the lower fractions of soil (Table 5) and only up to 10% of non ionic surfactant was leached out from the soil columns during 60 days.

2.3.3. Fluxes of pollutants and surfactants

Calculation of mass balance of anionic surfactants showed the highest degradation of anionic surfactants (about 86% of added surfactants) in the column of coarse-grained oil-polluted soil, while only 28.4% of anionic surfactants were degraded in the column of fine polluted soil (Table 2). Quite low degradation of anionic surfactants was determined in the columns of unpolluted soil (34.4% for coarse soil and 4.5% for fine soil) while added adsorbent significantly accelerated the degradation of anionic surfactants (65.3% for coarse soil and 58.6% for fine one).

The highest degradation of TPH (72%) was determined for the mixture of polluted coarse soil with adsorbent (Table 3) treated with SR-100 containing anionic surfactants. The treatment of polluted coarse soil with SR-100 reduced the content of TPH to 60%. In the case of fine soil the reduction of content of TPH was about 20% lower. Without added anionic surfactants the reduction of content of TPH was below 25%.

The cumulative amount of added Tween 80 was 116 mg CTAS and residual amount of non ionic surfactant was 66 mg CTAS and therefore 43% of non ionic surfactant was degraded during 60 days of experiments, while the leachate contained 9.7% of surfactant and therefore main part of Tween 80 biodegraded in soil compost during experiments. The other experiment also showed not so good biodegradation of Tween 80 due to its high molecular weight [113]. From biodegradability tests, both in liquid and in solid phase, Tween 80 resulted to be, in tested conditions, extremely biodegradable and mineralisable also by not specialized soil bacteria [68].

Calculation of mass balance of TPH showed that 22% of TPH was biodegraded in the column of soil compost treated with water and 23% of TPH was degraded through addition of solution of Tween 80. It means that non ionic surfactant had no accelerating effect on the biodegradation of TPH in soil compost.

3. Conclusion

Surfactants are used to increase the bioavailability of hydrophobic pollutants (hydrocarbons), but the added anionic surfactants were washed out of the upper layer of soil columns during the first 30 days regardless of the type of soil. After the experiments (60 days), the analysis of different soil fractions showed that up to 86% of anionic surfactants had degraded in the column of coarse-grained polluted soil while up to 28% of the added surfactants had degraded in the column of fine sandy soil. Higher amount of anionic surfactants was determined in the leachate of columns of coarse-grained soil and the higher porosity of soil could increase the leaching of surfactants due to the lower surface area of coarse-grained soil.

Addition of porous urea-formaldehyde adsorbent increased the mass of generated leachate (up to 25%) due to the higher porosity of soil but anionic surfactants were no leached out and the analysis of soil fractions indicated no significant accumulation of anionic surfactants in the upper layer of mixture of soil and adsorbent.

During the experiments similar amounts of leachate were generated from the soil compost through the addition of non ionic surfactant Tween 80 or water and therefore the non-ionic surfactant did not increase the amount of leachate during 2 months. The leachate had quite low content both of TPH and non ionic surfactant, but it was increased significantly for the last period through the added Tween 80, therefore the added non ionic surfactant can generate the leaching of petroleum hydrocarbon during longer period of treatment.

The analysis of compost fractions showed that both water and solution of Tween 80 reduced the content of petroleum products in the compost mixture about 20% and the reduction of hydrocarbon content was generated through biodegradation as less than 0.01% of hydrocarbons were leached out from the soil columns.

Calculation of mass balance of anionic surfactants showed 86% of degradation of anionic surfactants in the column of coarse-grained oil-polluted soil, while 72% degradation of TPH was determined for the mixture of polluted coarse soil with adsorbent treated solution of anionic surfactants. Calculation of mass balance indicated that 43% of non ionic surfactant Tween 80 was degraded during 60 days of experiments in soil compost, but non ionic surfactant had no accelerating effect on the biodegradation of TPH in soil compost.

