

Kinetics of reactive dyes adsorption on the bottom ashes

The aim of this paper is to present the adsorption kinetics of a typical textile reactive dye on the bottom waste ash, which can lead to valuable data related to the possibility of wider application, for example with purification of the dyed waste waters. Sorption kinetics, which describes the rate of adsorption of pollutants (dye), is one of the most important characteristic that defines the efficiency of sorption and the ability to use the adsorbent in controlling water pollution. In order to investigate the mechanism of adsorption of reactive dyes from the textile industry on the bottom ashes from city heating station by coal combustion, some characteristic constants of sorption are determined using Lagergren's equation for the pseudo-first and pseudo-second order. United, kinetic models of pseudo-first order and pseudo-second order can provide a simple but satisfactory explanation of the adsorption process for a reactive dye.

Key words: adsorption, ashes, kinetics, Lagergren's equation, reactive dye.

1. INTRODUCTION

Dye adsorption on the solid adsorbent, and consequently the process of decolorization is mainly related to the purification processes of wastewater, mainly of textile or some other industry. Residual dye is an important factor when it comes to security of wastewater before its discharge into waterways. Besides the aesthetic problem, the biggest concern regarding the dyes is their absorption and reflection of sunlight and therefore the disruption of photosynthesis of aquatic plants, which affects a significant increase in bacteria to the levels of insufficient biological degradation of contaminants in water, resulting in disruption of ecological balance.

Among the many techniques for removing dyes, adsorption process works best as it can be used to remove different types of dyeable materials. Most commercial systems use activated carbon as a sorbent for dye removal from wastewater, because of its excellent adsorption capability. Although the active carbon is given the priority as of the preferred sorbent, its widespread use is limited due to high prices.

Several researchers have suggested many unusual and low-cost adsorbents, including natural minerals, biosorbents and waste materials from industry and agriculture. These materials could be used as adsorbents for the removal of dyes from aqueous solution: a clay materials (bentonite, kaolinite), zeolite, silica materials (silicon granules, alunite, perlite), agricultural waste (biomass sugar cane, corn cob, rice husk,

coconut shell walnuts) industrial waste products (waste cement slurry, sludge metal hydroxide), biosorbents (chitosan, shake, and biomass) and others (starch, cyclodextrin, cotton) [1-5].

It is known that the adsorption from solution to solid surface begins to occur when the dipoles or charged types of adsorbents and adsorbates interact with each other. In addition, an exchange of anions and cations occurs when the neutral molecules get close enough to each other. So, in a similar way occur an interaction between dissolved organic compounds - dyes, solvent molecules - water and the surface of adsorbent - ash.

Since the introduction of the water-soluble dyes (e.g. reactive dyes), which are now widely used in industry, conventional biological treatment is not enough to achieve adequate removal of dye. Other common methods, such as physical coagulation - flocculation proved failure to eliminate today's most applicable reactive dyes.

The aim of this paper is to present the adsorption kinetics of a typical reactive dye on the bottom ash, which can lead to valuable data related to the possibility of wider application, for example with purification of the dyed waste waters. Sorption kinetics, which describes the rate of absorption of pollutants (dye), is one of the most important characteristic that defines the efficiency of sorption and the ability to use the adsorbent in controlling water pollution. Hence, the kinetics of removal of reactive dye was performed in order to understand the adsorption behavior of the adsorbent with respect to concentration and temperature.

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2. MATERIALS AND METHODS

As an adsorbent was used bottom ash from local city heating station attained by combustion of brown coal. After collecting and drying, sieving to the particle size of 0.5 mm is done. Crude ash was abundantly rinsed with distilled water, dried in the air, again sifted and used in the experiment.

In the process of adsorption was used reactive dye C.I. Reactive Blue 49 (hereafter in the text RB). The applied dye has in the structure a three sulphonated groups, which easily ionize in aqueous solution. One can say that we deal with an ionized compound, ie. it is an anionised dye.

Adsorption test was performed in a glass Erlenmeyer flask in which the adsorbent is suspended in the solution dye - adsorbate. Erlenmeyer flasks are placed on the shaker - shaker with 120 rpm at a certain temperature and kept in a specified time. Varied was the amount of ash in the amount of 1 to 4 g, while the solution in a constant volume of 100 cm³, contained concentrations of dye, 10, 30, 50, 70 and 100 mg/dm³. Processing time, with constant stirring, was 5, 10, 20, 30, 45 and 60 min.

