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ADSORPTION AND ELECTROADSORPTION OF TOLUENE ON SOME GRAPHITE/CLAY MATERIALS

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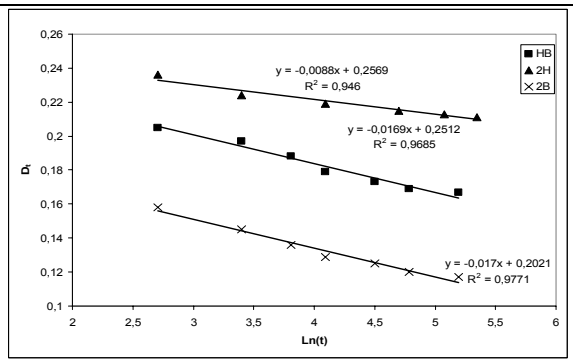
The adsorption of toluene from water/toluene systems on various graphite/clay materials has been investigated using the direct UV-photometry determination of adsorbate concentrations before, during, and after the adsorption. Various theoretical and semi-empirical models have been employed to verify their applicability to the description of adsorption dynamics. It has been found that the adsorption kinetics obeys the Elovich adsorption model and the final adsorption value is in the direct dependence on the graphite content in the adsorbent materials.
No influence of the 1V external voltage application on the adsorption process has been revealed for the water/ toluene/graphite/clay systems.



INTRODUCTION

Carbon and various carbon and non-carbon containing porous materials are used widely in many adsorption technologies, such as removal of organic and inorganic pollutants from liquids and gases,[1-3] extraction of rare and important elements,[4-5] water and wastewater decontamination[6, 7] and many more. As a result, a wide variety of extensive investigations of various adsorption phenomena are carried out by many scientific groups. The development of nanotechnologies has attracted extra interest to this field since carbon nanotubes, nanofibers and other nanomaterials exhibit new interesting and promising properties.[8-11]

In this context, the following directions of investigation of the porous materials adsorption application can be mentioned: extraction of gold from natural samples;[5,12,13] removal of organic pollutants by adsorption on the activated carbon samples;[14, 15] combined disinfection using carbon materials.[16, 17]

Electroadsorption is another interesting direction in the development of porous carbon materials with a wide array of potential applications.[18-21] Within this method, some voltage should be applied to the adsorption cell in order to facilitate better adsorption performance in the system. For instance, a significant increase in the performance of acilian blue removal has been reported for the system where the dye-containing solution was flowing through the reactor equipped with an activated carbon bed with potential difference (about 20 V) applied between the bed edges.[21]

It is well known that various carbon and graphite materials exhibit high efficiency in the organic compounds adsorption while the activity of

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the mineral adsorption substrates (like silica gel) is significantly weaker.

In this context, the aim of this investigation was to evaluate the dependence of the adsorption efficiency on the composition of graphite-containing materials and to discuss possible influence of the potential difference application (electroadsorption) on this process. The latter aim is based on the assumption that various electrochemical reactions running in the adsorption cell under the significant voltage of 20 V may have an effect on the increase in the adsorptive removal efficiency. This effect is likely to be much more influential than the electroadsorption itself, and the increase in the adsorption performance under an external voltage reported in[21] could be, in fact, caused by the interaction between the dye and the products of electrochemical reactions occurring in the cell.

MATERIALS AND EXPERIMENTAL MEHODS

Various graphite-clay mixtures were used as the adsorption substrate in this research. These substrates were developed from the raw material intended for the pencil rod production. It is known that some amounts of natural graphite and mineral alumo-silicate clay are present in these materials in such a way that the hardness grade of commercial pencils can be related to the ratio between the graphite and mineral components content (see Table 1).[22]

Therefore, this material can be considered suitable for the investigation of the influence the graphite composition content has on its adsorption activity. Three types of graphite composites with different hardness were selected in this research: 2H, HB and 2B. Their graphite/clay ratios can be found in the Table 1.

