



ADSORPTION KINETICS OF REACTIVE DYES ON ASH FROM TOWN HEATING PLANT

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Abstract: In order to investigate the mechanism of adsorption of reactive dyes from the textile industry on ash from heating plant produced by brown coal combustion, some characteristic sorption constants are determined using Langergren adsorption equations for pseudo-first and pseudo-second order. Combined 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. According to the characteristic diagrams and results of adsorption kinetic parameters of reactive dyes on ashes, for the applied amounts of the adsorbents and different initial dye concentrations, it can be concluded that the rate of sorption is fully functionally described by second order adsorption model. According to the results, the rate constant of pseudo-second order decreases with increasing initial dye concentration and increases with increasing amount of adsorbent – ash.

INTRODUCTION

Dye adsorption on a solid adsorbent, and consequently the process of decolorization is mainly related to the purification processes of wastewater, mainly from textile or some other industry. Residual dye is an important factor when it comes to security of wastewater before its discharge into waterways. Apart from 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.

Dyes can cause problems in several ways: they can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration. In addition, the dyes are characterized by sufficient stability to light and to oxidizing agents. Therefore, the presence of dye in watercourses will significantly reduce the quality of water and thus make it useless for any use. In addition, we found that dyes are dangerous substances with the ability to cause irritation to the gastrointestinal tract, shorter breathing and coughing [1, 2].

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

So far, studies were conducted and relatively numerous approaches for the development of cheaper and more efficient sorbents were made. 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: clay materials (bentonite, kaolinite), zeolite, silica materials (silicon granules, alunite, perlite), agricultural waste (sugar cane biomass, corn cob, rice husk, coconut shell) industrial waste products (waste cement slurry, metal hydroxide sludge), biosorbents (chitosan, shake, and biomass) and others (starch, cyclodextrin, cotton) [3–7].

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 an interaction occurs between dissolved organic compounds – dyes, solvent molecules – water and the surface of adsorbent – ash.

Therefore, it can be said that the adsorption of dissolved substances (adsorbate) from solution or suspension of solid material (adsorbent), takes place mostly in one of the following mechanisms: exchange of molecules from solution to adsorbent, physical adsorption – due to van der Waals's forces and chemisorptions.

Since the introduction of water-soluble dyes (e.g. reactive dyes), which are now widely used in industry, conventional biological treatment is not sufficient to achieve adequate removal of dye. Other common methods, such as physical coagulation – flocculation proved to be failure to eliminate today's most used reactive dyes [8].

The aim of this paper is to present the adsorption kinetics of a typical reactive dye on the 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 more important characteristics that define the efficiency of sorption and the ability to use the adsorbent in controlling water pollution. Hence, the kinetics of reactive dye removal was performed in order to understand adsorption behavior of the adsorbent with respect to concentration and temperature.

EXPERIMENTAL

Bottom ash produced by brown coal combustion from the town heating plant was used as an adsorbent. After collecting and drying, sieving to the particle size of 0.5 mm was 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 the reactive dye *C.I. Reactive Blue 221* from a textile company (hereafter *Reactive Blue*) was used.

Adsorption test was performed in glass Erlenmeyer flasks in which the adsorbent is suspended in dye solution – adsorbate. Erlenmeyer flasks are placed on the shaker

with 120 rpm at a certain temperature and kept for specified time. The amount of ash varied from 1 to 4 g, while the solution having constant volume of 100 cm³, contained the following dye concentrations, 10, 30, 50, 70 and 100 mg/dm³. Processing time, with constant stirring, was 5, 10, 20, 30, 45 and 60 min, while pH varied from 2 to 12, and was adjusted by adding 1M sulfuric acid or sodium hydroxide solutions.

The above dye concentrations were taken because they usually correspond to residual amounts of dye in dyeing solutions after wool dyeing. Practically, in the experiment matching concentrations of pure dye were used without usual dyeing additives. It was found that equilibrium adsorption time on ash was achieved in 60 min; the extension of treatment duration did not significantly alter adsorption.

Upon completion of adsorption, the dissolved dye and ash were filtered through a filter paper followed by analysis of solution absorption on the spectrophotometer UV-VIS (*Cary 100 Conc UV-VIS, Varian*) at 575 nm. Reproducibility of data varied in the range of ± 1.8%.