Mentioned dye concentration were taken from the reason that generally correspond to residual amounts of dye in the solution after the dyeing of wool textiles. Practically, in the experiment was used correspond-concentration of pure dye with no add-ons that typically go with dyeing. It was found that equilibrium adsorption time on the ashes of dye was achieved in 60 min, the extension of time of treatment did not significantly alter adsorption.

Upon completion of adsorption, the dissolved dye and ash are passed through a filter paper. The following is the determination of absorption solution on the spectrophotometer UV-VIS spectrophotometer (Cary 100 Conc UV-vis, Varian) at 575 nm. Reproducibility of data varied in the range of $\pm 1.8\%$.

SEM measurements were conducted on the device *VEGA TS 5130mm (TESCAN)* using a detector for secondary electrons. Ash used is relatively fine-bulk materials with heterogeneous particles of widespread shapes and forms that come from agglomerates of individual minerals, in general, less than 5 μm size.

SEM study (Fig. 1) of used bottom ash samples showed the appearance of particles, mostly incorrect - a characteristic oblong shape with surface macro-porosity materials.

Ash used is relatively fine-dispersed material presented heterogeneous particles of widespread shapes and forms that come from agglomerates of individual minerals. Left micrograph in Figure 1 gives a view with 1000x magnification.

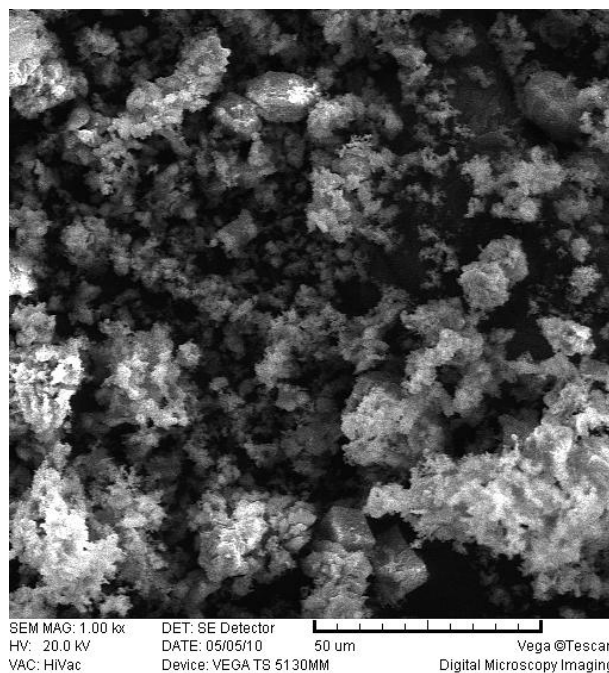


Figure 1 - Micrographs of the applied ash - adsorbent (1000x)

Diffraction measurements were performed on the *Bruker D8 Advance* diffractometer in θ/θ "scan-step" mode in the range of diffraction angles 2θ of 10° to 90° in steps of 0.05° and a total exposure of 5 s per step. On the diffractogram obtained using the *EVA software package v.9.0* into which is incorporated crystallographic database PDF-2, phase identification of adsorbent was carried out, made semi-quantitative phase analysis and the results of this analysis are shown in Figure 2.

Bands X-ray spectrum of the adsorbent, Fig. 2, reveal the presence of minerals, mainly dominated by calcite and quartz, and finally with a share below 10 % coming potassium calcium carbonate, fairchildite, butschlite, corundum, hematite, magnetite and wuestite.

From the point mineralogy, heating plant ash is essentially composed of three types of components: crystalline minerals (quartz, mullite, spinel ...), unburned carbon particles, and non-crystalline aluminosilicate glass. Data from various sources [1-3], including optical and electron microscopy, X-ray diffraction and geochemical data indicate that, while the crystalline fragments and crystal aggregates are abundant in one but not in the other ashes, and that different types of particles of unburned carbon may also be an important ingredient, while the glass is usually the dominant component is present in most samples of ash. Because of its abundance, but also of the disorder involved with the particle nature, the glass is usually considered a major component that could be included in the chemical reactions associated

with the use of ash plant, for example, in the production of cement in the concrete industry and the production of zeolites. In addition, the glass in the ashes has the ability to adsorb elements in traces

within the ash, some of which may be released into the environment, for example with leaching processes - extraction.

