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Effect of KOH treatment on bituminous coal for the effective removal of Basic Blue 41 dye from aqueous solutions

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ABSTRACT

Activated carbons (ACs) were produced from Zonguldak region bituminous coal using physical and chemical techniques and evaluated for the removal of a textile dye, Basic Blue 41 from aqueous solutions. The color removal performance of ACs prepared by physical activation (PAC), chemical activation with KOH (CAC), and the commercial AC were compared; and the effects of adsorbent preparation method, temperature, and initial dye concentration on adsorption were studied. BET surface areas of the PAC, AC, and CAC were determined as 52.6, 824, and 1,312 $m^2 g^{-1}$, respectively. Micropore volume of PAC determined by DR method was 0.02 $cm^3 g^{-1}$, whereas AC and CAC have values of 0.42 and 0.57 $cm^3 g^{-1}$. Thermal treatment with KOH resulted in enhancement of the porosity characteristics, particularly in micropores, and the surface area of the CAC samples. The batch adsorption experiments were carried out isothermally at 25–35˚C. The values for the adsorption capacity Q_0, determined from the Langmuir model at 25, 30, and 35˚C were 96.4, 52.1, 54.7 $mg g^{-1}$ for PAC; 262.5, 283.3, 293.3 $mg g^{-1}$, for AC; and 420.2, 427.4, 460.8 $mg g^{-1}$ for CAC, respectively. The increase in adsorption capacity with an increase in temperature for BB 41 onto CAC and AC indicated an endothermic chemisorption process, which was attributed to increased surface coverage at higher temperature and creation of reactive and active sites. For BB 41 adsorption onto PAC, the decrease in sorption capacity with increasing temperature indicated the exothermic behavior of the sorption process that is related to physisorption. The adsorption capacity of the obtained samples was found in the order of CAC > AC > PAC. Among the AC samples prepared by different methods, the highest value of the adsorption capacity obtained was 460.8 $mg g^{-1}$ at 35˚C for CAC. Kinetic data were adequately represented by the pseudo-first-order kinetic model. AC prepared from coal by CAC treatment was shown to be an effective adsorbent for the removal of BB 41.

Keywords: Basic Blue 41; Activated carbon; Adsorption; Coal; Dye

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1. Introduction

Chemical contamination of water is a serious environmental problem because of the many health hazards it causes. The textile and dying industries are the most polluting industries among all industrial sectors which generate large volumes of hazardous effluents [1–4]. Among a large variety of methods used for the removal of the dyes, adsorption is one of the most efficient processes for the treatment of wastewaters [5]. It has been widely applied in removing dyestuffs from textile industry wastewaters. Numerous studies have reported the adsorptive removal of dyes from aqueous solutions. Most of those were devoted to the development of low-cost materials from various sources, agricultural, or industrial by-products or wastes, treated and untreated activated carbons (ACs), various types of clays, sepiolite, perlite, and/or activated sludge. These materials were compared in terms of their adsorption capacities.

In a study by Sun and Xu [6], the adsorption capacity of sunflower stalks and its components for anionic dyes was obtained in the range of 15–76 mg g^{-1}. Palm fruit particles had adsorption capacities reported as 92–327 mg g^{-1} for basic dyes [7]. An industrial by-product, waste red mud which is formed during the bauxite ore processing, was reported to have an adsorption capacity of 4.05 mg g^{-1} for congo red [8]. A number of studies investigated color removal using coconut tree sawdust [9]; coconut shell, bamboo dust, rice husk, groundnut shell, straw [10], and orange peel [11] based ACs. The adsorption capacity of congo red by coir pith carbon was 6.7 mg g^{-1} [12]. In another study, monolayer saturation capacities for AC and "kudzu" reported were in the range of 720–860 and 160–220 mg g^{-1} for some basic dyes [13]. Doğan and Alkan [14] investigated the kinetics of methyl violet adsorption onto perlite. The sawdust and rice husk carbon were reported to have adsorption capacities of 183.8 and 86.9 mg g^{-1}, respectively, for Acid Yellow 36 [15]. Alkan et al. [16] assesed the adsorption capacity of sepiolite for Acid Yellow 49. The maximum adsorption capacities of powdered AC and sludge for Turquoise Blue-G were reported as 100 and 92 mg g^{-1}, respectively [17]. Attia et al. [18] used a commercial AC subjected to thermal treatment (400–600˚C, 2 h) for acid dyes. Methylene blue adsorption onto AC was investigated in various studies [19–23]. In some recent studies, the adsorption of cationic textile dyes Maxilon Blue 5G and Red GRL onto perlite and sepiolite was investigated [24,25]. Wawrzkiewicz et al. [26] investigated the adsorption of some acid, reactive and direct dyes using mixed silica–alumina oxide, and reported monolayer sorption capacities in the range of 41.4–49.2 mg g^{-1}. In a recent study, Basic Blue 41 dye by brick waste has an adsorption capacity of 60–70 mg g^{-1} [27].

In the present study, we have taken coal samples from a coal mine (Kilimli) in the city of Zonguldak, situated on the Black Sea Coast in Turkey, and used them for the synthesis of ACs. We produced AC samples by physical and chemical treatment techniques, denoted as PAC and CAC, respectively, and tested their performance in removing Basic Blue 41 (BB 41) dye from solution. The objective of this work was to examine the applicability of the ACs produced from coal in removing BB 41 from aqueous solutions. We studied the effects of different parameters including adsorbent production technique, temperature, and initial dye concentration in solution on the dye removal by adsorption. We investigated the adsorption kinetics and equilibrium, and analyzed the effects of activation conditions of the ACs from coal. We have compared the sorption capacities of PAC and CAC for BB 41 with that of commercial AC.