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

SEM study (Fig. 1) of used ash samples showed the appearance of particles mostly as irregular oblong shapes with characteristic surface macro-porosity. Left micrograph in Figure 1 gives a 1000× magnification view while the right micrograph refers to somewhat bigger plan, magnification of 5000×.

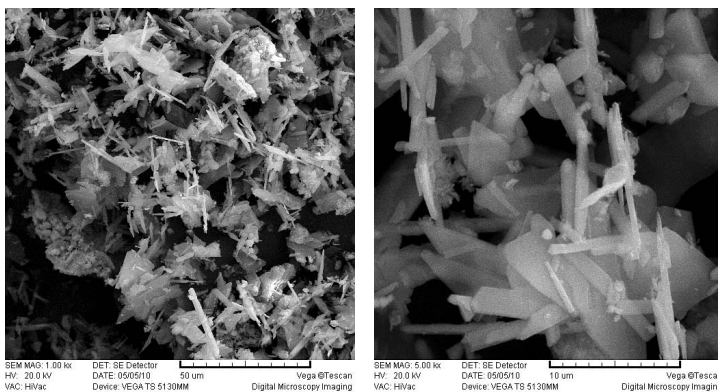


Fig. 1. Micrographs of used ash – adsorbent (left – 1000×, right – 5000×)

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 total exposure of 5 s per step.

Mainly dominated by gypsum and quartz, followed by calcite and aluminum hydrogen sulfate, and finally with a share below 10% coming ferchilidit, melanterit, oldhamit and iron sulfate, Table 1.

Table 1. The chemical composition of the ash according to diffraction measurements

Ingredients	Mass content, %
Ca(SO ₄) ₂ H ₂ O	28.5
SiO ₂	26.5
CaCO ₃	13.2
Al ₃ (HSO ₄)(SO ₄) ₄ ·9H ₂ O	13.0
K ₂ Ca(CO ₃) ₂	6.6
FeSO ₄ ·7H ₂ O	6.4
CaS	4.5
FeSO ₃	1.3

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 and pseudo-second order.

The equation of pseudo-first order

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

Lagergren equation is usually expressed as follows [13]:

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

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 $q_t = q_t$, the following equation 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 $\log(q_e - q_t)$ vs. 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 coefficient with experimental data. The rate change should be proportional to the first degree of concentration for strictly surface adsorption. However, the relationship between adsorbate initial concentration and the adsorption rate will not be linear when pore diffusion controls the adsorption process.

The equation of pseudo-second order

The model of pseudo-second order, which is usually given as follows [14], can describe adsorption kinetics:

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

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 (6) for the boundary conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$, and by linearization and rearrangement we obtain:

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

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

Intraparticle diffusion model

Intraparticle diffusion model was tested to identify the diffusion mechanism [9].

According to this theory:

$$q_t = k_p \cdot t^{1/2} \tag{6}$$

Where k_p (mg/g min^{1/2}), the intraparticle diffusion rate constant, is obtained from the slope of the straight line of q_t versus $t^{1/2}$.

RESULTS AND DISCUSSION

Figures 2–6 show diagrams and results related to sorption kinetics of reactive dye on the ash for the applied amount of adsorbent and different dye concentrations. According to the linear model forms of pseudo-first order and pseudo-second order, it can be concluded that the rate of sorption is fully functionally described with the second order model at given experimental conditions.

Models of pseudo-first order on diagrams in Figures 2 and 3 do not show good results for the entire period of sorption, unlike the pseudo-second order, which provide

functional straight line for all dye concentrations, as shown in Figures 4 and 5, which confirms its applicability (model pseudo-second order).