Water/toluene compositions were produced by mixing some amounts of toluene directly with water. To reach saturation, each mixture was then kept for 24 hours. After that, its optical density was measured using the LOMO SF-46 photometer against distilled water as a reference. All optical densities were measured on the wave length of 258 nm, which corresponds to the analytical peak of toluene absorbance.[23, 24] The initial absorbance was taken as zero value, and then some amount of the graphite material was added to the system. The concentration of toluene in the system was changing due to its adsorption by the graphite material, which causes some changes in the solution's optical density. Temporal changes in absorbance values were measured after certain periods of time, and the final absorbance was measured in 24 hours. All the mixtures were kept at 20 °C in inert plastic cells.

Electroadsorption experiments were carried out in a similar way, but the graphite/clay samples were fixed in the container's cover and then the potentials difference of 1 V was applied between the samples. This voltage is below the threshold of the electrolytic decomposition of water (ca 1.8 V) and, therefore, any influence of electrolysis does not make any effect on the process of toluene adsorption and/or changes in its concentration. On the other hand, in case of any direct influence of the voltage application on the adsorption, its effect will be seen through the deviation in the adsorption values for similar systems and conditions with and without an external voltage.

It should also be noted that the absorbance values are in linear dependence on toluene concentration and, since only relative changes and not absolute values of the concentrations are considered, the absorbance values can be used instead of real concentrations. According to this method, the initial absorbance of a sample is taken as a reference point and then all the following absorbance values should be normalized by the initial one. After that, the decrease in the absorbance divided by its initial value corresponds to the decrease in the optically active substance concentration. For instance, if the initial absorbance is 0.280 and the 30 minute absorbance is 0.2, the decrease in the toluene concentration can be calculated as (0.28 - 0.2) / 0.2 = 0.286 or 28.6 %.

RESULTS AND DISCUSSION

1. Simple adsorption

The results of the investigation of temporal changes in optical density for the samples containing various graphite compositions are shown in Table 2, while the final absorbance values (measured after 24 hours) are represented in Table 3. As stated above, for the reason of simplification, all the absorbance values are normalized by the corresponding initial value taken as 100 %. The values in Table 3 can be considered as the equilibrium adsorption since the process reaches its equilibrium state in 24 hours. All the data in Tables 2, 3 were obtained as averaged values of a series of 6 parallel experiments with a relative error value below 10 %.

Table 1

The ratio between the graphite and mineral clay parts in commercial pencil graphite rods

Commercial hardness grade	Ratio between carbon and SiO_2 (% / %)
6B	84/16
5B	81/19
4B	78/22
3B	75/25
2B	72/28
B	69/31
HB	66/34

Table 1 (continued)

H	63/37
2H	60/40
3H	57/43
4H	54/46
5H	52/48

Table 2

Temporal changes in the absorbance of various water/toluene mixtures and graphite/clay compositions

Graphite/clay grade	Adsorption time, min	Absorbance	Normalized absorbance, %
2H	0	0.262	100.00
	15	0.236	90.08
	30	0.224	85.50
	60	0.219	83.59
	110	0.215	82.06
	160	0.213	81.30
	210	0.211	80.53
HB	0	0.212	100.00
	15	0.205	96.70
	30	0.197	92.92
	45	0.188	88.68
	60	0.179	84.43
	90	0.173	81.60
	120	0.169	79.72
	180	0.167	78.77
2B	0	0.16	100.00
	15	0.158	98.75
	30	0.14	87.50
	45	0.137	85.63
	60	0.129	80.63
	90	0.125	78.13
	120	0.12	75.00
	180	0.117	74.05

Table 3

The final absorbance values for different graphite/clay compositions (measured after 24 hours)

Graphite/clay grade	Initial absorbance	Final absorbance	Normalized final absorbance, %
2H	0.262	0.184	70.23
HB	0.212	0.146	68.9
2B	0.160	0.11	68.7

As seen in Table 2 and 3, the harder material with lower graphite content exhibits lower toluene adsorption. The adsorption dynamics and the final adsorption values of the 2H material are lower than those for the 2B material. This result corresponds to the assumption that graphite, not the mineral part, has the leading role, in determining the adsorption characteristics of the material.

