DEGRADATION KINETICS OF TOTAL HYDROCARBONS IN THE BIOREMEDIATED SOIL LAYER

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Abstract:

The work presents kinetic parameters of the removal of the components with hydrocarbon functionalities and polar components in the course of bioremediation of the soil contaminated with crude and oil derivatives. In the course of a laboratory experiment that lasted 325 days it was found that content of the components with hydrocarbon functionalities decreased from 125 g/kg to 40-75 g/kg, depending on the mode of recirculation of water phase and sampling site (top, middle, or bottom of the bioreactor). A slower degradation process was observed compared to that of mineral oils along with the accumulation of polar components in the course of the bioremediation process.

Keywords:

bioremediation, hydrocarbons, soil, kinetics

1. INTRODUCTION

Hydrocarbons represent an extremely important and heterogeneous group of compounds that reach the environment by natural and anthropogenic ways. Among hydrocarbons, there are several groups of compounds that exhibit high toxicity (polycyclic aromatic hydrocarbons, PAHs, BTEX components, etc.). In the environmental samples, the majority of these compounds are analyzed by specific gas or liquid chromatography methods. In addition to the information about so specific sort of pollutants, the analyses of contaminated areas often contain also data obtained by IR spectrometric measurements, indicating total hydrocarbon content. According to Standard Methods, these measurements are carried out in the extracts (carbon tetrachloride or freon) after removal of polar components by adsorption on alumina or silica gel [2]. Kind of total petroleum hydrocarbons data can be obtained by gas-chromatographic measurments, also. The aim of this work was to determine kinetic parameters of degradation of the components with hydrocarbon functional groups, encompassing also polar structures that are not determined in routine

analyses. It is known that the biodegradation of hydrocarbons yields formation of polar products of metabolism [5] that can still have a high proportion of hydrocarbon structures, so that a better insight is thus obtained into the degree of degradation, i.e. persistence of hydrocarbon molecules.

2. MATERIALS AND METHODS

The experiments were carried out on samples of the contaminated soil brought from the internal dump of the Oil Refinery Novi Sad, where it was deposited immediately after the bombing in June 1999. Soil was directly contaminated with various petroleum products (gasoline, crude oil, kerosene, diesel fuel, black oil etc.) and products of their combustion due to frequent fires [1]. Real composite samples of the soil were put in two laborotory scale bioreactors (with continuous and discontinuous recirculation) [4]. Microorganisms previously adapted to specific pollution were applied on the soil together with nutrients. During the experiment (325 days) content of substances with hydrocarbon moieties was monitored at different heights of the bioreactors. IR spectrofotometric procedure was applied [2] with and without removal of polar compounds on Al_2O_3.

3. RESULTS AND DISCUSSION

Changes in the concentration of total hydrocarbons in soil with time are presented in Fig. 1.

