BIOREMEDIATION OF OIL-CONTAMINATED SOIL USING SURFACTANT AND ADSORBENTS.

Aare Selberg, Toomas Tenno

University of Tartu, Jakobi 2, 51014 Tartu, Estonia
e-mail: aare.selberg@mail.ee

Abstract

Bioremediation has become an important method for the restoration of oil-polluted environments. The emulsification of the hydrocarbons increases the degree of dispersion and changes the particles hydrophilic. But the oil pollution would be washed further down below the surface. Bioremediation of oil-contaminated soil from Ämari airport (northwest Estonia) was studied. Experiments were conducted in columns by using the emulsifying mixture that contains surfactant and nutrients. The solution was applied every 14 days for 3 consecutive applications. The hydrophobic and hydrophilic adsorbents were mixed with the soil. The amounts of the outflows and initial and residual total hydrocarbon concentrations were determined. After 60 days of column operations without an adsorbent the total extractable petroleum hydrocarbons (**TEPH**) concentration was reduced 20%. The medium dry residue of outflow was 3.04 g. In use of hydrophobic and hydrophilic adsorbents the TEPH concentrations reduced 60% and 40%, respectively. The dry residues of outflows were both times 1.60 g. Surfactants can emulsify hydrocarbons, thus enhance their water solubility, decrease surface tension and increase the displacement of oily substances from soil particles. Adsorbents can fix the emulsified hydrocarbons into the soil.

Introduction

Bioremediation methods use microorganisms that occur naturally in the environment and degrade (mineralize) contaminants to less toxic or harmless products like carbon dioxide and water. Biological processes have been used successfully to remediate soils contaminated with petroleum hydrocarbons and their derivatives (1). Several petroleum hydrocarbons can act as a source of carbon and energy for the growth of soil microorganisms.

The bioremediation rate is controlled by three major processes: a) the oxygen-transfer process from the air into the aqueous solutions, b) the oil-transfer process from the soil into the aqueous solutions, c) biodegradation rate of oil in aqueous solution (2, 3). In general the mass transfer rate of oil is smaller than either the oxygen transfer rate or the biodegradation rate, and it is the controlling step of bioremediation of oil-contaminated soil (3). The application of surfactants or emulsifying agents may decrease interfacial tension and enhance solubilization of hydrocarbons, thereby making the hydrophobic compounds more available for microbial degradation (4, 5, 6, 7). The sorption of surfactants by soil is affected by the type of surfactant, soil properties, and environmental factors (7), for example pH, amount of organic substance, amount and structure of clay minerals of soil (8). Anionic surfactants are usually chosen for surfactant-based remediation procedures because of their lower degree of adsorption on soil than that by cationic and nonionic surfactants (7). Anionic and nonionic surfactants are less likely to be adsorbed to the soil (1). Because anionic substances are weakly adsorbed by sandy soils with low amounts of organic matter, a leaching of surfactants to the subsoil and the groundwater is to be expected (8).

Materials and methods

The experiments were carried out with sandy soil and it contained 2% clay. The soil had pH of 7.0 (measured in $CaCl_2$), and contained 1.0 mg/kg available phosphorus and 0.12 mg/kg nitrate-nitrogen. The soil was sampled from Ämari airport (northwest Estonia) and it was contaminated with a mixture of jet fuel, diesel oil and lubricating oils. The content of total petrol hydrocarbons was between 450 and 3800 mg/kg dry soil. The polluted soil had the large number of slow-growing bacteria (9). In the latter experiments the soil was mixed with the porous adsorbents (10% v/v) prepared by modifying of the urea-formaldehyde resins.

The bioremediation of oil-polluted soil was studied in the columns in a vertical position. The columns were constructed of transparent Plexiglas cylinders (length 50 cm, inner diameter 6 cm, and wall thickness 0.5 cm). The view of column is presented in Figure 1. Plexiglas was found not to adsorb hydrophobic organic compounds (10). The volume of the columns was 1.4 liters and they contained 2.1 kg sandy soil. The bottoms of the columns were opened to register the outflows.

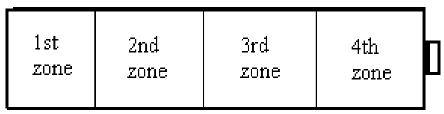

Figure 1. The view of column

Soil was treated with solution of emulsifying agent SR-100 (E-Tech, USA) every 14 days for 3 consecutive applications (11). The added solution of SR-100 contained 8% dry matter. 33 ml of distilled water was supplied every week to the surface of the soil. During treatment the outflows from columns were measured every day. The soil samples with and without adsorbents were treated in the columns by the same way.

After treatment the soil from the columns was divided to four parts according by the zones (Figure 1). The soil samples from different zones were extracted by shaking with methylene chloride and Soxhlet-extracted with n-hexane. Residues of hydrocarbons were determined gravimetrically as total extractable petroleum hydrocarbons (**TEPH**).

Results

At first the soil sample was treated with aerated water and the quantities of added water and outflows of the column are shown in Figure 2. The dry residue of the outflow was 2.015 g and it contained 1% of extractable hydrocarbons.