2. Materials and methods

2.1. Preparation and characterization of adsorbents

Three different kinds of adsorbents were used in this study: (i) commercial AC purchased from Aldrich, (ii) AC produced by physical activation (PAC) by thermal treatment from bituminous coal (PAC), and (iii) AC from coal produced by chemical activation with KOH (CAC). Coal samples for this research were taken from Kilimli coal mines in Zonguldak, which is situated on the northwestern coast of the Black Sea in Turkey. The surface characteristics, such as the surface areas, pore volumes, micropore volumes, pore sizes, and pore size distributions of all the samples produced were evaluated analyzing N_2 adsorption–desorption data obtained at 77 K. These experiments were conducted using a Quantachrome Gas Sorption Analyzer.

2.1.1. PAC of coal

Raw coal samples taken from the mine were crushed for a particle size range of 100–150 μm. In the first step, the ash content was decreased treating the raw coal with 15% HCl aqueous solution at 60˚C for 1 h. The resulting solution was filtered and washed with distilled water in order to remove the chloride ions contained in the filtrate solution. Then in the next step, the coal was treated with 25% HF (60˚C, 2 h) and then filtered and washed. The samples obtained were then subjected to pyrolysis in a tubular oven under N_2 flow, at a heating rate of 30˚C/min to 800˚C. The samples were kept at this temperature for 2 h and then left to cool under N_2 flow [28].

2.1.2. Chemical activation of coal with KOH

The resulting samples obtained by PAC were extracted with 1 M KOH solution with a KOH/coal mass ratio of 4:1 in a Soxhlet apparatus. Following the extraction, the samples obtained were dried at 120°C, and were then subjected to pyrolysis at 800°C under N_2 flow, in a temperature-controlled tubular oven for 2 h. After cooling the resulting chars with N_2 flow, they were washed with hot distilled water to eliminate the KOH content, until obtaining a neutral pH. They were then dried at 120°C for 1 d [28].

2.2. Basic Blue 41 dye

BB 41 dye was obtained from AK-Al Textile Company, which is situated on the Western Black Sea Region in Turkey. A BB 41 dye solution (1,000 mg l^{-1}) was prepared, and kept as a stock solution. Dye solution samples were prepared by diluting this stock solution to give the desired concentration.

2.3. Adsorption experiments

Before starting the measurements, a calibration curve was drawn to determine the concentration of BB 41 solution. The concentration of BB 41 in solution was measured spectrophotometrically at $\lambda_{max} = 610$ nm by withdrawing samples at different time intervals. A Shimadzu UV-1700 Model type Spectrophotometer was used for this purpose. Batch adsorption experiments were conducted at 25, 30, and 35°C using adsorbents PAC, AC, and CAC in order to investigate the effect of temperature and adsorbent type on the adsorptive removal of basic dye. For each experimental run, 200 ml of dye solution with an initial concentration in the range of 4–42 mg l^{-1} was prepared in a 500-ml stoppered flask and 10 mg of AC samples was added each time. The natural pH of BB 41 was measured as 7.7 initially, and the change in pH during an adsorption run was not more than 1.5%. This dye solution containing the AC particles was placed in a shaking water bath that was operated at a constant shaking speed. Samples withdrawn from the dye solution at different time intervals were analyzed for remaining dye concentration in solution. Adsorption rate of dye was investigated by analyzing the adsorptive uptake of BB 41 from solution with respect to time. In order to obtain the experimental adsorption isotherms, dye solutions of different initial concentrations each containing 10 mg of adsorbent samples were stirred (at 25, 30, and 35°C) until the equilibrium was achieved. The amount of dye adsorbed by the ACs at equilibrium was calculated as follows:

$$q_e = \frac{(C_0 - C_e)\,V}{W} \tag{1}$$

where q_e (mg g^{-1}) and C_e (mg l^{-1}) are the equilibrium values of adsorption capacity of carbon samples and BB 41 concentration in solution, respectively, V (l) is the volume of dye solution, and W (g) is the amount of adsorbent.

2.4. Adsorption isotherms

Experimental adsorption isotherm data were analyzed using the Langmuir and Freundlich isotherm models. These two models are widely used for analyzing the adsorption equilibrium related with many applications in wastewater treatment.

The Langmuir model is expressed as follows [11]:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{2}$$

where q_e (mg g^{-1}), and C_e (mg l^{-1}) are the amounts of BB 41 adsorbed per unit mass of AC samples, and concentration in solution at equilibrium, respectively. Q_0 (mg g^{-1}), and b (l mg^{-1}) are constants related to the affinity of the binding sites, and energy of adsorption, respectively.

The Freundlich isotherm, given below, is an empirical equation and gives satisfactory results at low concentrations [29]:

$$q_e = K_f\, C_e^{1/n} \tag{3}$$

here K_f is a constant related to the bonding energy. $1/n$, indicates the adsorption effectiveness [10]. Values of K_f and n can be evaluated from the intercept and slope of the plots, drawn ln q_e vs. ln C_e.

2.5. Kinetics of adsorption

In order to investigate the kinetics of the adsorption process in this study, adsorption rate data were analyzed using two models: the pseudo-first-order (Lagergren Model) and the pseudo-second-order kinetic models. The adsorption rate constants from these models were determined for 25, 30, and 35°C.

The first-order rate constant for adsorption of BB 41 on different ACs was determined using Lagergren's equation [30]:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

where q_e and q are the amounts of BB 41 adsorbed at equilibrium and at time t (mg g^{-1}), and k_1 is the rate constant (min^{-1}). The values of k_1 at different temperatures were calculated from the slopes of the respective linear plots of $\log(q_e - q)$ vs. t.

The pseudo-second-order kinetics equation is given below [31]:

$$\frac{1}{(q_e - q)} = \frac{1}{q_e} + k_2 t \tag{5}$$

here k_2 is the pseudo-second-order rate constant. From Eq. (5), k_2 can be obtained from the slope of the plot drawn from $1/(q_e - q)$ vs. t. The intercept of this linear relation gives $1/q_e$.