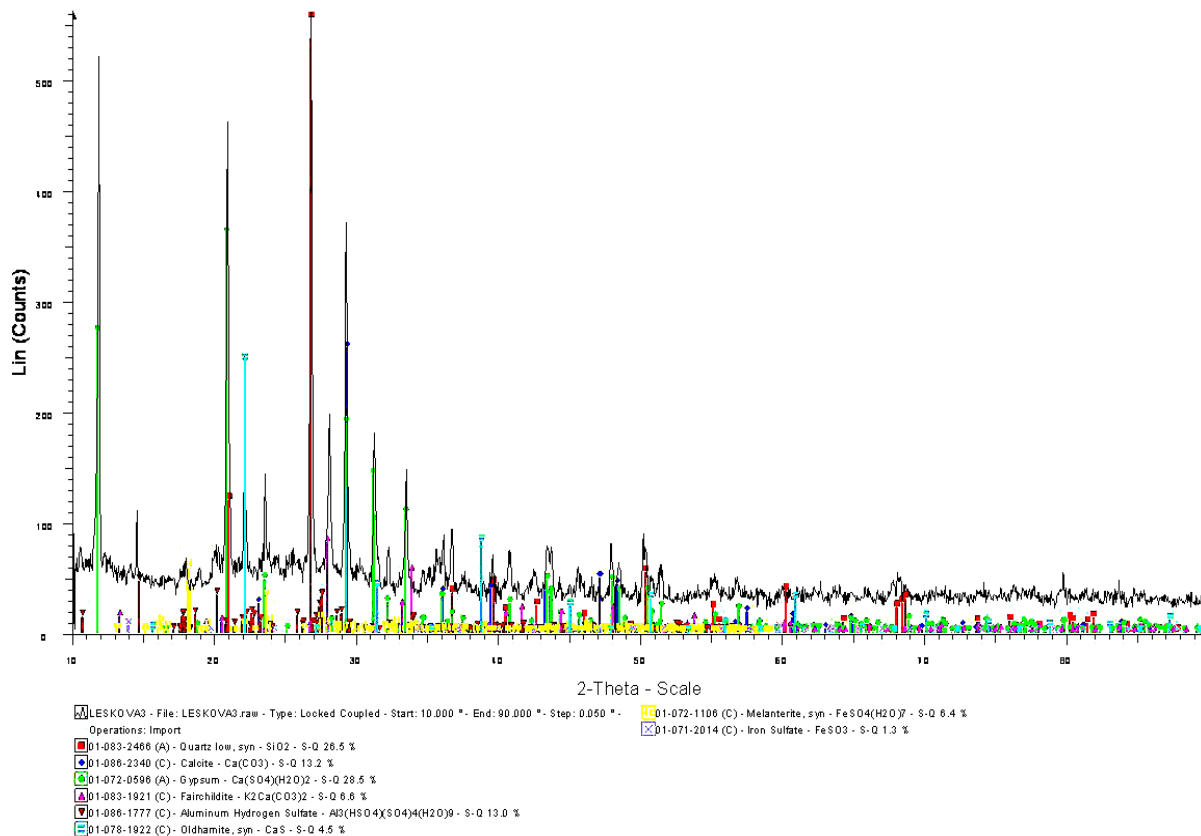


Figure 2 - X-ray diffractogram of the applied adsorbent

Also, the studies suggest that this is a waste material that by annealing at 450^oC and 1000^oC loses about 14, that is, 36 % of its mass, that 1 cm³ has a mass of 2.35 g to 1 g of an area of 8120 cm². The average particle size (based on average values of 100 microscopic measurements) is 2.7 μm.

Particle size may affect the amount of adsorbed dyes, as well as the sorption kinetics [6]. Outer surface of the particles increases with decreasing particle size, ie. surface mass transfer coefficient can be correlated with the mean particle size. However, in the literature can be found conflicting results regarding the effect of particle size on mass transfer during the sorption process. Basically, the more pronounced effects of particle size can be expected at relatively low concentrations of adsorbate and high doses of adsorbent [7].

Adsorption kinetic data were described using Lagergren's model of pseudo-first order, which is the earliest-known equations that describe the rate of adsorption based on adsorption capacity.

Lagergren's equation is usually expressed as follows [8]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where: q_e and q_t - adsorption capacity at equilibrium and after time t , respectively (mg/g), k_1 - adsorption rate constant of pseudo-first order (1/min).