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References

- [1] van Straalen, N.M. Assessment of soil contamination – a functional perspective. *Biodegradation* 2002; 13 41-52.
- [2] Nadim, F., Hoag, G.E., Liu, S., C, Carley, R.J., Zack, P. Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. *Journal of Petroleum Science and Engineering* 2000; 26 169-178.

- [3] Wei, Q.F., Mather, R.R., Fotheringham, A.F. Oil removal from used sorbents using a biosurfactant. *Bioresource Technology* 2005; 96 331-334.
- [4] Underwood, J., Debelak, K., Wilson, D, Means, J. Soil cleanup by in-situ surfactant flushing. *Separation Science and Technology* 1993; 28 1527-1537.
- [5] Zhang, C., Valsaraj, K.T., Constant, D., Roy, D. Surfactant screening for soil washing: comparison of foamability and biodegradability of a plant-based surfactants with commercial surfactants. *Journal of Environmental Science and Health A* 1998; 33(7) 1249-1273.
- [6] Semple, K.T., Reid, B.J., Fermor, T.R. Impact of composting strategies on the treatment of soils contaminated with organic pollutants. *Environmental Pollution* 2001; 112 269-283.
- [7] Alvarez, P.J.J., Illman, W.A. *Bioremediation and natural attenuation: process fundamentals and mathematical models*. Wiley-Interscience; 2006.
- [8] Bento, F.M., Camargo, F.A.O., Okeke, B.C., Frankenberger, W.T. Comparative bioremediation of soils contaminated with diesel oil by natural attenuation, biostimulation and bioaugmentation. *Bioresource Technology* 2005; 96 1049-1055.
- [9] Christofi, N., Ivshina, I.B. Microbial surfactants and their use in field studies of soil remediation. A review. *Journal of Applied Microbiology* 2002; 93 915-929.
- [10] Jørgensen, K.S., Puustinen, J., Suortti, A.-M. Bioremediation of petroleum hydrocarbon-contaminated soil by composting in biopiles. *Environmental Pollution* 2000;107 245-254.
- [11] Korda, A., Santas, P., Tenente, A., Santas, R. Petroleum hydrocarbon bioremediation: sampling and analytical techniques, in situ treatments and commercial microorganisms currently used. *Applied Microbiology and Biotechnology* 1997; 48 677-686.
- [12] Margesin, R. Potential of cold-adapted microorganisms for bioremediation of oil-polluted Alpine soils. *International Biodeterioration and Biodegradation* 2000; 46 3-10.
- [13] Balba, M.T., Al-Daher, R., Al-Awadhi, N., Chino, H., Tsuji, H. Bioremediation of oil-contaminated desert soil: the Kuwaiti experience. *Environment International* 1998; 24(1/2) 163-173.
- [14] Aguilera-Vazquez, L., Soto-Cruz, N.O., Saucedo-Castaneda, G., Gutierrez-Rojas, M. A model system for cocomposting hydrocarbon contaminated soil by using water activity and porosity as response variables. *Chemical Engineering Journal* 2001; 81 197-202.
- [15] Russell, D.L. *Remediation manual for contaminated sites*. CRC; 2012.
- [16] Caravaca, F., Roldan, A. Assessing changes in physical and biological properties in a soil contaminated by oil sludges under semiarid Mediterranean conditions. *Geoderma* 2003; 117 53-61.