It was also important to check if the Elovich equation can be applied for an adequate description of the adsorption processes similarly to how it was checked for the pure activated carbon adsorbent and water/toluene systems.[24]

Since this equation can be represented by $c_t = \left(\frac{1}{b}\right)\ln(ab) + \left(\frac{1}{b}\right)\ln t$, where c_t is the adsorbate concentration, t – time, a, b – empirical constants, we can verify its applicability by substituting concentrations with the normalized absorbance (D_t) and building the diagrams in the coordinates D_t vs $ln(t)$. The closer the pattern of the experimental dependencies is to the linear, the better is the applicability of the Elovich equation for the description of adsorption in experimental systems.

2. Electroadsorption

The results of a comparative study of influence of the potentials difference on the adsorption of toluene on various graphite/clay materials are shown in Table 4 and 5.

The Elovich equation is still applicable for the description of this kind of electroadsorption as it is

seen in the good agreement between the experimental points and the linear trends (Fig. 2).

As seen in Fig. 1, all three samples show the pattern that is very close to the linear, and the pair correlation coefficients are higher than 0.94 for all the samples.

As seen in the comparison between Tables 2 and 4, 3 and 5, no significant changes were registered in the systems with and without an external voltage applied. The dynamics of the adsorption, the final adsorption values for both types of the systems are quite close and lie within the experimental errors range. Moreover, the angle coefficients of the trend equations for the systems without an external voltage lie within the 0.0088-0.017 range, and for the system with an external voltage within the 0.0066-0.0143 range. Since the experimental error was under 10 %, the difference between these two ranges can not be considered as relevant. Besides, the final adsorption values for the systems with and without an external voltage (Tables 3 and 5) are very close.

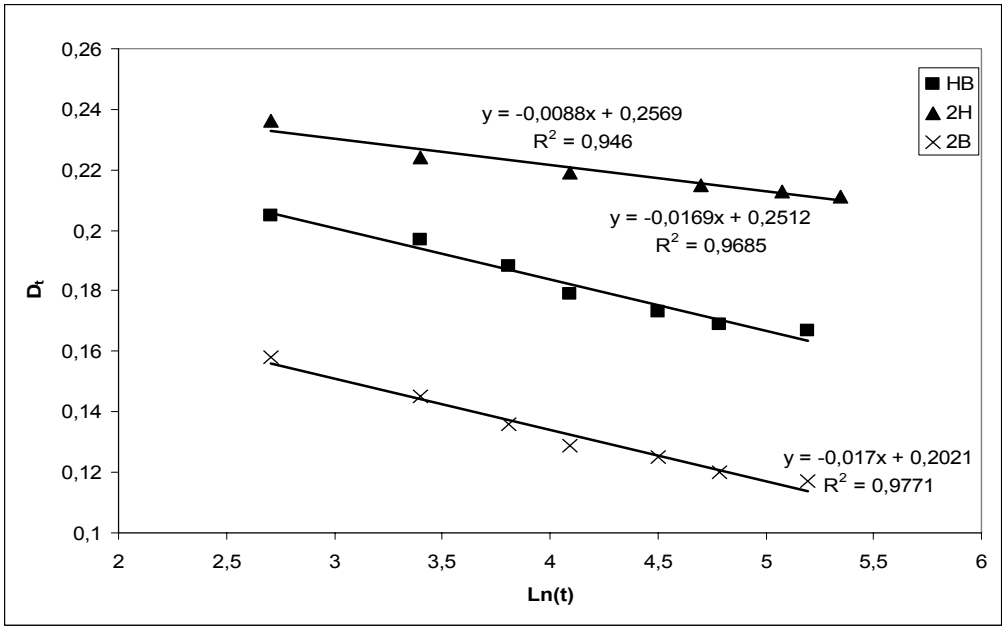

Fig. 1 – The verification of the Elovich equation applicability for the adsorption of toluene on various graphite/clay materials. The linear trends equations and the pair correlation coefficients are shown next to the corresponding dependencies.

