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Phenol and M-Crezol Sorption in Typical Black Earth, Brown Earth and Red Soils

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***Abstract*— According the studies regarding sorption of Phenol and m-crezol by ordinary black earth, typical brown and red earth soils, there is observed the dependence between reaction medium PH and dissociation degree, on content of the clay minerals, on the total amount of hummus and the fractional composition of the group. It was revealed, when soil contains low concentration of phenol and m-cresol sorption progresses chemically, but if concentration is high the process goes on the contrary. After multiple entries of phenol and m-cresol in the given samples of soils, first 30 days concentration of components is lower than in the beginning, but at the 40th day the amount exceeds the starting point. According the sorption of phenol and m-cresol, soils can be differentiated in the following way: ordinary black earth soil>typical brown earth soil>typical red earth soil.**

***Keywords*— soils, phenol, crezol, fraction, exothermal, isotherm, red soil, black soil.**

The modern epoch of the scientific-technical progress is being accompanied by the environmental pollution with different substances of exogenic origin including phenol compounds. They are widely spread in the waste waters of by-product coke plants, oil refineries and other manufacturing companies. They contain plant biome and many kinds of chemical protection preparations of the plant. They are characterized with good sustainability; they litter the environment – soil, atmosphere, drinking waters; they are toxic to live organisms and their major part is characterized with cancerogenity. Therefore, the utilization of these compounds is an urgent problem today [4,5,7,8, 11,12, 13,17, 26,27].

Migration-conversion process and the direction of phenolic compounds in soils depend on a number of characteristics. The most notable of them are the mineral composition of soils, PH- and redox potential impact, the content and structure of humus compounds, microbiological and Abiotic transformation [10,14,20,21,22,23].

From these processes the sorption processes of these substances are important, because as soon as they are placed in the soil, first of all, they are subjected to this transformation mechanism. In some cases these sorptive compounds are activated and therefore their decomposition, as compared with the free state, is more intense [16,21,24,25].

As phenol, the easiest representative of phenolic substances and m-Crezol have almost every feature typical for the group itself, on their examples we have studied the sorption phenomena in the upper -A- humus horizon of ordinary brown, gray and typical red soils. We studied the soil features with standard methods [1].

We placed 1.5 gram of soils in 50 ml flasks and included inside the increasing amount of phenol and of m-Crezol (1; 2; 3; 4; 5; 6; 7; 8) (respectively I, II, III, IV, V, VI, VII, VIII options). We add ach of them 15 ml of distilled water and in conditions of 20^0, 30^0, 45^0degree, we shake them during 24 hours. After the establishment of equilibrium between liquid and solid phases, we determined their amounts with the colorimetric method [3] in counteretch and discussed about the sorption with the K coefficient which was determined by the Freundlich equation solution [19]. Experiments were conducted in a 10-fold return. Obtained data were processed by methods of mathematical statistics [2].

From the obtained data we can see that phenol and m-Crezol are adsorbed more in ordinary black earth soils, then in typical gray soil and they are the least typical in red soil. This regularity is a true in conditions of different temperatures (20^0; 30^0; 45^0C).

It is known that phenol and m-Crezol reaction depends on the reaction capacity of the PH area. The more it is inclined toward neutral, the higher their impact is. Our data confirm this regularity. For example, PH of the ordinary squeezed water of the black earth soils varies within the limits of 7,1, in typical gray soils it is 5.6, while it is 4.5 in typical red soil (Table. N1).

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Table N1
Separate Characteristics of Soils

№	Soils	Rocks and minerals	Depths (cm)	"Content of physical clay (<0,01 mm)" (in %)	PH (H_2O)	Common content of humus in %	$C_H : C_F$
1	Ordinary Black Soil (Georgia, Shiraki)	Montmorill-onite Beidellite; Hydromicas	0-30	68,9	7,1	6,52	1,1
2	Typical brown soil (Georgia, Keda)	Hydromicas; Kaolin	0-25	47,5	5,6	4,61	0,39
3	Typical red soil (Georgia, Chakvi)	Kaolin; Kaolin -Haluazite; Chlorite	0-25	71,1	4,5	5,12	0,35

Therefore, when the sorption has a chemical character, the interaction of phenols with the adsorbent will be more intense in the ordinary brown soil than in the typical brown and red soils. It should be noted that along with the increase in acidity of the area (i.e., brown and red soils), the redox potential shifts toward the restoration processes, and therefore the oxidative processes, in which, the phenols can engage, will be of less intensity. In the black earth soils, on the contrary, the area reaction is a neutral-weak alkaline and oxidative processes dominate in this case.