- [17] Mohammed, D., Ramsubhag, A., Beskles, D.M. An assessment of the biodegradation of petroleum hydrocarbons in contaminated soil using non-indigenous, commercial microbes. *Water Air Soil Pollution* 2007; 182 349-356.
- [18] Cho, B.-H., Chino, H., Tsuji, H., Kunito, T., Makishima, H., Uchida, H., Matsumoto, S., Oyaizu, H. Analysis of oil components and hydrocarbon-utilizing microorganisms during laboratory-scale bioremediation of oil-contaminated soil of Kuwait. *Chemosphere* 1997; 35(7) 1613-1621.
- [19] Huesemann, M.H., Hausmann, T.S., Fortman, T.J. Does bioavailability limit biodegradation? A comparison of hydrocarbon biodegradation and desorption rates in aged soils. *Biodegradation* 2004; 15 261-274.
- [20] Balba, M.T., Al-Awadhi, N., Al-Daher, R. Bioremediation of oil-contaminated soil: microbiological methods for feasibility assessment and field evaluation. *Journal of Microbiological Methods* 1998; 32 155-164.
- [21] Divya, B., Kumar, M.D. Plant-microbe interaction with enhanced bioremediation. *Research Journal of Biotechnology* 2011; 6(4) 72-79.
- [22] Paria, S. Surfactant-enhanced remediation of organic contaminated soil and water. *Advances in Colloid and Interface Science* 2008; 138 24-58.
- [23] Salati, S., Papa, G., Adani, F. Perspective on the use of humic acids from biomass as natural surfactants for industrial application. *Bioresource Technology* 2011; 29 913-922.
- [24] Tadros, T.F. *Applied surfactants: principles and applications*. Wiley-VCH; 2005.
- [25] Ying, G.-G. Fate, behavior and effects of surfactants and their degradation products in the environment. *Environment International* 2006; 32 417-431.
- [26] de Jonge, H., Freijer, J.I., Verstraten, J.M., Westerveld, J., van der Wielen, F.W.M Relation between bioavailability and fuel oil hydrocarbon composition in contaminated soils. *Environmental Science and Technology* 1997; 31 771-775.
- [27] Westlake, D.W.S., Jobson, A.M., Cook, F.D. In situ degradation of oil in a soil of the boreal region of the Northwest Territories. *Canadian Journal of Microbiology* 1978; 24 254-260.
- [28] Margesin, R., Schinner, F. Bioremediation of diesel-oil-contaminated alpine soils at low temperatures. *Applied Microbiology and Biotechnology* 1997; 47 462-468.
- [29] Belousova, N.I., Baryshnikova, L.M., Shkidchenko, A.N. Selection of microorganisms capable of degrading petroleum and its products at low temperatures. *Applied Biochemistry and Microbiology* 2002; 38(5) 437-440.
- [30] Jobson, A., Cook, F.D., Westlake, D.W.S. Microbial utilization of crude oil. *Applied Microbiology* 1972; 23 1082-1089.

- [31] Walwort, J., Braddock, J., Wooland, C. Nutrient and temperature interactions in bio-remediation of cryic soils. *Cold Region Science and Technology* 2001; 32 85-91.
- [32] Panikov, N.S., Flanagan, P.W., Oechel, W.C., Mastepanov, M.A., Christensen, T.R. Microbial activity in soils frozen to below -39°C . *Soil Biology and Biochemistry* 2006; 38 785-794.
- [33] Volkering, F., Breure, A.M., Rulkens, W.H. Microbial aspects of surfactant use for biological soil remediation. *Biodegradation* 1998; 8 401-417.
- [34] Ferguson, S.H., Franzmann, P.D., Snape, I., Revill, A.T., Trefry, M.G., Zappia, L.R. Effects of temperature on mineralization of petroleum in contaminated Antarctic terrestrial sediments. *Chemosphere* 2003; 52 975-987.
- [35] Mohn, W.W., Stewart, G.R. Limiting factors for hydrocarbon biodegradation at low temperature in Arctic soil. *Soil Biology and Biochemistry* 2000; 32 1161-1172.
- [36] Zucchi, M., Angiolini, L., Borin, S., Brusetti, L., Dietrich, N., Gigliotti, C., Barbieri, P., Sorlini, C., Daffonchio, D. Response of bacterial community during bioremediation of an oil-polluted soil. *Journal of Applied Microbiology* 2003; 94 248-257.
- [37] Knox, A.S., Kaplan, D.I., Paller, M.H. Phosphate sources and their suitability for remediation of contaminated soils. *Science of Total Environment* 2006; 357 271-279.
- [38] Stelmack, P.L., Gray, M.R., Pickard, M.A. (1999) Bacterial adhesion to soil contaminants in the presence of surfactants. *Applied and Environmental Microbiology*, 65(1), 163-168.
- [39] Chaîneau, C.-H., Morel, J.-L., Oudot, J. Microbial degradation in soil microcosms of fuel oil hydrocarbons from drilling cuttings. *Environmental Science and Technology* 1995; 29 1615-1621.
- [40] Claassens, S., van Rensburg, L., Riedel, K.J., Bezuidenhout, J.J., van Rensburg, P.J.J. Evaluation of the efficiency of various commercial products for the bioremediation of hydrocarbon contaminated soil. *The Environmentalist* 2006; 26 51-62.
- [41] Erickson, L.E., Davis, L.C., Narayanan, M. Bioenergetics and bioremediation of contaminated soil. *Thermochimica Acta* 1995; 250 353-358.
- [42] Mortensen, G.K., Egsgaard, H., Ambus, P., Jensen, E.S., Grøn, C. Influence of plant growth on degradation of linear alkylbenzene sulfonate in sludge-amended soil. *Journal of Environmental Quality* 2001; 30 1266-1270.
- [43] Shukla, K.P., Sharma, S., Singh, N.K., Singh, V., Tiwari, K., Singh, S. Nature and role of root exudates: efficiency in bioremediation. *African Journal of Biotechnology* 2011; 10(48) 9717-9724.
- [44] Cohen, M.F., Yamasaki, H., Mazzola, M. Bioremediation of soils by plant-microbe systems. *International Journal of Green Energy* 2004; 1(3) 301-312.