By integrating equation (1) for the boundary conditions $t = 0$ to $t = t$ $q_t = 0$ to $q_t = q_t$ is obtained:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2,303}t \quad (2)$$

Equation (2) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2,303}t \quad (3)$$

Graph of $\log(q_e - q_t)$ towards t gives a linear dependence from which can be determined k_1 and q_e from the slope and intercept, respectively. If the intercept is not equal to q_e reaction time is probably not a first order reaction, although this graph has high correlation with experimental data. The change in speed should be proportional to the first level of concentration with a strictly surfaced adsorption. However, the relationship between initial concentration of adsorbate and the adsorption rate will be linear when pore diffusion limits the adsorption process.

Adsorption kinetics can be described by the model of pseudo-second order, which is usually given as follows [9]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

where: k_2 - rate constant of second order adsorption (g/mg·min), q_e and q_t - adsorption capacity at equilibrium and after time t , respectively (mg/g).

By integrating equation (4) for the boundary conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$, and linearization rearrangement we obtain:

$$\left(\frac{t}{q_t} \right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (5)$$

Graphics t/q_t to t gives a straight line for all the dye concentration, which confirms the applicability of equations of pseudo-second order. The values of k_2 and the equilibrium adsorption capacity of q_e were calculated from the intercept and slope of the curve t/q_t to t , respectively.

3. RESULTS AND DISCUSSION

The molecules of dye are linked (adsorb) to the adsorbent at a certain speed (depending on several factors) until it is reestablished the equilibrium between the dye concentration on adsorbent - ash and the dye concentration in solution. What follows is diffusing of dye molecules from the surface to the interior of the adsorbent while at the same time comes to their connection. Connections made are different and are characterized by a system of dyes - ash [6].

When the adsorbent finds itself in the solution with a dye, kinetically speaking, of interest are the following three stages in the system:

- diffusion of dye molecules in solution towards the surface of adsorbent,
- adsorption of dye molecules on the surface of an adsorbent,

- diffusion of dye molecules from the surface of a dye towards the interior of the adsorbent.

These phenomena are different and depend on the characteristics of the system. Their explanation requires knowledge of not only the nature of adsorbent and diffusion characteristics but also the structural and physical condition of the substrate - ash and other characteristics: affinity, diffusions distribution and nature of links between dye and substrate.

In the first phase of the transition of dye from the solution to the surface of adsorbent, adsorption rate depends on the degree of movement of dye solution. It reaches a maximum value during the energetic interference due to the existence of a barrier that opposes the diffusion of dye. With increasing solution flow rate, thickness of the boundary layer decreases and proportionate speed of the transition increases. The closing balance is achieved when the dye speed of transition becomes independent of further increase in speed of flow. When this condition is satisfied, the rate of adsorption is primarily determined by the speed with which dye can penetrate into the adsorbent interior.

The third process is characterized by intertwining of adsorbent with dye solution. Dye diffuses through the porous structure of ash and even more times depending on the share of force attachment exhibited by adsorbent. If this is considered a process of diffusion with simultaneous adsorption, penetration speed of dye is then defined not only, as the range in which the dye is adsorbed, but the resistance of structure of the adsorbent according to the movement of dye, as well.

In relation to the kinetic studies, several models can be used to verify the mechanism of adsorption of dissolved substances on the adsorbent. In order to investigate the adsorption mechanism, the characteristic constants were determined using Lagergen's equations of pseudo-first order based on the capacity of solid bodies with the assumption that the adsorption mechanism is the diffusion, controlled by equation of pseudo-second order based on the adsorption of solid phase with the assumption that the degree of limitations may be due to chemisorptions which includes valence forces through the sharing or exchange of electrons between adsorbent and adsorbate [6].

On Figures 3 and 4 are shown the diagrams with results that are related to the kinetics of sorption of RB dyes on the ashes for the applied amount of adsorbents and different dye concentration. According to the linear model forms of pseudo-first order and pseudo-second order, it can be concluded that the rate of sorption, when the experimental conditions are

given, is fully functionally described with the model of the second order.

Models of pseudo-first order from diagrams in Figure 3 do not show good results for the entire period of sorption, unlike the pseudo-second order, which

provide functional straight line for the dye concentration, as shown in Figure 4, which confirms its applicability (model pseudo-second order). Relations for the mass of the ashes of 3 and 4 g are not shown because no significant variation in the form of curves.