It is known that the sorption of substances depends on the mechanical composition of the soils [9,10,14,15,20]. There is a direct correlation between the content of sorption value and clay mineral. At the same time, the qualitative composition of the clay fraction is of great importance. In our case (table. N1) the ordinary black soil in the mechanical composition of 0-30 cm depth contains the fraction of physical clay (<0,01 mm) of 68.9%, which is mainly introduced by the secondary clay minerals: Montmorillonite, Beidellite, Hydromicas. Typical brown soil in the depth of 0-25 contains the physical clay fraction of 47.5%, which mainly consists of Hydromicas and

Kaolins and in the 0-25 cm depth of the typical red soil area the physical clay fraction is 71.1% which is represented by the secondary clay minerals: Kaolins, Kaolin-Haluazite, chlorite and Hydromicas.

Given the fact that the specific surface area of Montmorillonite is more than of Hydromicas and even more than of Kaolins and chlorite, therefore, due to participating in this process the amount of Phenols and m-cresols sorbated by the secondary clay minerals will be more in the black-earth ordinary soil, then in the typical brown soil, and at the end, in a typical red soil, as evidenced by the results obtained by us.

In conditions of sorption, the most important role is played by the organic substances of the soil [5,6,18,21], phenolic compounds interact with the humus substances of the soil and this process is more intense with humic acids than pulvilloric acid. Fractional composition of humus in the ordinary black soil is C_H:C_F=1,1, i.e., humic, while in the typical brown and red soils, this indicator is relatively close to each other (respectively 0,39 and 0,35), or is pulvilloric. It is therefore expected that the degree of sorption of Phenols and m-cresol will be a high in the ordinary black soil, while in the typical brown and red soils it will almost equal. As for the quantitative side it is in correlation with common humus content and since in the ordinary black soil this rate is 6,52% and 4,61% in the typical brown soil, while in the typical red soil of 5.12% (table.№1), so it is likely that the amount of sorbated Phenols and m-cresol will be more in ordinary black soil, then in the typical red soil and in the end in a typical brown soil.

Since the sorption is an exothermic process in the interaction area of components the temperature increase causes the physical sorption decreases, while the chemical sorption is increased. On this basis it is possible to distinguish the physical and chemical nature of the sorption.

The chemical nature of the sorption of Phenol and m-cresol is confirmed by the data that we obtained during studying in different (20^0, 30^0, 45^0C) temperat

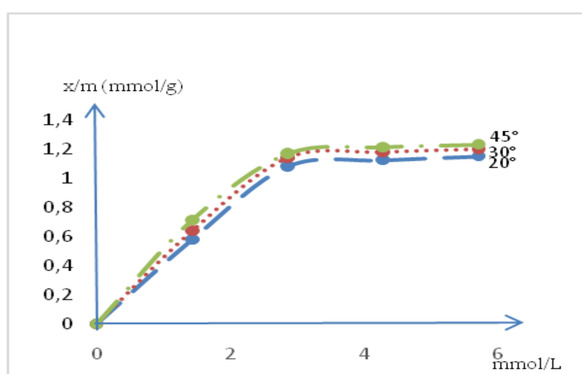

Diagram. 1. The isotherm of phenol sorption by ordinal black soil

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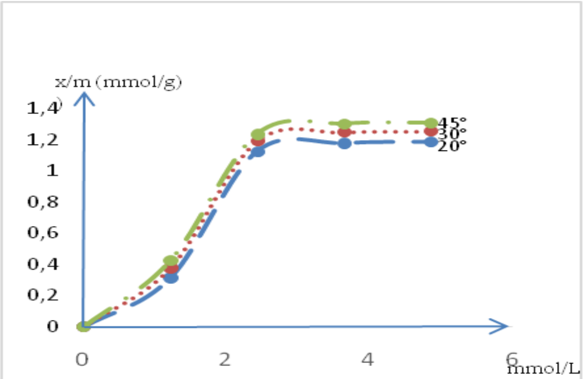