- [45] Kuiper, I., Lagendijk, E.L., Bloemberg, G.V., Lugtenberg, B.J.J. Rhizoremediation: a beneficial plant-microbe interaction. *Molecular Plant-Microbe Interactions* 2004; 17(1) 6-15.
- [46] Motoyama, T., Kadokura, K., Tatsusawa, S., Arie, T., Yamaguchi, I. Application of plant-microbe systems to bioremediation. *RIKEN Review* 2001; 42 35-38.
- [47] Obbard, J.P., Ng, K.L., Xu, R. Bioremediation of petroleum contaminated beach sediments: use of crude palm oil and fatty acids to enhance indigenous biodegradation. *Water, Air, and Soil Pollution* 2004; 157 149-161.
- [48] Nelson, E.C., Walter, M.V., Bossert, I.D., Martin, D.G. Enhancing Biodegradation of Petroleum Hydrocarbons with Guanidinium Fatty Acids. *Environmental Science and Technology* 1996; 30, 2406-2411.
- [49] Pereira, M.G., Mudge, S.M. Cleaning oiled shores: laboratory experiments testing the potential use of vegetable oil biodiesels. *Chemosphere* 2004; 54(3) 297-304.
- [50] Kosaric, N. Biosurfactants and their application for soil bioremediation. *Food Technology and Biotechnology* 2001; 39(4) 295-304.
- [51] Cort, T.L., Song, M.S., Bielefeldt, A.R. Non ionic surfactant effect on pentachlorophenol degradation. *Water Research* 2002; 36 1253-1261.
- [52] Makkar, R.S., Rockne, K.J. Comparison of synthetic surfactants and biosurfactants in enhancing biodegradation of polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry* 2003; 22(10) 2280-2292.
- [53] Mulligan, C.N., Yong, R.N., Gibbs, B.F. Surfactant remediation of contaminated soil: a review. *Engineering Geology* 2001; 60 371-380.
- [54] Holmberg, K. Natural surfactants. *Current Opinion in Colloid and Interface Science* 2001; 6 148-159.
- [55] Ron, E.Z., Rosenberg, E. Biosurfactants and oil bioremediation. *Current Opinion in Biotechnology* 2002; 13(3) 249-252.
- [56] Rosenberg, E., Ron, E.Z. High- and low-molecular-mass microbial surfactants. *Applied Microbiology and Biotechnology* 1999; 52 154-162.
- [57] Ahn, C.K., Kim, Y.M., Woo, S.H., Park, J.M. Soil washing using various non ionic surfactants and their recovery by selective adsorption with activated carbon. *Journal of Hazardous Material* 2008; 154 13-60.
- [58] Zheng, Z., Obbard, J.P. Polycyclic aromatic hydrocarbon removal from soil by surfactant solubilization and *Phanerochaete chrysosporium* oxidation. *Journal of Environmental Quality* 2002; 31 1842-1847.