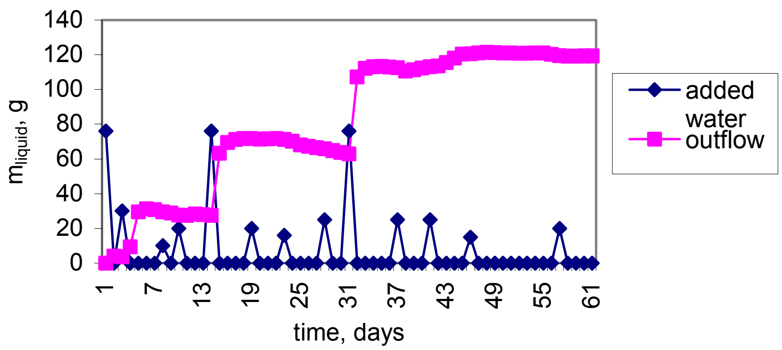

Figure 2. The temporal variation of the masses of added water and outflow

Next the soil samples were treated with the solution of SR-100. The quantities of outflow and the added solution and water are shown in Figure 3.

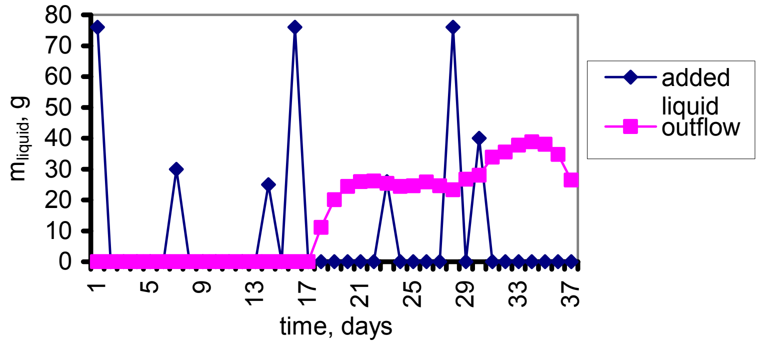

Figure 3. The temporal variation of masses of added liquids and outflow

The medium dry residue of outflows was 3.038 g and it contained 47% of extractable hydrocarbons. Figures 4 and 5 present the quantities of outflows and added solution of SR-100 and water for the columns with a mixture of soil and hydrophobic and hydrophilic adsorbents, respectively.

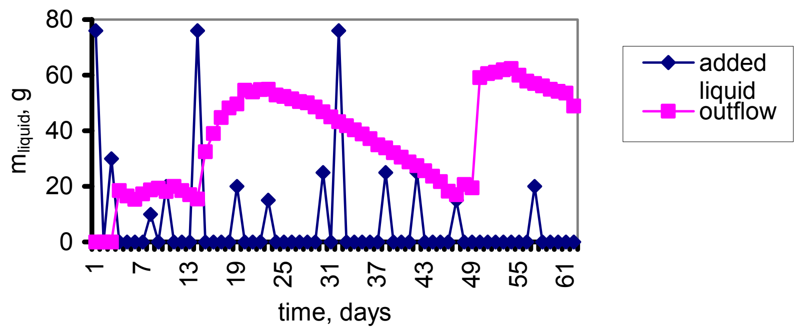

Figure 4. The temporal variation of masses of added liquids and outflow for hydrophobic adsorbent

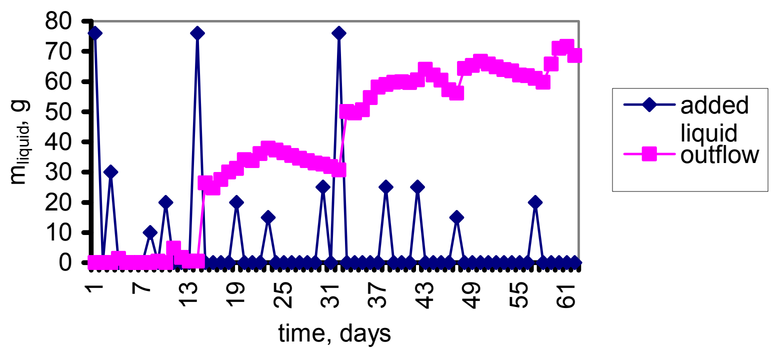

Figure 5. The temporal variation of masses of added liquids and outflows for hydrophilic adsorbent

The dry residue of outflow was 1.610 g for hydrophobic adsorbent and 1.596 g for hydrophilic adsorbent. Both times the dry residue contained less than 1% of extractable hydrocarbons. Figures 4 and 5 present the quantities of outflows and added solutions and water for the columns with a mixture of soil and adsorbents.

Table 1. TEPH concentrations after treatment with water or SR-100.

Zone	TEPH concentration			
	H_2O		SR-100	
	mg/kg	%	mg/kg	%
1st	1540	97	1240	78
2nd	1570	99	1270	80
3rd	1600	101	2140	135
4th	1570	99	1520	96

The TEPH concentrations in the columns with the adsorbents after treatment with the solution of SR-100 are shown in Table 2. Initial TEPH concentration was 570 mg/kg dry soil.