3. Results and discussion

3.1. Adsorbent characterization

Surface characteristics of adsorbents play a very important role in adsorption. Fig. 1a shows the N_2 adsorption–desorption isotherms obtained at 77 K, and Fig. 1b shows pore size distributions obtained by the NLDFT method of ACs used in this study. Surface characterization results such as the surface area, pore volume, micropore volume, and pore sizes of all the AC samples are shown in Table 1. The BET surface area of PAC, AC, and CAC samples were determined as 52.6, 824, and 1,312 m^2 g^{-1}, respectively. Micropore volume of PAC determined by DR method was found to be 0.02 cm^3 g^{-1}, whereas for AC and CAC values of 0.42 and 0.57 cm^3 g^{-1} were obtained. The surface area and micropore volume of CAC was much higher than PAC. Thermal treatment with KOH resulted in enhancement in the porosity characteristics, particularly in micropores, and the surface area of the CAC samples. Surface

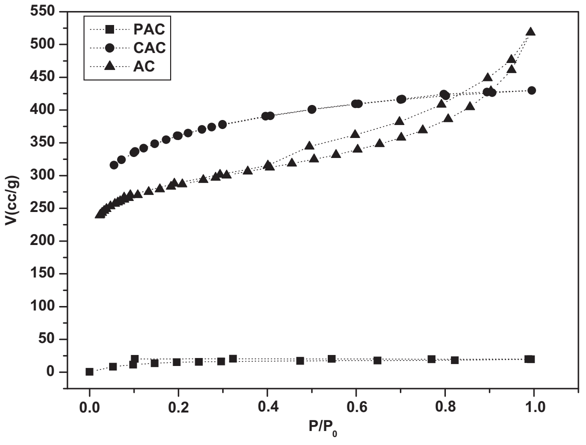

Fig. 1a. N_2 adsorption–desorption isotherms (77 K) on ACs.

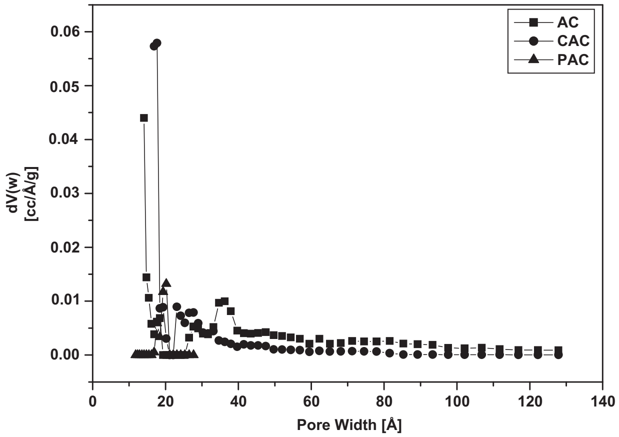

Fig. 1b. Pore size distributions (NLDFT method) of ACs.

Table 1
Surface properties of adsorbents

Adsorbent	Activated carbon prepared by physical activation (PAC)	Commercial activated carbon (AC)	Activated carbon treated by chemical activation (CAC)
BET surface area (m^2 g^{-1})	52.6	824	1,312
Langmuir surface area (m^2 g^{-1})	77.1	1,112	1,596
NLDFT cumulative (cm^3 g^{-1})	0.03	0.68	0.60
DR micropore volume (cm^3 g^{-1})	0.02	0.42	0.57
t-plot micropore volume (cm^3 g^{-1})	0.02	0.31	0.52
NLDFT pore size (Å)	20.2	14.1	17.7
DR pore size (Å)	23.3	16.7	21.1
Average pore size (Å)	23.1	37.2	20.3

analysis results have shown that PAC is not sufficient itself to enhance the surface area and the micropore volumes, but chemical treatment with KOH was a very effective way of increasing the micropores and the surface area of the coal particles.

3.2. Dye solution concentration, contact time, temperature

Initial concentration and contact time are important parameters for the design of effective adsorption systems to be used for wastewater treatment. The adsorption of BB 41 onto AC samples was studied at various initial concentrations as a function of contact time. The necessary adsorption equilibrium time was determined for each concentration. Rapid uptake and quick establishment of equilibrium time imply the efficiency of ACs in terms of their usage in adsorptive removal of dyes. Fig. 2 shows the effects of initial concentration and contact time on adsorption of BB 41 by ACs. The adsorption at different dye concentrations is rapid at the initial stages and then gradually decreases with the progress of adsorption until the equilibrium is reached. As shown in Fig. 2, the contact time needed for BB 41 solutions to reach equilibrium was 120 min for PAC; and 180 min for CAC and AC at 25℃. An increase in initial dye concentration resulted in increased dye uptake for all adsorbents used in this study (Fig. 3). For PAC, the adsorption capacity at equilibrium (q_e) increased from 35.3 to 73.5 mg g^{-1} with an increase in the initial BB 41 concentration from 9.7 to 34.9 mg l^{-1} at 25℃; increased from 23.3 to 51 mg g^{-1} when the initial BB 41 concentration was increased from 4.2 to 34.8 mg l^{-1} at 30℃; and increased from 25.9 to 58.3 mg g^{-1} with an increase in concentration from 4 to 30.3 mg l^{-1} at 35℃. For CAC, q_e increased from 296 to 446.5 mg g^{-1} with increasing initial concentration from 14.9 to 34.5 mg l^{-1} at 25℃; from 289.1 to 433.3 mg g^{-1} with an increase in the initial concentration from 14.7 to 29.8 mg l^{-1} at 30℃; and from 294 to 472 mg g^{-1} with increasing initial concentration from 14.8 to 33.7 mg l^{-1} at 35℃. For AC, q_e increased from 171.1 to 287.4 mg g^{-1} when the initial BB 41 concentration increased from 8.8 to 32.6 mg l^{-1} at 25℃, from 260 to 292.4 mg g^{-1} with increasing concentration from 14.2 to 32.5 mg l^{-1} at 30℃, and q_e increased from 180 to 322.8 mg g^{-1} when the concentration was increased from 9.1 to 28.7 mg l^{-1} at 35℃. It was seen that the dye removal depended on the concentration of the dye, and the initial adsorption rate was greater for higher initial dye concentrations. Similar results were also observed by Gök et al. [5] in their study investigating the effect of initial dye concentration.