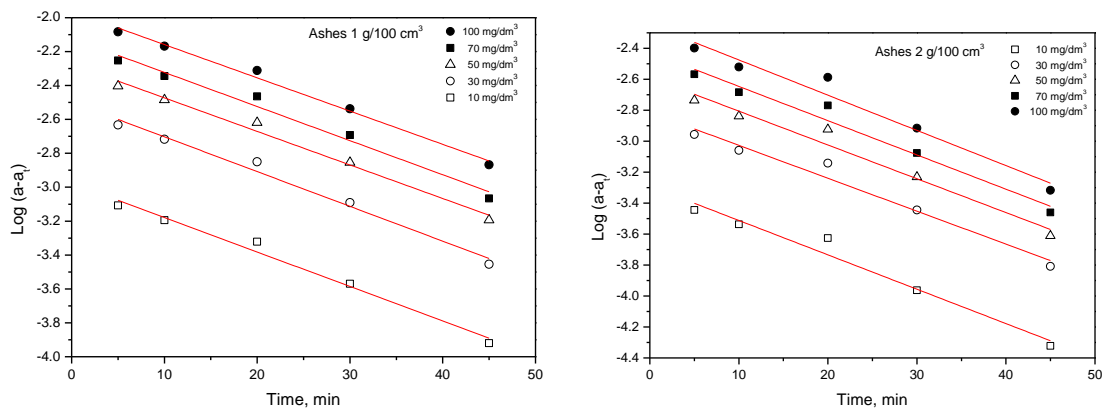


Figure 3 - Sorption kinetics of RB dye (pseudo-first order) for different dye concentration at 20°C

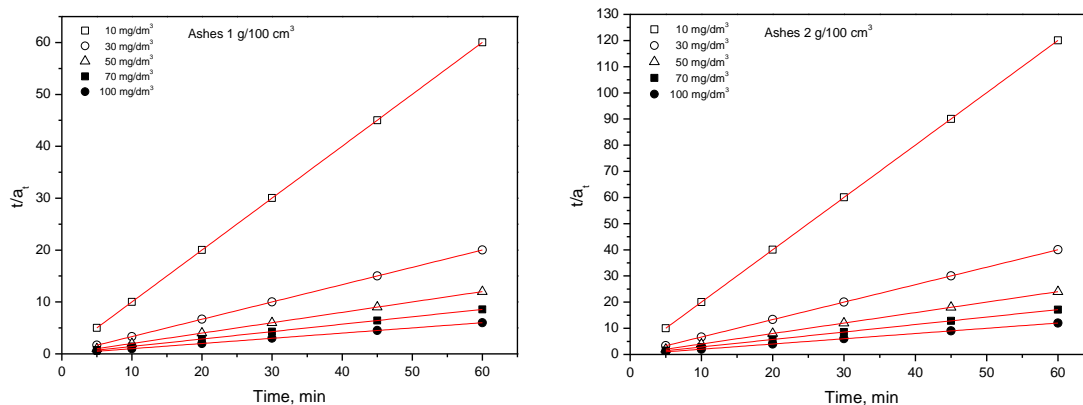


Figure 4 - Sorption kinetics of RB dye (pseudo-second row) for different dye concentration at 20°C

Tables 1 present the results of the kinetic parameters of the adsorption of RB dye on ashes (the equilibrium rate constant kinetic pseudo-first and second order) for all the used amount of adsorbent, initial concentration of the dye, all temperatures and values for the parameter q (calculated - q_{cal} and experimental - q_{exp}).

Although the coefficients of determination R^2 for the kinetic model of pseudo-first order generally greater than 0.9, for all amounts of adsorbent, as the dye concentration and temperature, however, much lower values of the calculated parameters are obtained (q_{cal}) compared to those for the experimental parameter (q_{exp}). Therefore, adsorption cannot be best described using a kinetic model of pseudo-first order, because in many cases the first-order equation does not adequately cover the entire range of contact time.

In contrast, the kinetic model of pseudo-second order is in all cases $R^2 = 1$, which is achieved when

the full functionality of a model can be used to describe the adsorption process of a dye on the ashes. In addition, the differences between the parameters q_{cal} and q_{exp} are minimal, for this model practically insignificant.

Thus, the pseudo-first order of kinetic model does not describe adequately the kinetics of adsorption for the dye system - adsorbent because the experimental values q_{exp} don't agree with calculated values q_{cal} obtained from Lagergen's chart with a lower coefficient of determination lower than 1.