Table 2. TEPH concentration in the columns with adsorbents.

Zone	TEPH concentration			
	hydrophobic		hydrophilic	
	mg/kg	%	mg/kg	%
1st	110	19	330	58
2nd	140	25	340	60
3rd	220	39	380	67
4th	130	23	230	40

Discussion

The outflows were collected into the open flask and evaporation of water occurred during the experiments. The constant mass of outflow showed that the rates of flowing and evaporation were equal.

The amount of outflow grew almost immediately after adding the bigger amount of water (Fig. 2) and it showed that the sandy soil had good permeability for water. The dry residue of outflow contained 1% extractable compounds and the TEPH concentrations were very similar in the different zones of column (Table 1). It means that petroleum hydrocarbons did not leach by water.

The liquid started flowing more than 2 weeks after the beginning of treatment with the solution of SR-100 (Fig. 3) because the surfactant adsorbed in soil. At the same time the mass of dry residue of outflow was bigger and it contained 47% extractable hydrocarbons. It showed leaching of petroleum hydrocarbons by the surfactant and it would have a risk for groundwater. The TEPH concentrations (Table 2) showed that petrol hydrocarbons leached down in soil and TEPH accumulated into the 3rd zone. It was hard to identify the reason of reduction of TEPH: degradation or leaching.

The properties of the adsorbent influenced the amount of outflow. The mixture of soil and hydrophobic adsorbent did not adsorb the solution of SR-100 in the beginning of treatment (Fig. 4) but during treatment the adsorption of surfactant grew. The mixture of soil and hydrophilic adsorbent adsorbed the added solution well in the beginning of treatment (Fig. 5) but later the adsorption of solution was smaller. The adsorbent saturated with water and the solution flowed through the soil. The dry residue of outflow was almost equal for both adsorbents and it contained less than 1% extractable hydrocarbons. It means that adsorbents adsorbed the petroleum hydrocarbons. TEPH concentrations (Table 3) in the different zones showed that hydrocarbons were biodegraded during treatment but the accumulation of them occurred in the 3rd zone. The using of hydrophobic adsorbent led to the faster degradation of hydrocarbons but the degree of accumulation was also higher than it was for hydrophilic adsorbent. The lack of oxygen can be the reason for the accumulation of hydrocarbons into the 3rd zone. The bottom of the column was opened and oxygen diffused into the 4th zone. The hydrophobic adsorbent adsorbed the emulsified hydrocarbons and it enhanced the bioavailability and biodegradation of hydrocarbons.

Conclusion

The column tests were carried out to examine the effects of surfactant and adsorbents on the biodegradation of petroleum hydrocarbons in sandy soil. The experiments showed the leaching of hydrocarbons in soil by treatment with the solution of surfactant. The leaching disturbed the examination of biodegradation of pollutants. Adding of adsorbents decreased the leaching and fixed the petroleum hydrocarbons into the soil. The rate of biodegradation of contaminants was higher for additives of hydrophobic adsorbent, in comparison to hydrophilic adsorbent.

Acknowledgements

The authors thank World Federation of Scientists for support.

References

1. C.N. Mulligan, R.N. Yong and B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review. Engineering Geology, **60**, 371-380 (2001).
2. K.Y. Li, T. Xu, W.A. Cawley et al. Field test and mathematical modeling of bioremediation of an oil-contaminated soil – part 2: Mathematical modeling. Waste Management, **14**, 571-579 (1994).
3. K.Y. Li, Y. Zhang and T. Xu, Bioremediation of oil-contaminated soil – a rate model. Waste Management, **15**, 335-338 (1995).
4. L. Bardi, A. Mattei, S. Steffan et al. Hydrocarbon degradation by a soil microbial population with β-cyclodextrin as surfactant to enhance bioavailability. Enzyme and Microbial Technology, **27**, 709-713 (2000).
5. J.C. Fountain, A. Klimek, M.G. Beikerch et al. The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer. Journal of Hazardous Materials, **28**, 295-311 (1991).
6. I.S. Kim, J.-S. Park and K.-W. Kim, Enhanced biodegradation of polycyclic aromatic hydrocarbons using nonionic surfactants in soil slurry. Applied Geochemistry, **16**, 1419-1428 (2001).
7. D.-H. Lee, R.D. Cody, D.-J. Kim et al. Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil. Environment International, **27**, 681-688 (2002).
8. T. Küchler, W. Schnaak, Behaviour of linear alkylbenzene sulphonates (LAS) in sandy soils with low amounts of organic matter, Chemosphere, **35**, 153-167 (1997).
9. A. Selberg and T. Tenno, Bioremediation of oil-contaminated soil: effects of emulsifying agent. Environmental Science and Pollution Research, **3**, 242 (2002).
10. E.P. Kuhn, P.J. Colberg, J.L. Schnoor et al. Microbial transformations of substituted benzenes during infiltration of river water to groundwater: laboratory column studies, Environmental Science and Technology, **19**, 961-968 (1985).
11. SR-100 Series. Emulsifying Soil Remediation Agent and Structured Deactivation Technology. Technical Bulletin, Ecology Tech of California