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INVESTIGATION ON APPLYING NATURAL SORBENTS FOR DECOLOURISATION OF DYE SOLUTIONS

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ABSTRACT

The present work investigates the adsorption properties of the Grus material, of bentonite "Zelenika" and their heat-treated forms towards 12 direct and 15 acid dyes. Based on the results obtained, it was concluded that the Grus material manifests better adsorption properties. The types of isotherms describing the adsorption process for the different types of dye have been established.

Keywords: Grus material, bentonite, direct dyes, acid dyes, adsorption.

INTRODUCTION

Dyes are one of the main pollutants of wastewaters from textile finishing and coloration processes. These waters need to pass through several stages of complex purification, which requires special installations and equipment. One of the stages involves the use of different types of sorbents, most often activated carbon [1-6]. However, an increased use is observed of alternative natural and artificial sorbents of non-carbon composition, such as clay, zeolite, natural bentonite and some others [7-12] in the process of treatment of wastewaters from textile processing. The use of these sorbents is justified by their high adsorption capacity, selectivity, the cation exchanging properties of some of them as well as their generally low cost. The goal of the present work is to investigate the adsorption properties of the Grus material and the bentonite "Zelenika", which are sorbents of natural origin, as well as their heat-treated forms towards water solutions of direct and acid dyes, which are generally used for coloring and printing of cellulosic, and woolen and polyamide textile material.

The Grus material has a polymineral composition. It is a calcium-alkaline formation from the mountain of Stara Planina in Bulgaria obtained as a result of weather processes. By the means of Rö analysis it is established that the material contains the primary minerals quartz, feldspat, and amphibole, and the secondary minerals clay, mica, and chlorides [13].

The formation of the bentonite is most often explained as the result of a secondary transformation of a site of volcanic ashes. It has increased plasticity compared to other clays formed under similar conditions. The main component of bentonite is montmorillonite. It is characterized by a very high cation capacity – 80-150 mgequ/100 g. It also has the capability to adsorb large quantities of water and swell.

EXPERIMENTAL

The following four natural sorbents were used in the experiment: Grus material (I), a heat-treated form of the Grus material (II) bentonite "Zelenika" (III) and a heat-treated form of the bentonite "Zelenika" (IV).

The Grus material and the bentonite "Zelenika" have been heat-treated at 80°C for 24 hours. All four sorbents are in the form of particles with diameter < 0.5 mm, that have been isolated after a grain-size analysis.

The experiments were carried with 0.1 g of sorbent in 50 ml of water dye solutions with concentration as follows: 10.10^{-3} g l^{-1}, 5.10^{-3} g l^{-1}, $2,5.10^{-3}$ g l^{-1} and $1,25.10^{-3}$ g l^{-1}. The adsorption equilibrium has been reached at T = 25°C for one week. 12 direct and 15 acid dyes have been investigated. The quantity of the adsorbed dye is determined via spectrophotometer with Spekol 11. First the values of the luminous adsorption of the dye solutions have been established. Based on the results and using previously calculated standard straight curves, the quantity of the adsorbed dye has been found.

The quantity of adsorbed dye from 1 g adsorbent (Γ) is calculated by the equation:

$$\Gamma = (C_o - C_e)V/A, \text{ g } g_{ads}^{-1} \quad (1)$$

where: C_o – initial dye concentration in the solution, g l^{-1}

C_e – equilibrium concentration, g l^{-1}

A – mass of the adsorbent, g

V – operating volume, l

The relative quantity of the adsorbed dye (C') towards C_o is calculated according to:

$$C' = (C_o - C_e)100/ C_o \text{ , \%} \quad (2)$$

RESULTS AND DISCUSSION

As expected, for all sorbents and for both types of dye, the common trend is that the quantity of the adsorbed dye increases with the augmentation of the initial concentration of the dying solution. Under the same conditions the relative quantity of the adsorbed dye decreases. The results are illustrated in Tables 1 and 2.

Tables 3 and 4 represent the values of adsorptive capacity when the concentration of the dying solution is of 10.10^{-3} g l^{-1}. The results from the experiment show that for 9 (75 %) out of 12 investigated direct dyes (Table 3), the desired effect is observed, when sorbents I and III are used (Grus material and bentonite "Zelenika"). The heat-treated sorbents (II and IV) are effective for 5 of the dyes, i.e. about 42 %. There is a trend showing that the quantity of the adsorbed direct dye by the Grus material is higher than that adsorbed by the bentonite. The adsorption capacity of the heat-treated Grus material (II) is higher than that of the non-treated. This can not be said for the heat-treated bentonite "Zelenika" for which the values of Γ are lower than that of the non-treated. The quantity of the adsorbed dye by IV is lower than that adsorbed by II, i.e. the trend to obtain higher values of Γ from the Grus material compared to the bentonite "Zelenika" is maintained after heat treatment as well.