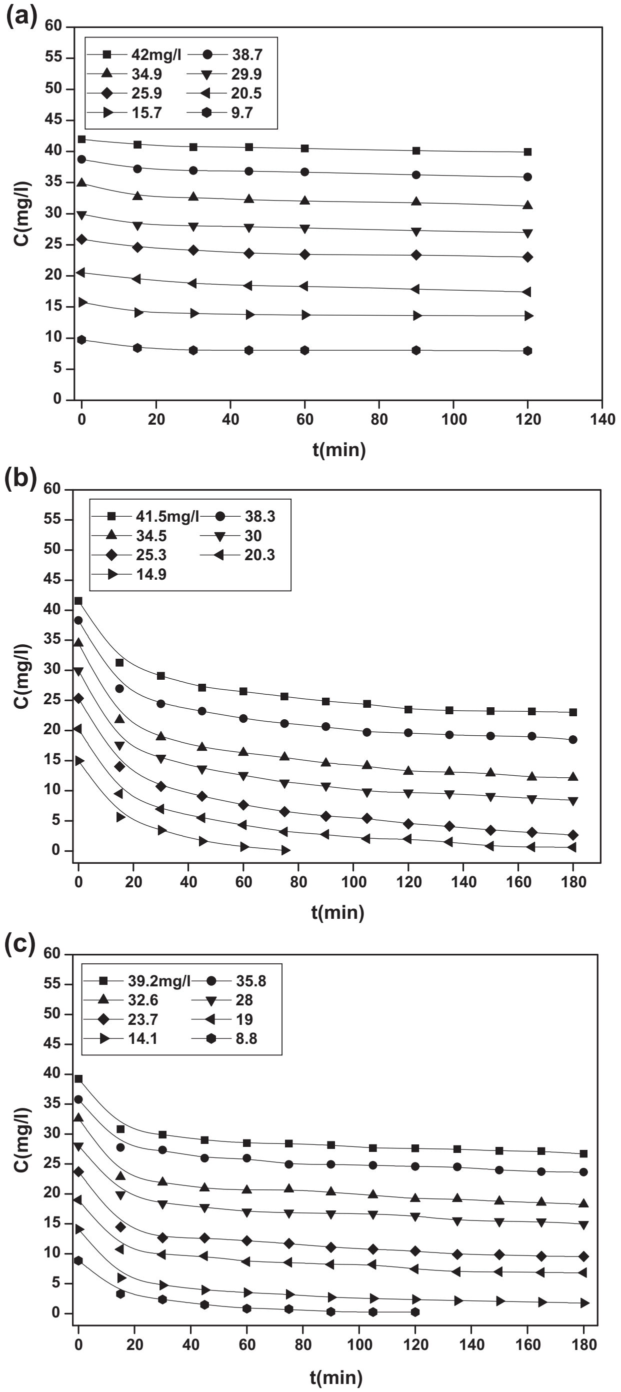

Fig. 2. Change of BB 41 solution concentration with time for adsorption onto ACs (T: 25℃; W: 10 mg; V: 0.2 l) (a) PAC, (b) CAC, (c) AC.

The other important parameter during the adsorption process is the temperature of solution. Effect of temperature assists in understanding the type of adsorption. For this reason, batch adsorption studies were conducted at three different temperatures over a

