Study of the Immobilizing Capacity of Humic Substances in Soils at Oil Contamination

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Abstract. Agro- and physico-chemical analysis of three types of soils was carried out. It has been shown that the pH value for dark gray soil is 5.5 and characterizes it as more acidic compared to gray soil (pH = 6.0) and black soil (Rich soil) (pH = 6.5). Molecular masses and sizes of colloidal micelles of humic substances from soil samples were determined. It is shown that the size of humic micelles in three types of soils is different and is inversely related to pH - the lower the pH value, the larger the micelles. The presence of a direct relationship between the efficiency of immobilization of oil particles in soil and the size of micelles of humic structures was revealed. This factor determines the effectiveness of oil pollution remediation. New dependencies have been obtained that can be used to predict the consequences of oil pollution, as well as to develop a targeted action technology for soil cleaning. The prospects of using the scientific approach for practical purposes are shown. Knowing the obtained dependencies, it is possible to control the formation of large micelles and create optimal technological conditions for the sorption of oil by particles in each type of soil. The results are of fundamental importance, contribute to the ecological chemistry of soils and contribute to an in-depth understanding of the interaction of bioremediates with oil.

1. Introduction

Oil and its refined products belong to the most common class of pollutants [1]. This is due to the huge volumes of its production, which is associated with great environmental risks. In particular, due to the danger of oil entering the environment as a result of accidents at boreholes, as well as spills from oil pipelines, oil transportation facilities, gas stations, oil depots, oil storage facilities, etc. The entry of oil into the soil leads to changes in its physical, chemical and microbiological properties, deforms the structure of biocenoses, leads to the loss of its natural biospheric buffer properties and violates the ecological safety of the territory [2, 3]. Existing methods of eliminating the consequences of soil pollution by oil include mechanical, physicochemical and biological methods of remediation and the use of various sorbents [4, 5].

However, this does not always meet the requirements of economy and environmental safety, in particular, due to the threat of secondary pollution. Considering the scale of oil production and flow into environmental objects, the search for effective and environmentally friendly methods of remediation of oil-contaminated soils is a very acute and urgent task [6]. This is also consistent with the need to follow the modern concept of best available technology (BAT) in order to protect the environment.
One of the environmentally safe methods is the remediation of oil-contaminated soils using humates or sorbents based on them [6, 7, 8]. Humic substances are the main natural matrix of soil organic matter, which are not only ameliorants. They are primarily responsible for the biodegradation of petroleum hydrocarbons [9,10,11]. Due to the presence of ion-exchange groups, humic substances are able to effectively sorb oil hydrocarbons, increase the activity of soil microflora, and accelerate the processes of hydrocarbon destruction and their humification.

However, due to the variability of soil properties, there is no clear understanding of the mechanism of interaction of oil with humic substances, which may cause different efficiency of its immobilization. These processes are poorly studied, as well as oil dispersion under the influence of organomineral particles and humic substances.

The lack of scientific understanding of the mechanism of such interaction leads to contradictory conclusions regarding the practical use of sorbents based on humates for cleaning oil-contaminated soils. This, in turn, will reduce the effectiveness of the technologies used in practice for soil remediation in case of oil spills. These circumstances determine the fundamental scientific prospects for studying the interaction of oil particles with humic substances of soils.

It should be emphasized that in ecological soil chemistry, the problem of studying the types of interactions between substances is fundamental and is at the stage of accumulating results for the formation of scientifically grounded ideas about the types of physicochemical interactions in the soil pool.

The purpose of the research: on the basis of studying the agro- and physicochemical parameters of three types of soils and model laboratory experiments with artificially contaminated soil with oil, to reveal the empirical dependence of the efficiency of immobilization of oil particles on the size of the resulting humus micelles of soils.

The tasks of the work included:
- to obtain agro- and physico-chemical parameters of three types of soils.
- to isolate and determine the average molecular weight, as well as the size (diameter) of colloidal micelles of humic substances in three types of soils;
- to determine the effect of the pH of the soil on the size of micelles of humic substances;
- to evaluate the efficiency of oil binding by humic micelles of different sizes.