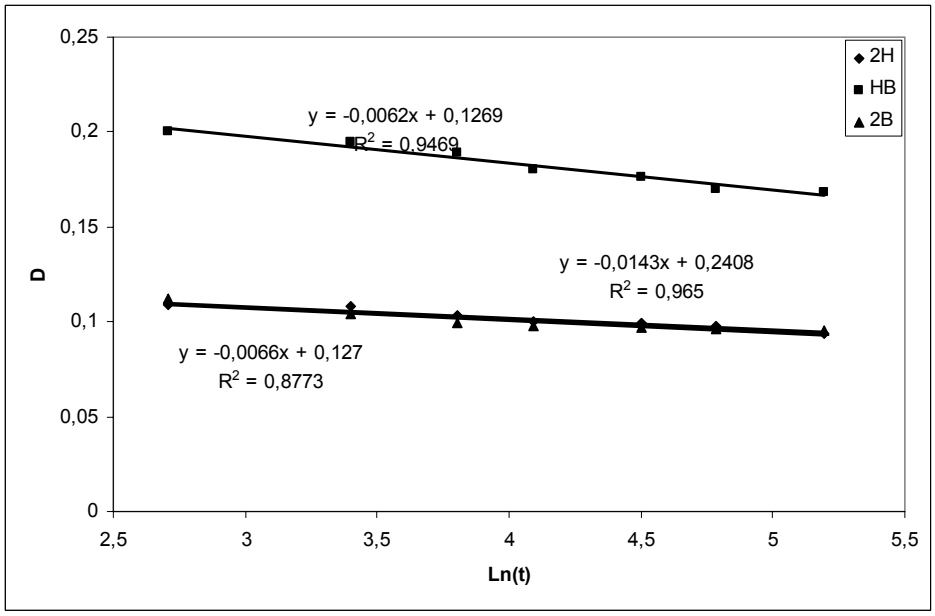

Fig. 2 – The verification of the Elovich equation applicability for the adsorption of toluene on various graphite/clay materials under external voltage 1 V.

Table 4

Temporal changes in the absorbance of various water/toluene mixtures and graphite/clay compositions under an external potentials difference of 1V

Graphite/clay grade	Adsorption time, min	Absorbance	Normalized absorbance, %
2H	0	0.11	100.00
	15	0.109	99.09
	30	0.108	98.18
	45	0.103	93.64
	60	0.1	90.91
	90	0.099	90.00
	120	0.098	89.09
	180	0.094	85.45
HB	0	0.204	100.00
	15	0.2	98.04
	30	0.195	95.59
	60	0.189	92.65
	110	0.18	88.24
	160	0.176	86.27
	210	0.17	83.33
2B	0	0.128	100.00
	15	0.112	87.50
	30	0.104	81.25
	45	0.099	77.34
	60	0.098	76.56
	90	0.097	75.78
	120	0.096	75.00
	180	0.095	74.22

Table 5

The final absorbance values for different graphite/clay compositions (measured after 24 hours) under an external potentials difference of 1V

Graphite/clay grade	Initial absorbance	Final absorbance	Normalized final absorbance, %
2H	0.11	0.080	72.7
HB	0.204	0.138	67.7
2B	0.128	0.11	65.6

Therefore, our results prove that no significant changes can be found for systems containing a water/toluene mixture and a graphite/clay adsorbent with and without external voltage application. In our opinion, the significant rise in the adsorption value after the application of 20 V reported in[21] can be caused by the electrodecomposition of the dye, the influence of oxygen and hydrogen released in the course of water electrolysis.

No significant influence of the application of the potentials difference (1 V) on the process of adsorption was revealed. Both the adsorption dynamics and the final adsorption values remain similar to those for the systems without the external voltage application. The previously reported adsorption intensification under an external voltage can in fact be caused by the effects of the water electrolysis products facilitating additional decomposition of the adsorbate in the system.

CONCLUSION

Graphite/clay materials exhibit adsorption activity in water/toluene systems, and the value of this activity is determined by the graphite content. However, the regularities of the adsorption interaction in the above system obey the Elovich equation for all the compositions involved in this investigation.

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