The results for the 15 analyzed acid dyes (Table 4) show that the Grus material is effective for 11 of them (73 %), while the bentonite – for 9 (60 %). Heat-treated sorbents act positively on smaller number of dyes – this number is 8 (54 %) for sorbent II and 6 (40 %) for sorbent IV. It is observed that for certain acid dyes such as Acid chrome Black TDS, Nylon fast Yellow GR, Nylon fast Red MPG and Nylon fast Red S2B the bentonite shows better adsorption capabilities than the Grus material. However, the adsorption capabilities of the Grus material increase after heat treatment. For some acid dyes, the same trend is observed for the bentonite "Zelenika" as well.

For both the direct and acid dyes the quantity of the adsorbed dye varies in wide limits, regardless of the type of the sorbent. These results can be explained with the different chemical composition of the dyes which is a corporate secret of the producers and is therefore unknown.

The better adsorption abilities of the heat-treated Grus material compared to that of the non-treated is most probably due to the increased sponginess of the Grus material after the treatment and therefore its enlarged adsorption surface. As for the heat-treated bentonite, it probably loses some of its swelling abilities after the treatment which influences negatively its adsorption capabilities and they decrease.

Table 1. Data for the system, Direct Dark Green B/bentonite "Zelenika".

No	$C_o.10^3$,g l^{-1}	$C_e.10^3$,g l^{-1}	C', %	$\Gamma.10^3$,g/g_{ads}
1.	10.00	5.40	46.0	2.30
2.	4.90	3.15	35.7	0.87
3.	2.80	2.10	25.0	0.35
4.	1.25	0.65	4.8	0.30

Table 2. Data for the system, Acid Chrome Black TDS/heat-treated Grus material.

No	$C_o.10^3$,g l^{-1}	$C_e.10^3$,g l^{-1}	C', %	$\Gamma.10^3$,g/g_{ads}
1.	10.00	3.65	63.5	3.17
2.	5.10	2.25	55.8	1.42
3.	2.50	1.95	22.0	0.27
4.	1.65	1.48	10.00	0.08

Table 3. Comparison of the adsorption capacity of the studied direct dyes.

No	Direct Dyes	$\Gamma.10^3$, g.g_{ads}^{-1}			
		Adsorbents			
		I	II	III	IV
1.	Direct Yellow TG 130%	0.00	0.00	0.32	0.36
2.	Direct Bordeaux B	0.89	1.26	0.37	0.32
3.	Direct Dark Green B	1.19	1.86	2.30	1.20
4.	Direct brill. Blue B	7.00	0.00	0.40	0.00
5.	Direct Black VSF 600	0.73	0.00	0.42	0.00
6.	Direct Yellow 11	0.17	0.00	0.00	0.00
7.	Direct Black 22	0.00	0.50	0.00	0.00
8.	Priamoi geltii K 200%	0.00	0.00	0.95	0.00
9.	Priamoi krasnii 2C 170%	0.18	0.68	0.00	0.00
10.	Priamoi fioletovii C 200%	0.50	0.42	0.52	0.35
11.	Priamoi sinii 125%	0.46	0.00	0.18	0.00
12.	Priamoi tshernii 2C 275%	0.93	0.00	0.68	0.24

Table 4. Comparison of the adsorption capacity of the studied acid dyes.

No	Acid Dyes	$\Gamma.10^3$, g.g_{ads}^{-1}			
		Adsorbents			
		I	II	III	IV
1.	Acid Yellowbrown EL	0.00	0.00	0.00	0.00
2.	Acid Orange II	0.00	0.00	0.00	0.00
3.	Acid brill. Scarlet 3R	0.17	0.00	0.00	0.00
4.	Acid Chrome Black TDS	0.30	3.15	1.10	1.49
5.	Acid Black GLF conc.	0.00	0.63	0.32	0.76
6.	Acid Black GRL	0.00	2.10	0.47	0.49
7.	Acid fast Black SB 200%	0.37	1.04	0.00	1.44
8.	Nylon fast Yellow L-PRL	0.32	0.00	0.25	0.00
9.	Nylon fast Yellow GR	0.14	0.00	0.40	0.00
10.	Nylon fast Red S2B	0.87	1.45	1.30	1.20
11.	Nylon fast Red MPG	0.22	2.21	1.80	1.39
12.	Nylon fast Violet R	0.24	0.67	0.00	0.00
13.	Acid Yellow G	0.51	0.00	0.00	0.00
14.	Acid Orange II	0.23	0.00	0.17	0.00
15.	Acid Black 1	1.39	0.40	0.25	0.00

To clarify the trends, an investigation was carried of the adsorption equilibrium of the system "dye solution – sorbent". The Freundlich and BET models have been used for the description of the equilibrium. This investigation established the type of the adsorbent isotherms describing the equilibrium. For the Grus material and its heat-treated form it is the isotherm of Freundlich, while for the two forms of bentonite – the isotherm of BET. The experimental isotherms of the Grus material are illustrated on Fig. 1 and Fig. 2, and those of the heat treated Grus material – on Fig. 3 and Fig. 4. The data on Fig. 2 and Fig. 4 confirm the validity of the isotherm of Freundlich.

$$\Gamma = kC_e^n, \qquad (3)$$

where: Γ – the quantity adsorbed by an adsorption unit; C_e- equilibrium concentration of the adsorbed substance; k and n – empirical constants.