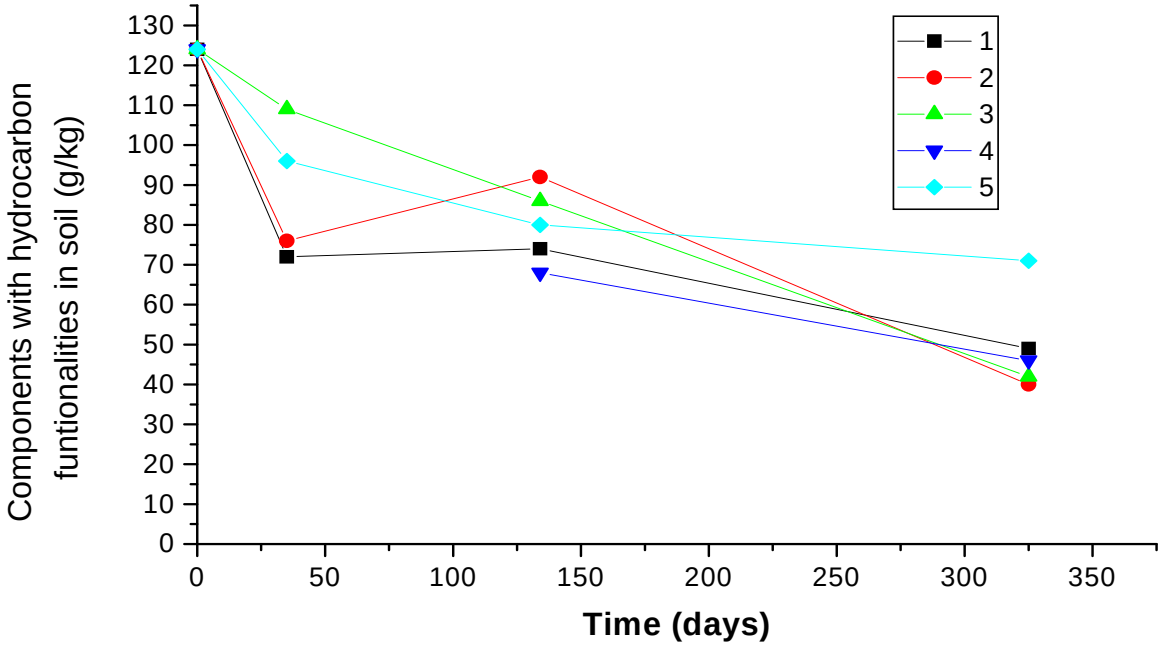

Fig. 1*.Concentration change of matter containing hydrocarbon functionalities in soil in the course of 325 days; 1-top of the reactor with continuous recirculation, 2- bottom of the reactor with continuous recirculation, 3-top of the reactor with discontinuous recirculation, 4-middle of the reactor with discontinuous recirculation, 5- bottom of the reactor with discontinuous recirculation*

Functional dependence of the concentration change with time can be described by the following equation:

$$\ln Y = A + B*X^{0.5} \qquad (1)$$

with the correlation coefficients from 0.9330 to 0.9995 (depending on the measured parameter and sampling site), where :

Y - concentration of total hydrocarbons in g/kg of dry soil,

X - time (in days) needed to reduce the concentrations of components with hydrocarbon groups to the natural level (25 mg/kg),

A – ordinate intercept,

B – rate coefficient of the change of total hydrocarbon content in soil ($day^{-1/2}$) .

The values of the slope (B) and correlation coefficient (R), as well as the time (x) needed to achieve the reduction of the concentration of hydrocarbons to natural level are presented in Table 1. The estimated time needed for removal of hydrocarbon components from the soil, i.e to reduce their contents to the natural level, is from 44 to 184 years, which is significantly longer than the estimated value for mineral oils (32 to 59 years) [3], depending on the wetting conditions and site of sampling.

Table 1. *Kinetic parameters of hydrocarbon degradation*

Constant	Content of components with hydrocarbon functionalities			
	1	**2**	**4**	**5**
A	4.8	4.8	4.8	4.8
-B ($day^{-1/2}$)	0.050	0.067	0.054	0.033
R	0.9330	0.9925	0.9995	0.9856
X (year)	79	44	69	184

The rate of removal of components with hydrocarbon functionalities is the lowest at bottom of the reactor with discontinuous recirculation, it is eqaul at the top of the reactor with continuous recirculation and in the middle of the reactor with discontinuous recirculation, whereas it is highest at the bottom of the reactor with continuous recirculation. Changes in the concentration of hydrocarbons adsorbed on alumina (polar compounds) in soil with time are presented in Figure 2. The concentration of polar components shows first a decrease except for the anaerobic bottom, where it constantly increases (probably because of migration), and then increases everywhere, and after 150 days a decreasing trend is observed. On the basis of the rate of removal of components with hydrocarbon functionalities and mineral oils, as well as trends of the changes of polar components concentration, it can be concluded that polar groups that can represent degradation products of hydrocarbon pollutants decelarate significantly the process of their complete removal.

4. CONCLUSION

In the course of the laboratory experiment lasting 325 days it was found that contents of the components with hydrocarbon functionalities decreased from 125 g/kg to 40-75 g/kg, depending on the mode of water recirculation and sampling site (top, middle or bottom of the bioreactor). It was found that the rate of biodegradation is slower compared to that observed for mineral oils and that the components accumulate in the process of biodegradation. In both bioreactors, biodegradation can be described by equation: $\ln y = a+bx^{0.5}$ with high correlation cefficient r^2=0.93-0.99. Using this equation it was calculated that the level of pollution could reach background value of the area (25 mg/kg) in 44-184 years, depending on the conditions involved. It can be supposed that this is a consequence of accumulation hydrocarbon components with polar groups, as the experiment showed they can also

accumulate in soil. Such a result indicates at the same time that once contaminated with hydrocarbons, the soil can be very slowly brought to the previous state, and only under the condition that no new contamination occurred.