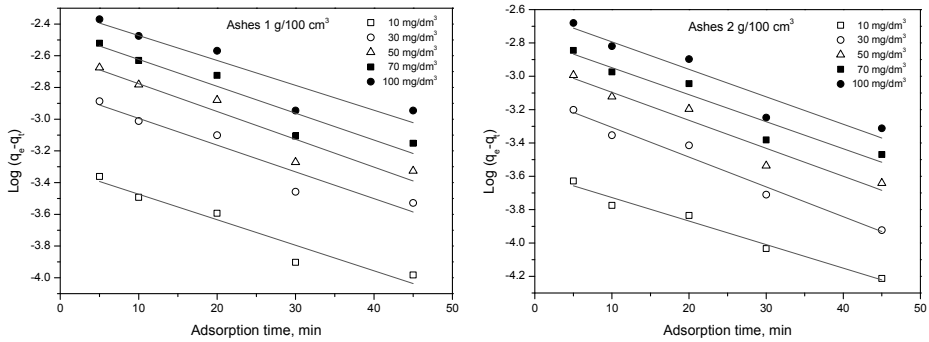


Fig. 2. Sorption kinetics of *Reactive Blue* dye (pseudo-first order) adsorption on the ashes concentration of 1 and 2 g/100 cm³ at 20°C

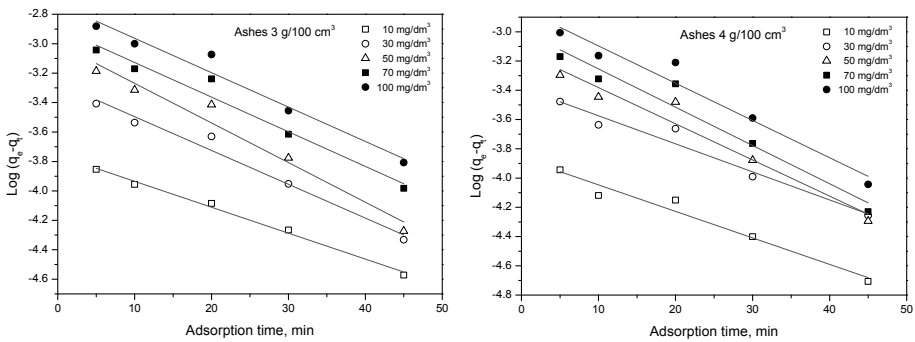


Fig. 3. Sorption kinetics of *Reactive Blue* dye (pseudo-first order) adsorption on the ashes concentration of 3 and 4 g/100 cm³ at 20°C

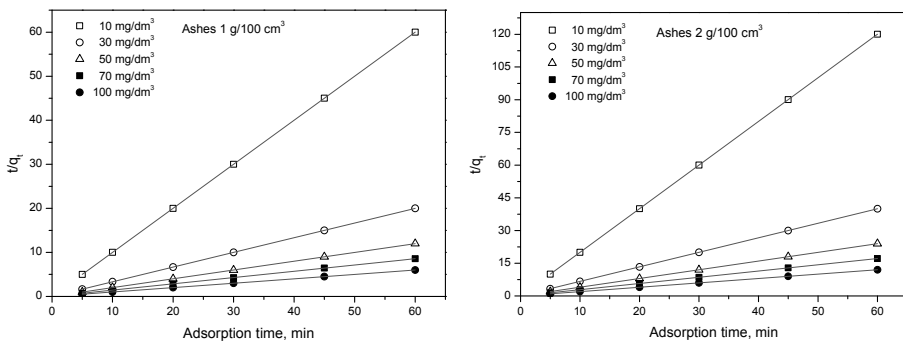


Fig. 4. Sorption kinetics of *Reactive Blue* dye (pseudo-second order) adsorption on the ashes concentration of 1 and 2 g/100 cm³ at 20°C

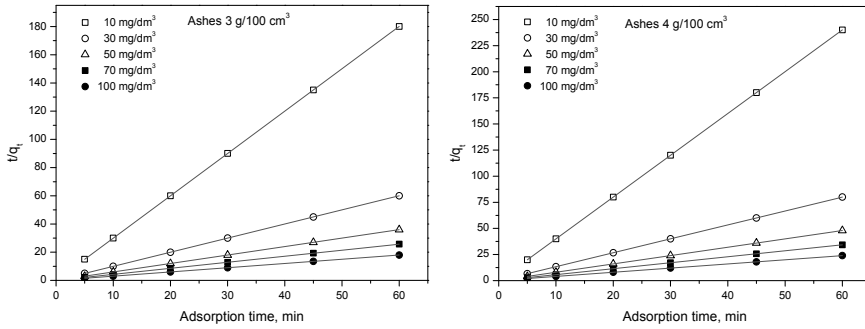


Fig. 5. Sorption kinetics of *Reactive Blue* dye (pseudo-second order) adsorption on the ashes concentration of 3 and 4 g/100 cm³ at 20°C