Dye concentration decreases rapidly during the initial absorption before diffusion inside the particles begin to control the kinetics of adsorption in all cases. Increasing of the contact time (or speed reduction of external diffusion) reduces the resistance of the boundary layer and thus enhances the mobility of dye during the adsorption.

Table 1 - Kinetic parameters of RB dye adsorption on the ashes of the 20°C

Quantity of adsorbent, g	Concentration of dye, mg/dm ³	q_{exp} , mg/g	Pseudo I order			Pseudo II order		
			k_1 , min ⁻¹	q_{isz} , mg/g	R^2	k_2 , g/mg·min	q_{isz} , mg/g	R^2
1	10	0.998	0.046	0.0012	0.885	126.24	1.000	1
	30	2.996	0.047	0.0033	0.985	42.58	2.998	1
	50	4.995	0.043	0.0051	0.987	24.94	4.997	1
	70	6.994	0.045	0.0077	0.981	18.62	6.996	1
	100	9.993	0.044	0.0106	0.990	12.45	9.995	1
2	10	0.501	0.050	0.0007	0.971	272.25	0.500	1
	30	1.497	0.048	0.0014	0.873	88.62	1.498	1
	50	2.496	0.050	0.0027	0.970	53.44	2.498	1
	70	3.496	0.050	0.0039	0.971	37.50	3.498	1
	100	4.992	0.048	0.0054	0.964	25.21	4.996	1
3	10	0.335	0.042	0.0004	0.964	410.41	0.331	1
	30	0.997	0.044	0.0008	0.866	138.35	1.000	1
	50	1.667	0.044	0.0015	0.965	82.85	1.663	1
	70	2.335	0.045	0.0020	0.965	56.25	2.330	1
	100	3.330	0.043	0.0030	0.964	41.45	3.334	1
4	10	0.254	0.044	0.0003	0.913	610.44	0.251	1
	30	0.752	0.050	0.0008	0.944	187.74	0.755	1
	50	1.247	0.047	0.0013	0.945	111.62	1.246	1
	70	1.749	0.050	0.0018	0.944	78.78	1.746	1
	100	2.496	0.045	0.0025	0.852	57.22	2.498	1

4. CONCLUSION

The kinetic factors that affect the process of dye adsorption in aqueous solution using bottom ash as adsorbent were studied. It is shown that by-product of city heating station is a good adsorbent. United, kinetic models of pseudo-first order and pseudo-second-order without doubt, can provide a simple but satisfactory explanation of the adsorption processes in many systems.

Based on experimental results the following conclusions can be drawn:

- **Kinetics of dye adsorption followed the model of pseudo-second order:** q_{exp} experimental values are fully consistent with the calculated values q_{cal} , coefficient of determination in all cases of the model of pseudo-second order for dye is $R^2 = 1$ (the model of pseudo-first-order R^2 is below 1 or below 0.9).

- **The rate constant of pseudo-second order decreases** with an increasing initial concentration of both dyes and increases with an increasing amount of adsorbent - ash and temperature.

- **Based on kinetic data,** it can be concluded that physical adsorption dominates; for the applied dye since, according to the model of pseudo-second order, there were no restrictions due to possible chemisorptions, which would include valence forces through the sharing or exchange of electrons between adsorbent and adsorbate.

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IZVOD

KINETIKA ADSORPCIJE REAKTIVNE BOJE NA KOTLOVSKOM PEPELU

Cilj ovog rada je da predstavi kinetiku adsorpcije tipične reaktivne boje za tekstil na kotlovskom otpadnom pepelu, što može dovesti do dragocenih podataka koji se odnose na mogućnost šire primene, na primer, za prečišćavanje obojenih otpadnih voda. Kinetika sorpcije, koja opisuje brzinu adsorpcije zagađivača (boja) je jedna od najvažnijih karakteristika koja definiše efikasnost sorpcije i mogućnost korišćenja adsorbenta u kontroli zagađenja voda. U cilju istraživanja mehanizma adsorpcije reaktivne boje iz tekstilne industrije na kotlovski pepeo dobijen posle sagorevanja uglja iz gradske toplane, određene su karakteristične konstante sorpcije korišćenjem Lagergren-ove jednačine za pseudo-prvi i pseudo-drugi red. Zajedno, kinetički modeli pseudo-prvog i pseudo-drugog reda mogu obezbediti jednostavno ali zadovoljavajuće objašnjenje procesa adsorpcije reaktivne boje.

Ključne reči: adsorpcija, pepeo, kinetika, Lagergren-ova jednačina, reaktivna boja.

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