2. Materials and methods

The object of the study was natural soils of three sections, as well as samples of these soils artificially contaminated with oil - chernozem, dark gray soil, gray light loamy soil. The field, theoretical, physicochemical, chemical, biological, statistical methods were used with the use of modern analytical equipment and generally accepted methods in soil analysis [12].

Soil samples were taken to a depth of 20 cm in accordance with the standards. IR spectrometry using the AN-2 analyzer was used to determine oil products in soils. The extraction of petroleum products was carried out with carbon tetrachloride. The end of the analysis is the chromatographic separation of petroleum products from associated organic compounds of other classes from oil-saturated soils [13, 14]. Micellar humic formations and the molecular weight distribution of micelles were determined using in-plane gel filtration in a thick layer (h = 1 mm) on Sephadex G-50 dextran gel (thin). Determination of the size of structured colloidal micelles of humic substances (the size of associates) was carried out on a universal laser diffraction particle size analyzer SALD-2201 (Shimadzu, Japan).

EXCEL statistics to process the results were used.

3. Research results

The table shows the physicochemical and agrochemical parameters of soils.

The table shows the following physical and chemical parameters of soils:
1, 2 - pH_{H_2O} и pH_{KCl} – determined potentiometrically;
3 - Ca^{2+} и Mg^{2+} – determined titrimetrically;
4 - Cation exchange capacity;
5 – V, degree of saturation, %
6 - granulometric composition by pipet method according to Kachinsky;
7 - hygroscopic moisture - determined by thermostat-weight method ;
8 - loss on ignition in a muffle at 900 ° C.
9 - organic carbon content according to Tyurin;
10 - group composition of humus according to Kononova-Belchikova.

Table 1. Physicochemical properties of the studied soils in the 20 cm layer.

| Index | Soil types          | Gray soil | Dark gray soil | black soil (rich soil) |
|-------|---------------------|-----------|----------------|-----------------------|
| 1     | pH<sub>H2O</sub>    | 5.5       | 6.0            | 6.5                   |
| 2     | pH<sub>KCl</sub>   | 5.8       | 6.4            | 6.7                   |
| 3     | S (Ca+Mg), mg-eq / 100 g of soil | 21.9 | 27.0 | 44.2 |
| 4     | CEC, mg-eq / 100 g of soil | 27.2 | 30.2 | 45.4 |
| 5     | V (degree of saturation), % | 80.5 | 89.4 | 95.4 |
| 6     | Fraction content <0,01 mm, % | 27 | 31 | 38 |
| 7     | Hygroscopic moisture, % | 4.15 | 4.52 | 5.21 |
| 8     | loss on ignition , % | 8.56 | 9.81 | 10.71 |
| 9     | C<sub>r</sub> % | 3.62 | 4.17 | 3.82 |
| 10    | C humic acids /C fulvic acids | 1.21 | 1.65 | 1.38 |

Figure 1 shows the average molecular masses of humic substances for three types of soils, namely, from the upper horizon: 1- AYG (gray-humus); 2- AU D (dark gray humus); 3 - AU B (black soil).

Figure 2 shows, respectively, the average size of colloidal micelles of humic substances for the same soil types.

Figure 1. Molecular weight of humic substances of three types of soils, kDalton.

Figure 2. Size (diameter) of colloidal micelles of humic substances of three types (1-3) of soils, µm.

Taking into account the high sensitivity of the structural and chemical stability of micelles to environmental influences, the dependences of the sizes of micellar colloids under different conditions, primarily on soil pH, were studied [15] figure 3. It was revealed that the size of colloidal micelles of humic substances is directly dependent on the pH of the medium - the higher the acidity, the larger the size of micellar formations of humic substances.
4. Discussion
As shown in the table, the pH value (indicator 1) for dark gray soil is 5.5 and characterizes it as more acidic in comparison with neutral gray soil (6.0) and especially with black soil (6.5).

The content of exchangeable Ca\(^{2+}\) and Mg\(^{2+}\) (index 2) in black soil is the highest (two times), which may indicate an increased salt content. This is consistent with the values of the sum of exchangeable bases in a row (indicator 4) and the degree of saturation of three soils with bases,\(\%\) (indicator 5).