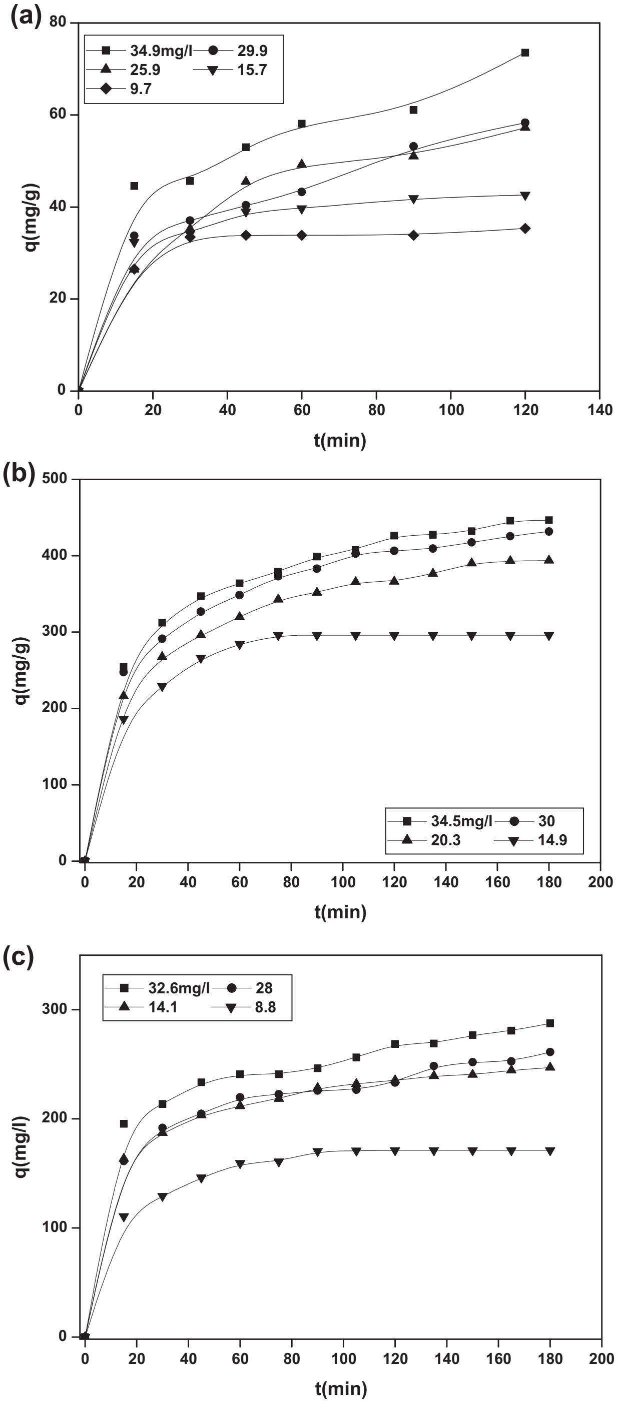

Fig. 3. Change of adsorbed BB 41 concentration onto ACs with respect to time (*T*: 25°C; *W*: 10 mg; *V*: 0.2 l) (a) PAC, (b) CAC, (c) AC.

range of initial dye concentrations for all of adsorbents used. The adsorption capacity may increase or decrease at higher temperatures, depending on the nature of the reaction and other controlling variables. Effect of temperature on the capacity of adsorbent indicates the nature of adsorption: whether the process is endothermic or exothermic. If adsorption capacity increases with an increase in temperature, then the adsorption process is endothermic; which may be attributed to increased surface coverage at

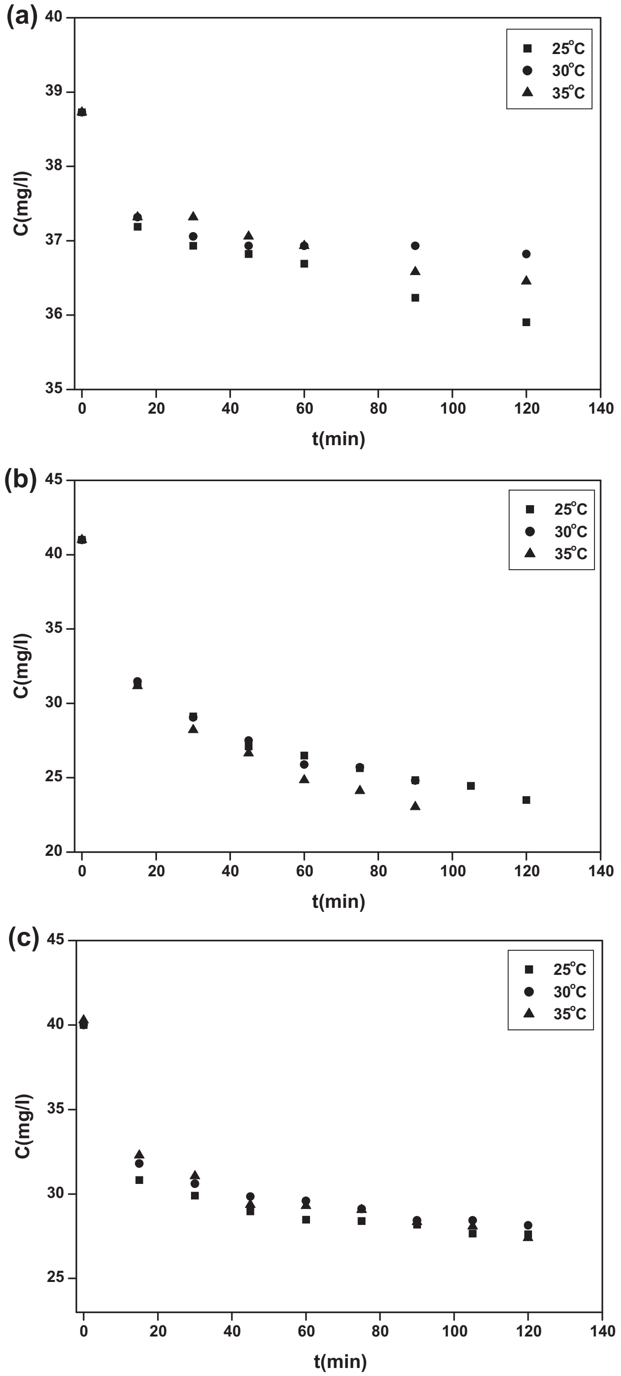

Fig. 4. Effect of temperature for BB 41 adsorption onto ACs (*W*: 10 mg; *V*: 0.2 l) (a) PAC (C_0: 38.7 mg l^{-1}), (b) CAC (C_0: 41 mg l^{-1}), (c) AC (C_0: 40 mg l^{-1}).

Table 2
Adsorption isotherm constants for BB 41 adsorption onto PAC, AC, and CAC (*W*: 10 mg, *V*: 0.2 l)

	PAC			AC			CAC		
Isotherm models	25℃	30℃	35℃	25℃	30℃	35℃	25℃	30℃	35℃
Langmuir model									
Q_0 (mg g^{-1})	96.4	52.1	54.7	262.5	283.3	293.3	420.2	427.4	460.8
b	0.07	0.28	0.32	9.36	8.98	15.84	24.2	11.47	18.02
r^2	0.94	0.89	0.93	0.95	0.96	0.95	0.89	0.93	0.96
Freundlich model									
K_f	12.89	20.80	20.11	211.8	230.3	238.3	372.98	366.45	395.6
n	2.05	4.13	3.56	12.70	13.45	12.40	22.25	18.74	17.04
r^2	0.93	0.73	0.89	0.82	0.78	0.83	0.62	0.68	0.72