Diagram. 2. M-crezol sorption isotherm by ordinal black soil

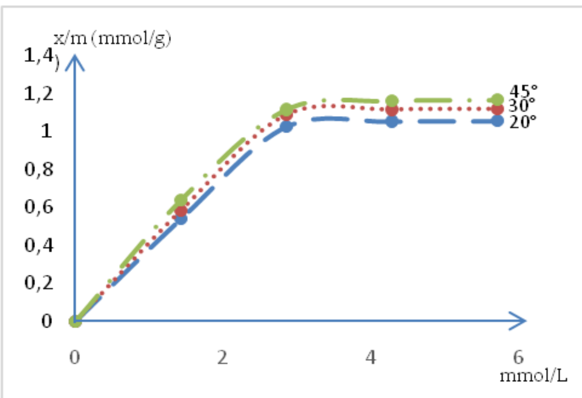

Diagram. 3. Phenol sorption isotherm by typical brown soil

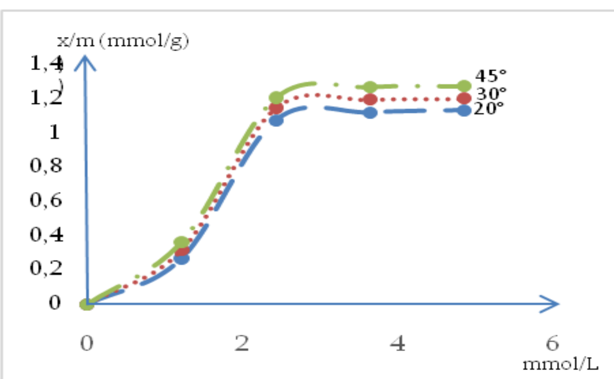

Diagram. 4. M-crezol sorption isotherm by typical brown soil

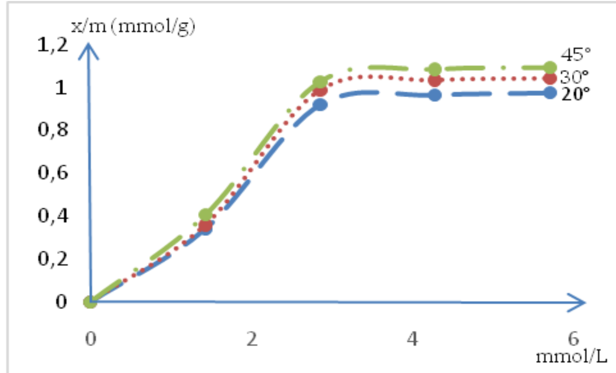

Diagram. 5. Phenol sorption isotherm by typical red soil

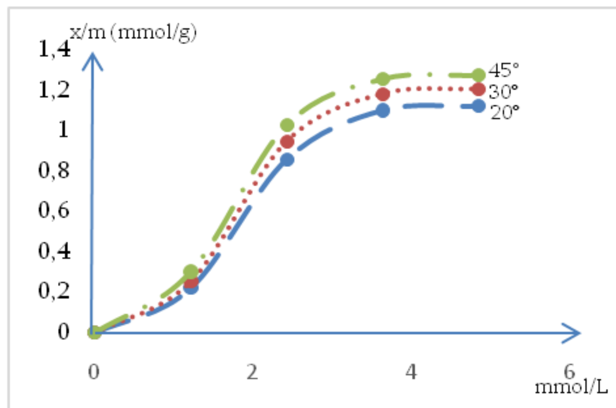

Diagram. 6. M-crezol sorption isotherm by the red soil

From the diagrams (№1,2,3,4,5,6) we can see that along with the temperature increase, the amount of phenol and m-cresol sorbated by soils also increases. The chemical nature of the process is conditioned by the chemically high activity of the abovementioned compounds, i.e. their ability to produce hydrogen bonds with soil colloids and organic substances.

№1,3,5 diagrams show that the amount sorbated phenol in ordinary of black typical, brown and typical red soils reaches a maximum in the VI variant (when 6.0 mg of phenol is brought in the 1.5 g of soil). In the case of m-cresol (diagrams №2,4,6) the sorbated amount is maximum in case of any soil in VII variant (when 1.5 grams of soil contained to 7.0 mg of m-cresol).

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Further increase in the concentration of substances does not increase their sorbated amount, which means that all centers participating in the process of sorption is saturated. At the same time, the obtained data (diagrams №1,2,3,4,5,6) show that the m-cresol is more bound by the soils than by phenol.