Interpretation of intraparticle diffusion model is graphically presented in Figure 6. As can be seen, the linear line did not pass through the origin and this deviation from the origin or near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [10]. Values of intercept, C , ($q_t = kp \cdot t^{1/2} + C$), give an idea about the thickness of boundary layer, i.e., larger the intercept, greater is the boundary layer effect. Also, there may be a present multi linearity, which indicates that two or more steps occur in the adsorption processes. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate controlled. The third portion is the final equilibrium stage, where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution [11, 12]. The results for the adsorbent amount of 2 and 3 g are not shown in order not to burden the work since it is similar results.

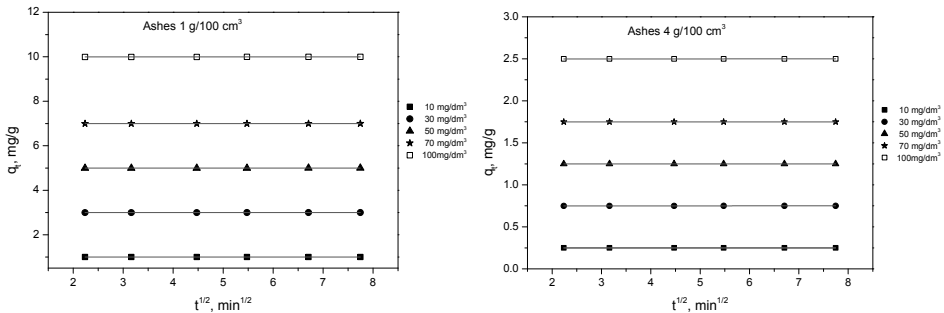


Fig. 6. Sorption kinetics of *Reactive Blue* dye (intra-particle diffusion model) adsorption on the ashes concentration of 1 and 4 g/100 cm³ at 20°C

Tables 2–5 present results of kinetic parameters of the adsorption process of reactive dye on ash (the equilibrium rate constant for pseudo-first and second order kinetics) for all adsorbent amounts used, all initial dye concentrations, all temperatures and parameter q values (calculated – q_{cal} and experimental – q_{exp}).

Although the coefficients of determination R^2 for the kinetic model of pseudo-first order were generally greater than 0.9, for all amounts of adsorbent, all initial dye concentrations and temperatures, much lower values of the calculated parameter (q_{cal}) were obtained (q_{cal}) compared to those of 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 shows in all cases $R^2 = 1$, achieving full functionality of the model; then it can be used to describe the adsorption process of a dye on the ash. In addition, the differences between parameters q_{cal} and q_{exp} are minimal for this model and practically insignificant. The advantage of our derivation is that it shows when the initial concentration of solute is not too high, that the sorption process obeys the pseudo-second-order model. Our results show that the observed rate constant of the second order model (k_2) is a complex function of the initial concentration of solute, which agrees with many studies [15–17].

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

According to the results in Tables 2–4, rate constant of pseudo-second order decreases linearly with increasing initial dye concentration and increases with an increasing amount of adsorbent – ash. In addition, with an increasing temperature from 20 through 40 to 60°C, the rate constant of pseudo-second order shows continued growth.

Table 2. Kinetic parameters of *Reactive Blue* 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_{cal} , mg/g	R^2	k_2 , g/mg·min	q_{cal} , mg/g	R^2
1	10	0.9997	0.037	0.0005	0.939	248.88	0.9998	1
	30	2.9992	0.039	0.0015	0.925	82.35	2.9993	1
	50	4.9987	0.040	0.0025	0.913	49.81	4.9987	1
	70	6.9981	0.039	0.0035	0.908	34.92	6.9984	1
	100	9.9973	0.036	0.0048	0.878	24.61	9.9980	1
2	10	0.4999	0.032	0.0003	0.977	435.87	0.4999	1
	30	1.4996	0.041	0.0007	0.971	168.43	1.4997	1
	50	2.4994	0.039	0.0012	0.940	103.95	2.4994	1
	70	3.4991	0.037	0.0016	0.932	73.58	3.4992	1
	100	4.9987	0.038	0.0023	0.920	51.87	4.9987	1
3	10	0.3333	0.041	0.0002	0.994	715.60	0.3333	1
	30	0.9998	0.053	0.0005	0.977	267.49	0.9998	1
	50	1.6663	0.062	0.0010	0.967	162.23	1.6664	1
	70	2.3328	0.054	0.0013	0.967	113.43	2.3329	1
	100	3.3325	0.054	0.0019	0.967	77.62	3.3327	1