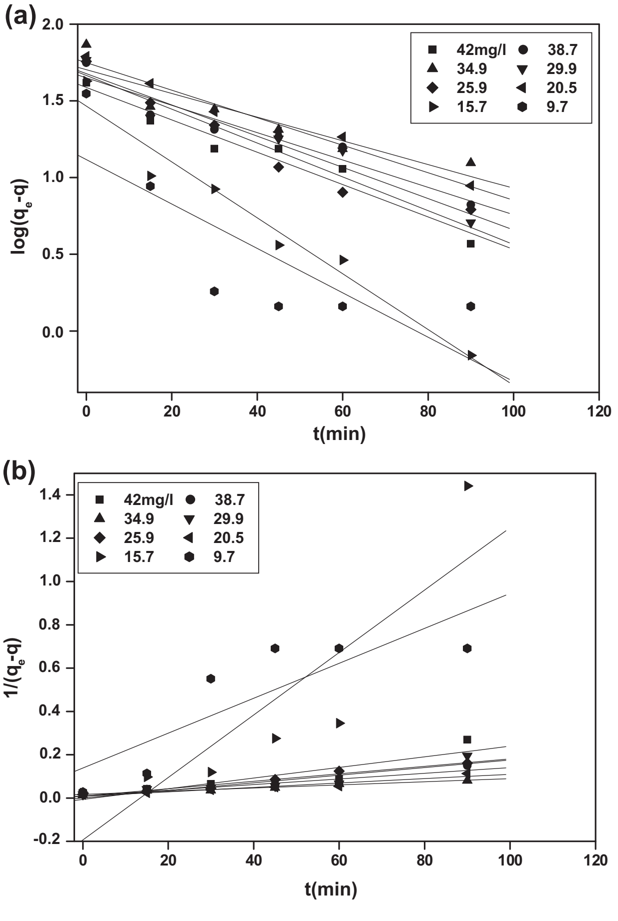

Fig. 5. Rate curves for BB 41 adsorption onto PAC at different initial dye solution concentrations (*T*: 25℃; *W*: 10 mg; *V*: 0.2 l) (a) pseudo-first-order rate, (b) pseudo-second-order rate.

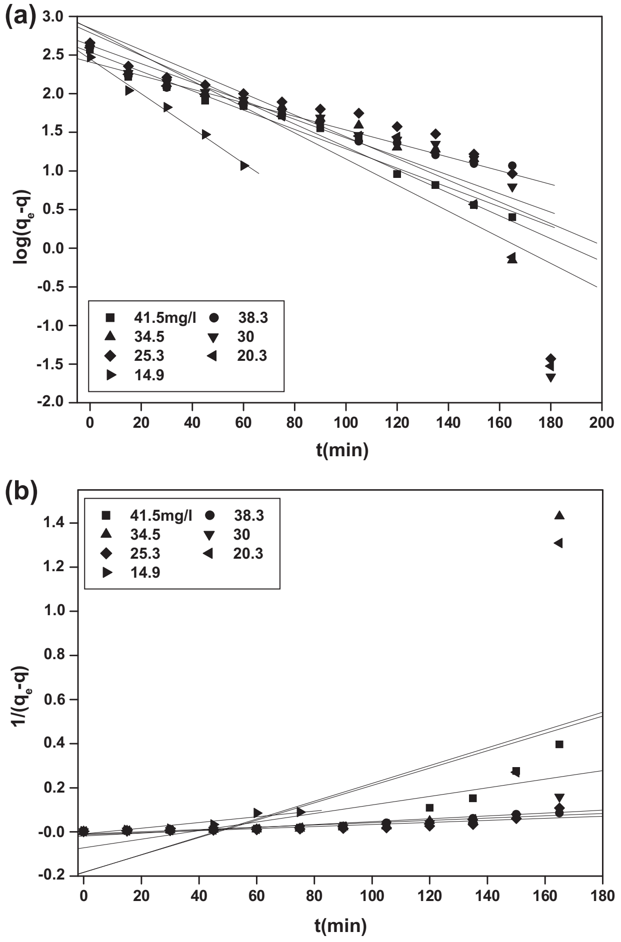

Fig. 6. Rate curves for BB 41 adsorption onto CAC at different initial dye solution concentrations (*T*: 25℃; *W*: 10 mg; *V*: 0.2 l) (a) pseudo-first-order rate, (b) pseudo-second-order rate.

higher temperature, and expansion and creation of reactive and active sites. If the capacity of adsorbent decreases with an increase in temperature, then it denotes an exothermic reaction. Physical adsorption decreases with increasing temperature, and chemical adsorption increases as the temperature increases. In the liquid phase, adsorption phenomena are sometimes endothermic, and therefore higher adsorbed