It is also seen that the ratio of the sum of exchange bases to the cation exchange capacity is the smallest for gray soil - 80\%, while for black soil this characteristic is equal to 95\%. Those soils differ in their ability to absorb oil on their organo-mineral complex in each case. In addition, the loss on ignition of LOI (indicator 8) also gives an idea of the amount of mineral salts in three types of soils, which can be an additional factor for the intermolecular interaction of oil particles and salt ions.

However, it is known that the physicochemical and biochemical mechanisms of the processes of biodegradation of hydrocarbons in soils are mainly in the absorption of oil hydrocarbons by molecules of humic substances. Oil hydrocarbons interact with functional molecular groups, ligands of humic acids form new structures of compounds, which contributes to the process of destruction and humification of oil-contaminated lands and, accordingly, to reduce environmental hazard [16, 17, 18].

The antidote activity of humic compounds in relation to oil products is based on their ability to act mainly as surface-active agents, complexing agents and molecular destructors of toxic oil products [19, 20, 21].

To clarify the relationship between the saturation of the soil with the humic complex and the level of immobilization of oil particles, molecular weights were isolated and determined, and the sizes of colloidal micelles of humic substances were determined. It has been shown that the molecular weights of micelles from gray and dark gray soils are in the range of 15-17 kDa, while the molecular weights of micelles of black soil are much less - by 4 kDa. At the same time, the size (diameter) of colloidal micelles for gray and dark gray soils is 8.9 and 8.4 \(\mu\)m, respectively, and exceeds that for black soil, for which the size does not exceed 7.0 \(\mu\)m.

However, the studied soils have different acidity-pH values. Taking into account the sensitivity of the humic complex to acid-base properties, the empirical dependence of the size of the formed micellar particles on the acidity of the medium was determined. It was shown that the lower the pH,
the larger the micelles figure 3. Obviously, this factor is dominant and determines the efficiency and size of micelles of humic substances. The revealed features of structure formation can explain the potential sorption properties of the soil layer in each case.

Under the conditions of a laboratory model experiment with artificial soil contamination with crude oil at the same concentrations of 100 mg / kg, the amounts of oil sorbed by each of the three types of soils were determined in three replicates.

After keeping the contaminated soil in water for several days, followed by washing the soil with water (simulating the natural conditions of the natural washing regime), after drying and subsequent extraction of petroleum products in carbon tetrachloride, their concentrations were determined by IR spectroscopy.

This made it possible to evaluate the efficiency of oil (petroleum hydrocarbons) immobilization by each type of soil. In figure 4 shows the empirical dependence of the immobilized oil on the size of humic micelles. It was found that the larger the size of micellar structural formations, the greater the concentration of oil that can be fixed on them and then humified. The greatest amount of oil can be fixed on micelles of gray soil, then dark gray, and finally in black soil.

Thus, new factors of intrasoil interactions and dependences with the participation of micelles of humic substances and petroleum products (oil) were revealed. Knowing such dependences, it is possible to control the formation of large micelles in practice by adjusting the pH of the medium and to create optimal conditions for oil sorption in practice.

5. Conclusion

Agro- and physico-chemical analysis of three types of soils was carried out. It is shown that the pH value for dark gray soil is 5.5 and characterizes it as more acidic in comparison with gray soil and chernozem. The molecular weights and sizes of colloidal micelles of humic substances from soil samples were isolated and determined.

It was shown that the size of humic micelles depends on the pH of the soil medium - the lower the pH value, the larger the micelles. This factor must be taken into account when assessing the efficiency of micelle formation of humic substances, since it is this factor that determines the process of immobilization of oil particles.

The presence of a relationship between the efficiency of immobilization of oil particles in the soil and the size of micelles of humic substances was revealed. The obtained dependences can be used to predict the consequences of oil pollution, as well as to develop a targeted action technology for the remediation of contaminated soil. It is shown that this approach is promising for practical purposes.

New dependencies have been obtained that make it possible to control the formation of large micelles and to create optimal technological conditions for the sorption of oil by soil particles. The results are of fundamental scientific importance, since they contribute to the ecological chemistry of soils and contribute to an in-depth understanding of the influence of the properties of the soil pool on the efficiency of the interaction of bioremediates with oil.

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