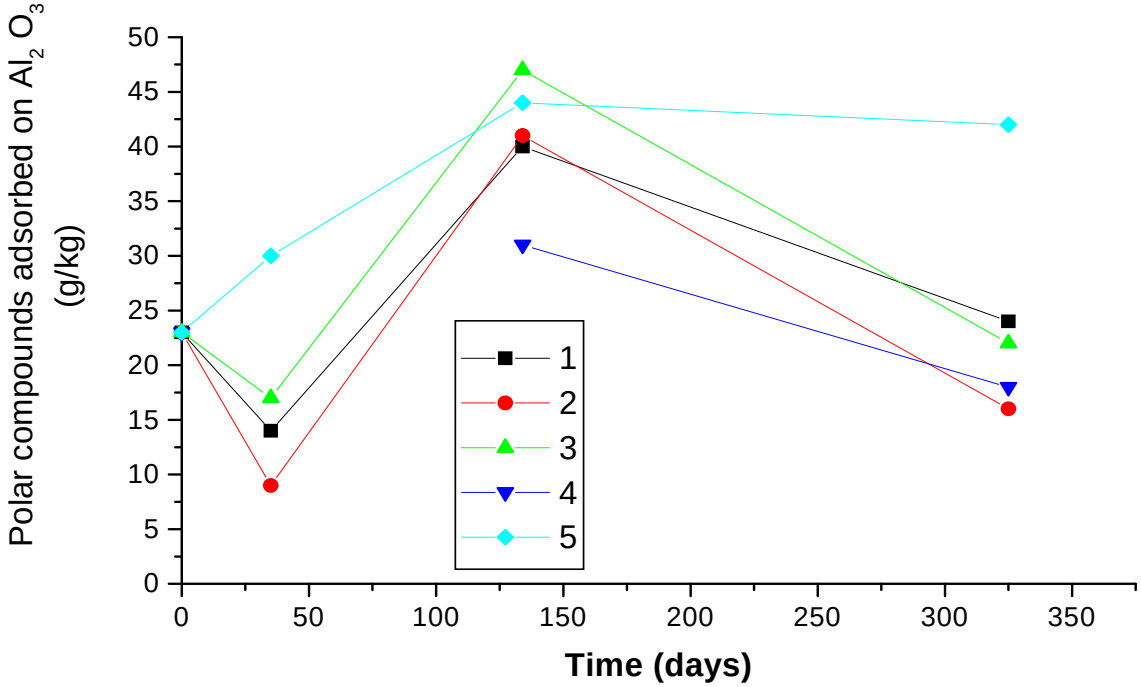

Fig. 2. *Changes in polar compounds concentration during experiment*

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5. REFERENCES

1. Anon. Protection of Water Supply Source "Ratno Ostrvo" in Novi Sad, Institute for Water "Jaroslav Cerni", Belgrade, 1999.
2. Anon. Standard Methods for the Examination of Drinking Water, Federal Institute of Public Health, (Skunca-Milovanovic, S., Feliks, R., Djurovic B., Eds) Belgrade, 1990.
3. DALMACIJA B., IVANČEV-TUMBAS I., RONČEVIĆ S., PETROVIĆ O. Bioremediation of polluted soil after NATO bombing in Novi Sad, Yugoslavia in Abstract Book from 12th International Biodeterioration and Biodegradation Symposium, Prague, Czech Republic, 14-18 July, 2002.
4. RONCEVIC S. Kinetics of bioremediation processes in soil polluted with oil and oil derivatives, Master thesis, Faculty of Sciences and Mathematics, Novi Sad, 2002.
5. WATKINSON R.J. Developments in Biodegradation of Hydrocarbons. Applied Science Publishers, London, 1974.