- [59] Volkering, F., Breure, A.M., van Andel, J.G., Rulkens, W.H. Influence of non ionic surfactants on bioavailability and biodegradation of polycyclic aromatic hydrocarbons. *Applied and Environmental Microbiology* 1995; 61 1699-1705.
- [60] Lu, L., Zhu, L. Effect of soil components on the surfactant-enhanced soil sorption of PAH. *Journal of Soils and Sediments* 2012; 12 161-168.
- [61] Huesemann, M.H., Moore, K.O.J. Compositional changes during landfarming of weathered Michigan crude oil contaminated soil. *Journal of Soil Contamination* 1993; 2 245-264.
- [62] Nocentini, M., Pinelli, D., Fava, F. Bioremediation of a soil contaminated by hydrocarbon mixtures: the residual concentration problem. *Chemosphere* 2000; 41 1115-1123.
- [63] Urum, K., Pekdemir, T. Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere* 2004; 57 1139-1150.
- [64] Veenanadig, N.K., Gowthaman, M.K., Karanth, N.G.K. Scale up studies for the production of biosurfactant in packed column bioreactor. *Bioprocess Engineering* 2000; 22 95-99.
- [65] Harwell, J.H., Sabatini, D.A., Knox, R.C. Surfactants for ground water remediation. *Colloids and Surface A* 1999; 151 255-268.
- [66] Elgh-Dalgren, K., Arwidsson, Z., Camdzija, A., Sjöberg, R., Ribe, V., Waara, S., Al-lard, B., von Kronhelm, T., van Hees, P.A.W. Laboratory and pilot scale soil washing of PAH and arsenic from a wood preservation site: Changes in concentration and toxicity. *Journal of Hazardous Materials* 2009; 172 1033-1040.
- [67] Yuan, T., Marshall, W.D. Optimizing of washing procedure to mobilize polycyclic aromatic hydrocarbons (PAHs) from a field-contaminated soil. *Industrial and Engineering Chemistry Research* 2007; 46 4626-4632.
- [68] Franzetti, A., Gennaro, P.D., Bevilacqua, A., Papacchini, M., Bestetti, G. Environmental features of two commercial surfactants widely used in soil remediation. *Chemosphere* 2006; 62 1474-1480.
- [69] Suchanek, M., Kostal, J., Demnerova, K., Kralova, B. Use of sodium dodecyl sulphate for stimulation of biodegradation of n-alkanes without residual contamination by the surfactant. *International Biodeterioration and Biodegradation* 2000; 45 27-33.
- [70] Mulligan, C.N., Yong, R.N., Gibbs, B.F. Removal of heavy metals from contaminated soil and sediments using the biosurfactant surfactin. *Journal of Soil Contamination* 1999; 8(2) 231-254.
- [71] Mulligan, C.N., Yong, R.N., Gibbs, B.F. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology* 2001; 60(1-4) 193-207.