On the basis of the mutual comparison of the isotherms of the adsorption of Phenol and m-cresol we can see that in conditions of the low concentration of the substances in three types of soils, the adsorbed amount of phenol exceeds the amount of m-cresol. This can be explained by the fact that the dissociation of phenol is equal to 1.3. 10-10, and cresol's is even less and equals to 8.1 10-11. Therefore, if a chemical adsorption has a chemical character, then the phenol generates hydrogen bonds easier than m-cresol. With increasing concentrations (V, VI, VII, VIII variants of the experiments) the picture of sorption of these materials change and the adsorbed amount of m-cresol exceeds Phenol's amount. This result can be explained by the fact that in conditions of the low concentrations (when 1.5 mg to 4 mg of phenol and m-cresol was brought in 1,5-1,5 g of soil samples), the sorption is basically of a chemical character. During further increase of the concentration of substances, we think that the chemical sorption centers are being saturated and the subsequent sorption subordinates to the physical mechanism. This opinion can be confirmed after discussing the diagrams N1,2,3,4,5,6. They clearly identify that in conditions of the low concentrations the increase of the sorbated substances can be observed along with the temperature increase. On the last sections of the diagrams the abovementioned regularity is violated, which indicates that the physical sorption exceeds the chemical one.

The results about the sorption should be noted that we obtained in conditions of multiple fertilization of the soil with Phenol and m-cresol. In this regard, we brought certain amount of Phenol and m-cresol in 100-100 g soil samples. We moisture the soils up to 70% and placed them in thermostat in 20^0C conditions. The process was proceeding in the darkness. In order to determine the sorbated substances we took first sample after bringing in the phenolic materials. Then on every 10-th day we added new doses of these substances. The obtained results showed that (table N2) the amounts of sorbatedPhenol and m-cresol again are reduced during bringing in for the second time.

Table №2
The amounts of again sorbated Phenol and m-cresol in black, brown and red soils

№	Soil type	The phenols	The phenols (mg)	Initial value of Sorption (mg)	The amounts of again sorbatedPhenol and m-cresol (mg)			
					X Today	XX Today	XXX Today	XXXX Today
1	Ordinary black soil	phenol m-cresol	2 2	0,51± 0,011 0,47± 0,009	0,44 ± 0,008 0,43 ± 0,01	0,46 ± 0,007 0,44 ± 0,005	0,50 ± 0,009 0,46 ± 0,01	0,53 ± 0,01 0,49 ± 0,008
2	Typical Brown soil	phenol m-cresol	2 2	0,42 ± 0,014 0,32 ± 0,01	0,39 ± 0,011 0,28 ± 0,006	0,38 ± 0,01 0,28 ± 0,005	0,40 ± 0,01 0,30 ± 0,009	0,43 ± 0,0011 0,33 ± 0,0011
3	Typical Red soil	phenol m-cresol	2 2	0,39 ± 0,013 0,30± 0,012	0,33 ± 0,009 0,26 ± 0014	0,37 ± 0,011 0,27 ± 0,012	0,38 ± 0,0012 0,27 ± 0,0014	0,40 ± 0,0014 0,29 ± 0,0013

Then, it increases (during 20, 30, 40 days) gradually and in the end the sorbated amounts exceed their initial values. We believe that in the course of the experiment the cultivation of Phenol depletion microorganisms takes place, therefore, the speed of collapsing phenolic substances the in soils gradually increase.

Based on the results of the research we can make the following conclusions:

1. According to the sorbation of Phenol and m-cresol the soils deploy as following: Ordinary Black soil> typical brown soil > typical red soil:
2. During the sorption of phenol and m-cresol by the ordinary black soil, a typical brown and red soils one can observe the dependence on the PH of the reaction area and on the dissociation quality.
3. There is a direct correlation between the value of sorption and the content of clay minerals in the ordinary black soil, a typical brown and typical red soils;
4. There is a direct correlation between the value of the sorption and the overall amount of humus and the group fractional composition of the ordinary black soil, typical brown and typical red soils.
5. It was found out that the sorption of phenol and m-cresol by the ordinary black, typical brown and typical red soils has a chemical and physical nature. At the same time, in conditions of a low concentration the sorption basically continues in a chemically, and in high concentration conditions the physical sorption exceeds the chemical sorption.

6. It was found out that during multiple fertilization with phenol and m-cresol in the ordinary black, typical brown and typical red soils, during the first 30 days it is less than the initial amounts, while for the 40^{th} day exceeds it.

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