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_{cal} , mg/g	R^2	k_2 , g/mg·min	q_{cal} , mg/g	R^2
4	10	0.2499	0.042	0.0001	0.965	920.68	0.2500	1
	30	0.7499	0.044	0.0004	0.960	310.89	0.7499	1
	50	1.2498	0.057	0.0007	0.954	204.55	1.2498	1
	70	1.7496	0.060	0.0010	0.951	153.36	1.7497	1
	100	2.4995	0.059	0.0014	0.958	107.43	2.4996	1

Table 3. Kinetic parameters of *Reactive Blue* dye adsorption on the ashes of the 40°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_{cal} , mg/g	R^2	k_2 , g/mg·min	q_{cal} , mg/g	R^2
1	10	0.9998	0.031	0.0004	0.886	279.44	0.9998	1
	30	2.9993	0.034	0.0014	0.923	82.96	2.9994	1
	50	4.9988	0.036	0.0023	0.917	51.31	4.9990	1
	70	6.9982	0.036	0.0032	0.912	36.37	6.9984	1
	100	9.9974	0.035	0.0046	0.907	25.58	9.9980	1
2	10	0.4999	0.035	0.0003	0.963	429.74	0.4999	1
	30	1.4997	0.038	0.0007	0.971	167.78	1.4997	1
	50	2.4994	0.042	0.0012	0.946	108.89	2.4995	1
	70	3.4991	0.040	0.0016	0.938	77.05	3.4993	1
	100	4.9988	0.038	0.0023	0.934	53.06	4.9990	1
3	10	0.3333	0.058	0.0002	0.988	785.47	0.3333	1
	30	0.9998	0.052	0.0005	0.975	263.95	0.9999	1
	50	1.6663	0.062	0.0010	0.969	165.97	1.6664	1
	70	2.3328	0.053	0.0012	0.966	117.04	2.3329	1
	100	3.3326	0.053	0.0018	0.969	81.85	3.3328	1
4	10	0.2499	0.055	0.0001	0.901	954.10	0.2500	1
	30	0.7499	0.049	0.0004	0.969	320.39	0.7499	1
	50	1.2498	0.062	0.0007	0.941	213.41	1.2498	1
	70	1.7496	0.062	0.0010	0.946	164.15	1.7497	1
	100	2.4995	0.058	0.0013	0.951	114.33	2.4996	1

Table 4. Kinetic parameters of *Reactive Blue* dye adsorption on the ashes of the 60°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_{cal} , mg/g	R^2	k_2 , g/mg·min	q_{cal} , mg/g	R^2
1	10	0.9998	0.031	0.0004	0.823	293.35	0.9998	1
	30	2.9994	0.034	0.0013	0.929	85.51	2.9994	1
	50	4.9988	0.036	0.0022	0.902	55.01	4.9990	1
	70	6.9983	0.036	0.0030	0.897	39.21	6.9984	1
	100	9.9976	0.036	0.0045	0.909	26.67	9.9980	1
2	10	0.4999	0.039	0.0003	0.956	462.51	0.4999	1
	30	1.4997	0.037	0.0007	0.980	168.41	1.4997	1
	50	2.4994	0.040	0.0011	0.945	111.94	2.4995	1
	70	3.4992	0.040	0.0016	0.938	80.07	3.4993	1
	100	4.9988	0.039	0.0022	0.936	55.17	4.9990	1
3	10	0.3333	0.058	0.0002	0.988	794.42	0.3333	1
	30	0.9998	0.053	0.0005	0.979	270.36	0.9999	1
	50	1.6663	0.061	0.0009	0.965	171.49	1.6664	1
	70	2.3329	0.053	0.0012	0.969	120.88	2.3329	1
	100	3.3326	0.053	0.0017	0.971	84.94	3.3328	1
4	10	0.2499	0.105	0.0002	0.813	1092.90	0.2500	1
	30	0.7499	0.049	0.0004	0.969	324.48	0.7499	1
	50	1.2498	0.062	0.0007	0.943	220.76	1.2499	1
	70	1.7496	0.065	0.0010	0.945	172.83	1.7497	1
	100	2.4995	0.058	0.0013	0.953	119.45	2.4996	1