- [72] Zhang, G.-L., Wu, Y.-T., Qian, X.-P., Meng, Q. Biodegradation of crude oil by *Pseudomonas aeruginosa* in the presence of rhamnolipids. Journal of Zhejiang University SCIENCE 2005; 6B(8) 725-730.
- [73] Roch, F., Alexander, M. Biodegradation of hydrophobic compounds in the presence of surfactants. Environmental Toxicology and Chemistry 1995; 14(7) 1151-1158.
- [74] Berna, J.L., Ferrer, A., Moreno A., Prats, D., Bevia, F.R. The fate of LAS in the environment. Tenside Surfactants Detergents 1989; 26 101-107.
- [75] Mezzanote, V., Castiglioni, F., Todeschini, R., Pavan, M. Study on anaerobic and aerobic degradation of different non-ionic surfactants. Bioresource Technology 2003; 87 87-91.
- [76] Jayashree, R., Vasudvan, N. Effect of Tween 80 added to the soil on the degradation of endosulfan by *Pseudomonas aeruginosa*. International Journal of Environmental Science and Technology 2007; 4 203-210.
- [77] Zhang, D., Zhu, L. Effects of Tween 80 on the removal, sorption and biodegradation of pyrene by *Klebsiella oxytoca* PYR-1. Environmental Pollution 2012; 164 169-174.
- [78] Abd-Allah, A.M.D., Srorr, T. Biodegradation of anionic surfactants in the presence of organic contaminants. Water Research 1998; 32(3) 944-947.
- [79] Gonzales, M.M., Martin, J., Camacho-Munoz, D., Santos, J.L., Aparicio, I., Alonso, E. Degradation and environmental risk of surfactants after the application of compost sludge to the soil. Waste Management 2012; 32 1324-1331.
- [80] Bardi, L., Mattei, A., Steffan, S., Marzona, M. Hydrocarbon degradation by a soil microbial population with β -cyclodextrin as surfactant to enhance bioavailability. Enzyme and Microbial Technology 2000; 27 709-713.
- [81] Hua, Z., Chen, J., Lun, S., Wang, X. Influence of biosurfactants produced by *Candida antarctica* on surface properties of microorganism and biodegradation of *n*-alkanes. Water Research 2003; 37 4143-4150.
- [82] Gejlsbjerg, B., Madsen, T., Andersen, T.T. Comparison of biodegradation of surfactants in soils and sludge-soil mixtures by use of ^{14}C -labelled compounds and automated respirometry. Chemosphere 2003; 50 321-331.
- [83] Di-Toro, D.M., Dodge, L.J., Hand, V.C. A model for anionic surfactant sorption. Environmental Science and Technology 1990; 24 1013-1020.
- [84] Rodriguez-Cruz, M.S., Sanchez-Martrin, M.J., Sanchez-Camazano, M. A comparative study of adsorption of an anionic and a non-ionic surfactant by soils based on physicochemical and mineralogical properties of soils. Chemosphere 2005; 61 56-64.
- [85] Jacobsen, A.M., Mortensen, G.K., Hansen, H.C.B. Degradation and mobility of linear alkylbenzene sulfonate and nonylphenol in sludge-amended soil. Journal of Environmental Quality 2004; 33 232-240.

- [86] Kirchmann, H., Ewnetu, W. Biodegradation of petroleum-based oil wastes through composting. *Biodegradation* 1998; 9 151-156.
- [87] Beaudin, N., Caron, R.F., Legros, R., Ramsay, J., Ramsay, B. Identification of the key factors affecting composting of a weathered hydrocarbon-contaminated soil. *Biodegradation* 1999; 10 127-133.
- [88] Diaz, L.F., de Bertoldi, M., Bidlingmaier, W., Stentiford, E. *Compost science and technology*. Elsevier; 2007.
- [89] Al-Daher, R., Al-Awadhi, N., El-Nawawy, A. Bioremediation of damaged desert environment using the windrow soil pile system in Kuwait. *Environment International* 1998; 24(1/2) 175-180.
- [90] van Gestel, K., Mergaert, J., Swings, J., Coosemans, J., Ryckeboer, J. Bioremediation of diesel oil-contaminated soil by composting with biowaste. *Environmental Pollution* 2003; 125 361-368.
- [91] Namkoong, W., Hwang, E.-Y., Park, J.-S., Choi, J.-Y. Bioremediation of diesel-contaminated soil with composting. *Environmental Pollution* 2002; 119 23-31.
- [92] Brusseau, M.L., Jessup, R.E. Rao, S.C. Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes. *Environmental Science and Technology* 1991; 25 134-142.
- [93] Piatt, J.J., Brusseau, M.L. Rate limiting sorption of hydrophobic organic compounds by soils with well characterized organic matter. *Environmental Science and Technology* 1998; 32 1604-1608.
- [94] Neilson, A.H., Allard, A.-S. *Environmental degradation and transformation of organic chemicals*. CRC Press; 2008.
- [95] Laine, M.M., Ahtiainen, J., Wagman, N., Öberg, L.G., Jørgensen, K.S. Fate and toxicity of chlorophenols, polychlorinated dibenzo-p-dioxins, and dibenzofurans during composting of contaminated sawmill soil. *Environmental Science and Technology* 1997; 31 3244-3250.
- [96] Laine, M.M., Jørgensen, K.S. Effective and safe composting of chlorophenol-contaminated soil in pilot scale. *Environmental Science and Technology* 1997; 31 371-378.
- [97] Bruns-Nagel, D., Dryzyzga, O., Steinbach, K., Schmidt, T.C., von Löw, E., Gorontzy, T., Blotevogel, K.-H., Gemsa, D. Anaerobic/aerobic composting of 2, 4, 6-trinitrotoluene-contaminated soil in a reactor system. *Environmental Science and Technology* 1998; 32 1676-1679.
- [98] Kirk, J.L., Klironomos, J.N., Lee, H., Trevors, J.T. The effects of perennial ryegrass and alfalfa on microbial abundance and diversity in petroleum contaminated soil. *Environmental Pollution* 2005; 133 455-465.