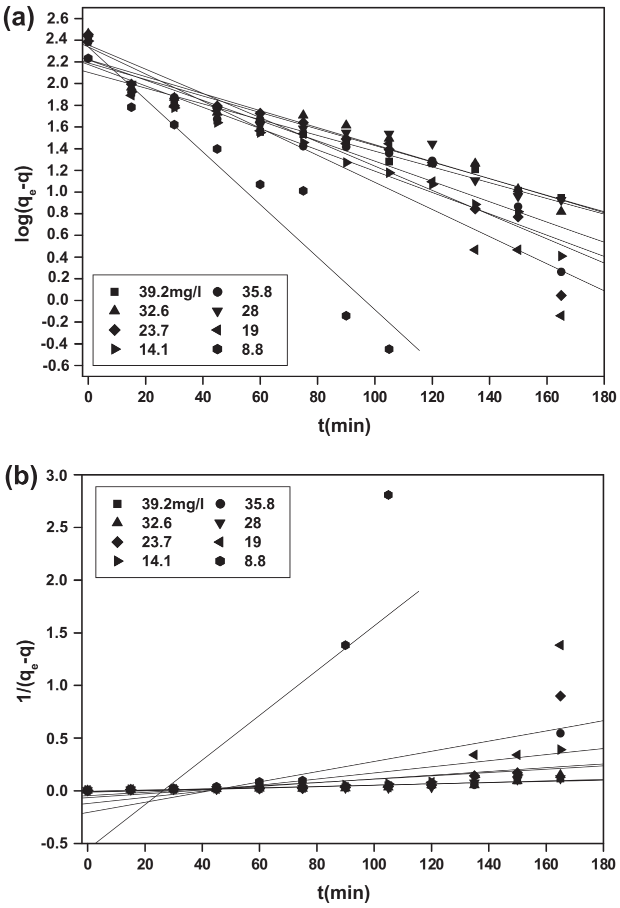

Fig. 7. Rate curves for BB 41 adsorption on AC at different initial dye solution concentrations (T: 25°C; W: 10 mg; V: 0.2 l) (a) pseudo-first-order rate, (b) pseudo-second-order rate.

amounts are obtained at higher temperature, which is the usual behavior of chemisorption.

The effects of temperature were studied at 25, 30, and 35°C for BB 41 adsorption onto AC, CAC, and PAC. Concentration changes with respect to time at different temperatures are illustrated in Fig. 4. Fig. 4(b) and (c) show that the adsorption of BB 41 increases with an increase in temperature. This indicates the endothermic nature of the adsorption reaction of BB 41 onto CAC and AC. The increase in adsorption capacity with an increase in temperature, indicating the endothermic nature of the process, was also supported by Ahmad and Kumar [32]. This has been widely observed in many studies [14,33–37].

The effect of temperature on BB 41 adsorption onto PAC was given in Fig. 4(a). From this figure, it can be seen that the adsorption of BB 41 onto this adsorbent decreased with an increase in temperature from 25 to 30°C, indicating the exothermic behavior as also reported in many studies [38–40]. On the other hand, when the temperature was raised from 30 to 35°C, the effect of temperature was not significant. For low concentrations, the effect of temperature on the adsorption equilibrium becomes insignificant.

3.3. Analysis of adsorption isotherms

The adsorption equilibrium data were compared with two isotherm models. The Langmuir and the Freundlich isotherm models were used for BB 41 adsorption onto PAC, CAC, and AC at 25, 30, and 35°C. Model constants and r^2 values were all evaluated and the results are presented in Table 2 for BB 41 onto PAC, CAC, and AC. The best fit was obtained with the Langmuir model with an r^2 value of 0.96 for BB 41 adsorption onto CAC and AC at 35 and 30°C, respectively. The values of the Langmuir adsorption isotherm constant corresponding to the maximum BB 41 surface

Table 3
Adsorption rate constants at different initial concentrations of BB 41 onto PAC (pH 7.7; W: 10 mg; V: 0.2 l)

C_0 (mg l^{-1})	k_1 (min^{-1})	r^2	k_2 (g mg^{-1} min^{-1})	r^2
T: 25°C				
42	2.43×10^{-2}	0.97	2.46×10^{-3}	0.89
38.7	2.21×10^{-2}	0.96	1.31×10^{-3}	0.93
34.9	1.78×10^{-2}	0.92	0.72×10^{-3}	0.98
29.9	2.34×10^{-2}	0.96	1.76×10^{-3}	0.90
25.9	2.54×10^{-2}	0.97	1.72×10^{-3}	0.99
20.5	2.07×10^{-2}	0.99	1.02×10^{-3}	0.96
15.7	4.19×10^{-2}	0.98	1.44×10^{-3}	0.88
9.7	3.34×10^{-2}	0.81	8.07×10^{-3}	0.85
Average	2.92×10^{-2}		2.31×10^{-3}	
T: 30°C				
38.7	3.03×10^{-2}	0.86	5.41×10^{-3}	0.89
34.8	1.96×10^{-2}	0.97	1.20×10^{-3}	0.97
30.6	2.34×10^{-2}	0.94	1.92×10^{-3}	0.99
25.7	9.78×10^{-2}	0.91	8.29×10^{-3}	0.94
20.8	2.43×10^{-2}	0.96	2.08×10^{-3}	0.94
15.4	1.38×10^{-2}	0.77	0.88×10^{-3}	0.78
9.9	2.03×10^{-2}	0.86	2.26×10^{-3}	0.95
4.2	3.79×10^{-2}	0.99	14.5×10^{-3}	0.92
Average	3.34×10^{-2}		4.57×10^{-3}	
T: 35°C				
38.7	2.82×10^{-2}	0.97	3.69×10^{-3}	0.87
34.5	1.61×10^{-2}	0.92	0.90×10^{-3}	0.98
30.3	5.29×10^{-2}	0.96	0.90×10^{-3}	0.98
25.1	6.34×10^{-2}	0.83	1.32×10^{-3}	0.95
20.6	1.81×10^{-2}	0.84	1.2×10^{-3}	0.93
15	2.26×10^{-2}	0.93	2.08×10^{-3}	0.96
9.7	5.67×10^{-2}	0.92	5.67×10^{-3}	0.96
4	3.66×10^{-2}	0.99	9.45×10^{-3}	0.90
Average	3.68×10^{-2}		3.15×10^{-3}	

coverage Q_0 at 25, 30, and 35°C were found as 96.4, 52.1, 54.7 mg g^{-1} for PAC adsorbent; 420.2, 427.4, and 460.8 mg g^{-1} for CAC; and 262.5, 283.3, and 293.3 mg g^{-1} for AC, respectively. The results have shown that the adsorption capacity of the adsorbent sample is greatly related to the surface area. The BET surface area of PAC, AC, and CAC samples obtained were 52.6, 741, and 1,325 m^2 g^{-1}, respectively. The lowest surface area sample PAC showed the lowest dye adsorption capacity. The commercial AC had a surface area of 15 times larger than that of phyically treated samples PAC, and had dye adsorption capacities about 2.7–5.4 times higher than that of PAC samples. Applying chemical treatment by use of KOH addition resulted in AC samples having 25 times larger surface area than that of PAC samples, and about 2 times larger surface area than the commercial AC samples. The highest BB 41 dye adsorption capacities were obtained with this KOH-treated AC sample produced. The increase in Q_0 with an increase in temperature indicates that at higher temperatures a greater number of dye molecules penetrated the pores.