The presented results show that unlike the Grus material and its heat-treated form, the adsorption of the bentonite "Zelenika" is polymolecular. Regardless

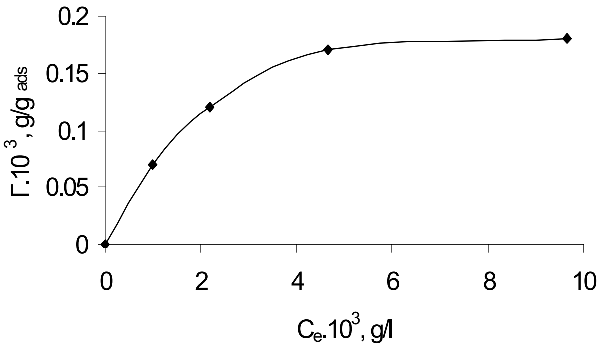

Fig. 1. Dependence of the quantity of adsorbed dye from the equilibrium concentration (Grus material, Priamoi krasnii 2C 170 %).

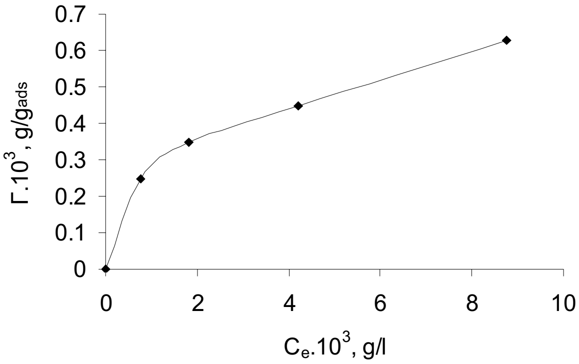

Fig. 2. Dependence of the quantity of adsorbed dye from the equilibrium concentration (heat-treated Grus material, Acid Black GLF conc.).

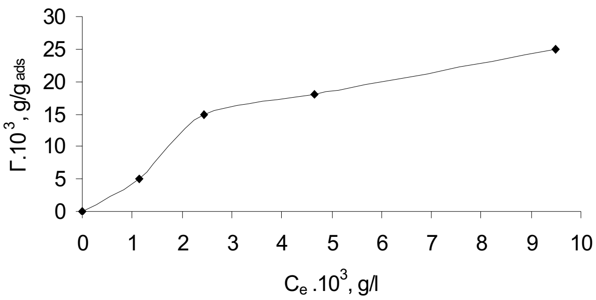

Fig. 3 Dependence of the quantity of adsorbed dye from the equilibrium concentration (bentonite “Zelenika”, Nylon Fast Yellow L-RPL)

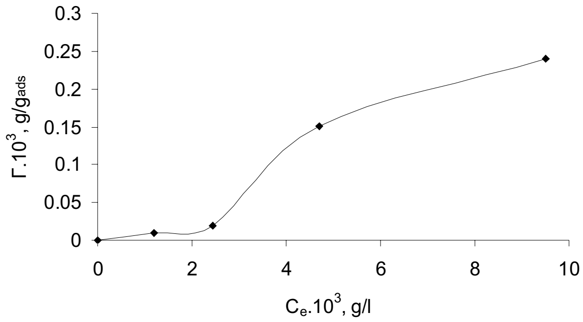

Fig. 4. Dependence of the quantity of adsorbed dye from the equilibrium concentration (heat-treated bentonite “Zelenika”, Priamoi tshernii 2C 275 %).

of this fact, its adsorption ability towards the investigated dyes is lower than that of the Grus material.

CONCLUSIONS

The present work studied the adsorption abilities of the Grus material and bentonite “Zelenika” as well as their heat-treated forms towards 12 direct and 15 acid dyes.

It was established that in considerable number of cases the sorbents manifest adsorption abilities. These abilities are higher for Grus material.

Heat treatment influences positively the adsorption abilities of the Grus material.

It was also established that the adsorption equilibrium in the system “Grus material – dye solution” is described by the isotherm of Freundlich, while the equilibrium in the system “bentonite “Zelenika” – dye solution” is described by the isotherm of BET.

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