- [99] Willey, N. *Phytoremediation: Methods and Reviews*. (Methods in Biotechnology, 23) Humana Press; 2007.
- [100] Wang, Z., Xu, Y., Zhao, J., Li, F., Gao, D., Xing, B. Remediation of petroleum contaminated soils through composting and rhizosphere degradation. *Journal of Hazardous Materials* 2011; 190 677-685.
- [101] Selberg, A., Budashova, J., Tenno, T. Column study of the leaching and degradation of anionic surfactants in oil-polluted soil. *Proceeding of Estonian Academy of Science. Chemistry* 2007; 56 87-97.
- [102] *Standard Methods for the Examination of Water and Wastewater*. APHA, 1985, 16th Edition
- [103] Salanitro, J.P., Diaz, L.A. Anaerobic biodegradability testing of surfactants. *Chemosphere* 1995; 30 813-830.
- [104] Zhang, C., Valsaraj, K.T., Constant, W.D., Roy, D. Aerobic biodegradation kinetics of four anionic and non ionic surfactants at sub- and supra-critical micelle concentrations (CMCs). *Water Research* 1999; 33 115-224.
- [105] Koga, M., Yamamichi, Y., Nomoto, Y. et al. Rapid determination of anionic surfactants by improved spectrophotometric method using Methylene Blue. *Analytical Science* 1999; 15 563-568.
- [106] Hayachi, K. A rapid determination of sodium dodecyl sulfate with methylene blue. *Analytical Biochemistry* 1975; 67 503-506.
- [107] n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons). USEPA Method 1664. EPA-821-B-94-004b.
- [108] Strotmann, U., Reuschenbach, P., Schwarz, H., Pagga, U. Development and evaluation of an online CO₂ evolution test and a multicomponent biodegradation test system. *Applied and Environmental Microbiology* 2004; 70 4621-4628.
- [109] Reuschenbach, P., Pagga, U., Strotmann, U. A critical comparison of respirometric biodegradation tests based on OECD 301 and related test methods. *Water Research* 2003; 37 1517-1582.
- [110] Binner, E., Böhm, K., Lehner, P. Large scale study on measurement of respiration activity (AT₄) by Sapromat and OxiTop. *Waste Management* 2012; 32 1752-1759.
- [111] Selberg, A. Evaluation of environmental quality in Northern Estonia by the analysis of leachate. PhD Thesis. University of Tartu; 2010.
- [112] Juuram, K. Assessment of the windrow composting of oil polluted soil and its enhancement. Master's Thesis. University of Tartu; 2012. (In Estonian, Summary in English)

- [113] Kim, I.S., Park, J.-S., Kim, K.-W. Enhanced biodegradation of polycyclic aromatic hydrocarbons using non ionic surfactants in soil slurry. *Applied Geochemistry* 2001; 16 1419-1428.

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