Dye concentration decreases rapidly during initial absorption before diffusion inside particles begin to control adsorption kinetics in all cases. Increasing contact time (or decreasing rate of external diffusion) reduces the resistance of the boundary layer and thus enhances the mobility of dye during the adsorption. The results show that increased dye concentration led to lower initial rate while change in temperature from 20 to 60°C increased external diffusion. It is clear that external mass transfer resistance cannot be ignored even at high mixing speed, although the resistance is significant only for an initial period of sorption.

Generally, the driving force changes with the dye concentration in bulk solution. The increase in dye concentration results in the increase of driving force, which consequently increases the diffusion rate of the molecular dye from bulk phase to the exterior surface of adsorbent. According to the results in Table 5, the effect of the initial dye concentration k_p was not significant. It is assumed that the diffusion resistance which is caused by the size

of the adsorbate molecule and the pore-size distribution of the adsorbent is larger than the driving force of diffusion. Finally, the increase in the driving force of diffusion can be neglected when the dye diffuses in the pores of the particles. The R^2 values (Table 5) obtained were lower compared to those obtained from pseudo-second-order kinetic model, however, the calculated and experimental q values agreed satisfactorily well for intraparticle diffusion model.

Table 5. Kinetic parameters – intraparticle diffusion model of *Reactive Blue* dye adsorption on the ashes of the 20°C

Quantity of adsorbent, g	Concentration of dye, mg/dm ³	q_{exp} mg/g	Intraparticle diffusion model		
			k_p , mg/g min ^{1/2}	q_{cal} mg/g	R^2
1	10	0.9998	$7.51 \cdot 10^{-5}$	0.9997	0.970
	30	2.9994	$2.28 \cdot 10^{-4}$	2.9992	0.967
	50	4.9988	$3.78 \cdot 10^{-4}$	4.9986	0.964
	70	6.9983	$5.28 \cdot 10^{-4}$	6.9944	0.963
	100	9.9976	$7.51 \cdot 10^{-4}$	9.9972	0.958
4	10	0.2499	$1.95 \cdot 10^{-5}$	0.2499	0.967
	30	0.7499	$5.86 \cdot 10^{-5}$	0.7499	0.963
	50	1.2498	$9.27 \cdot 10^{-5}$	1.2497	0.956
	70	1.7496	$1.24 \cdot 10^{-4}$	1.7496	0.954
	100	2.4995	$1.80 \cdot 10^{-4}$	2.4994	0.959

CONCLUSION

The kinetic factors affecting the process of dye adsorption in aqueous solution using ash as adsorbent were studied. It is shown that by-product of town heating plant is a good adsorbent. Combined, 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. In recent years, the pseudo-second-order rate expression has been widely applied to the adsorption of pollutants from aqueous solutions. The advantage of using this model is that there is no need to know the equilibrium capacity from the experiments, as it can be calculated from the model. The pseudo-second-order rate expression was used to describe chemisorptions involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange.

Based on experimental results the following conclusions can be drawn:

- Kinetics of dye adsorption followed the model of pseudo-second order: experimental q_{exp} values are fully consistent with the calculated q_{cal} values, coefficient of determination in all cases of the model of pseudo-second order for dye is $R^2 = 1$. (With pseudo-first order model 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. The k_2 constant value is usually strongly dependent on the applied initial solute concentration. It decreases with the increasing initial solute concentration as a rule, which is a commonly known fact related to the interpretation of k_2 as a time-scaling factor (obviously, the higher the initial solute concentration value, the longer time is required to reach equilibrium). This is in agreement with the results of most theoretical interpretations, predicting such dependence of k_2 on initial solute concentration.
- Intraparticle diffusion model of textile dyeing give an idea about the thickness of boundary layer, i.e., larger the intercept, greater is the boundary layer effect.
- Based on kinetic data, it can be concluded that physical adsorption prevails because according to the pseudo–second order model there were no limitations due to chemisorption that includes valence forces and exchanging and sharing of electrons between adsorbent and adsorbate.

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