Table 2 shows that there is a decrease from 96.4 to 52.1 mg g^{-1} in the adsorption capacity of BB 41 onto PAC as temperature increases. The decrease in sorption effectiveness with increasing temperature can be attributed to the exothermic nature of the sorption process. There is no further change when the temperature increases from 30 to 35°C. For CAC and AC, it was observed that the adsorption capacity increased with increase in temperature ranging from 25, 30, 35°C, indicating the endothermic nature of the adsorption reaction of BB 41 onto CAC and AC as shown in Table 2.

3.4. Kinetics of adsorption

Typical Lagergren plots corresponding to the pseudo-first-order adsorption kinetics and pseudo-

Table 4
Adsorption rate constants at different concentrations of BB 41 onto CAC for natural pH (pH 7.7; *W*: 10 mg; *V*: 0.2 l)

C_0 (mg l^{-1})	k_1 (min^{-1})	r^2	k_2 (g mg^{-1} min^{-1})	r^2
T: 25°C				
41.5	2.88×10^{-2}	0.99	1.94×10^{-3}	0.83
38.3	2.02×10^{-2}	0.99	0.51×10^{-3}	0.95
34.5	2.77×10^{-2}	0.91	0.42×10^{-3}	0.93
30	3.41×10^{-2}	0.82	0.65×10^{-3}	0.80
25.3	2.24×10^{-2}	0.81	0.46×10^{-3}	0.81
20.3	3.89×10^{-2}	0.89	4.03×10^{-3}	0.59
14.9	5.18×10^{-2}	0.99	1.26×10^{-3}	0.89
Average	3.20×10^{-2}		1.32×10^{-3}	
T: 30°C				
40.7	3.22×10^{-2}	0.77	0.37×10^{-3}	0.86
37.7	1.81×10^{-2}	0.99	0.35×10^{-3}	0.88
33.5	2.60×10^{-2}	0.94	1.78×10^{-3}	0.61
29.8	2.20×10^{-2}	0.99	0.61×10^{-3}	0.81
24.1	2.16×10^{-2}	0.96	0.74×10^{-3}	0.65
20.2	2.54×10^{-2}	0.99	0.68×10^{-3}	0.84
14.7	5.22×10^{-2}	0.99	1.37×10^{-3}	0.89
Average	2.82×10^{-2}		0.84×10^{-3}	
T: 35°C				
40.7	1.76×10^{-2}	0.99	0.28×10^{-3}	0.93
37.4	2.77×10^{-2}	0.83	0.23×10^{-3}	0.94
33.7	1.98×10^{-2}	0.99	0.36×10^{-3}	0.92
29.8	1.85×10^{-2}	0.99	0.29×10^{-3}	0.91
24.8	1.84×10^{-2}	0.99	0.3×10^{-3}	0.93
19.8	2.39×10^{-2}	0.98	0.85×10^{-3}	0.79
14.8	5.22×10^{-2}	0.99	2.19×10^{-3}	0.88
Average	2.54×10^{-2}		0.64×10^{-3}	

Table 5
Adsorption rate constants at different concentrations of BB 41 onto AC for natural pH (pH 7.7; *W*: 10 mg; *V*: 0.2 l)

C_0 (mg l^{-1})	k_1 (min^{-1})	r^2	k_2 (g mg^{-1} min^{-1})	r^2
T: 25°C				
39.2	1.67×10^{-2}	0.96	0.59×10^{-3}	0.94
35.8	2.15×10^{-2}	0.94	1.77×10^{-3}	0.64
32.6	1.81×10^{-2}	0.96	0.67×10^{-3}	0.85
28	1.75×10^{-2}	0.96	0.63×10^{-3}	0.88
23.7	2.57×10^{-2}	0.95	2.9×10^{-3}	0.62
19	2.87×10^{-2}	0.94	4.84×10^{-3}	0.66
14.1	2.26×10^{-2}	0.98	1.57×10^{-3}	0.79
8.8	5.58×10^{-2}	0.96	21.2×10^{-3}	0.76
Average	2.58×10^{-2}		4.27×10^{-3}	
T: 30°C				
39.7	1.75×10^{-2}	0.97	0.65×10^{-3}	0.83
36.7	1.94×10^{-2}	0.97	0.76×10^{-3}	0.87
32.5	2.26×10^{-2}	0.97	1.28×10^{-3}	0.74
28.9	7.55×10^{-2}	0.85	0.31×10^{-3}	0.97
23.9	1.45×10^{-2}	0.96	0.56×10^{-3}	0.91
19.3	1.78×10^{-2}	0.97	0.95×10^{-3}	0.86
14.2	2.09×10^{-2}	0.98	1.32×10^{-3}	0.80
9.3	2.20×10^{-2}	0.98	1.98×10^{-3}	0.90
Average	2.63×10^{-2}		0.98×10^{-3}	
T: 35°C				
40.3	5.74×10^{-2}	0.92	$0.58 \text{ x } 10^{-3}$	0.94
36.6	1.56×10^{-2}	0.96	0.40×10^{-3}	0.96
33.4	3.18×10^{-2}	0.76	0.54×10^{-3}	0.91
28.7	1.97×10^{-2}	0.93	0.96×10^{-3}	0.62
25	3.86×10^{-2}	0.91	1.61×10^{-3}	0.78
19.6	2.49×10^{-2}	0.95	1.6×10^{-3}	0.75
14.8	2.53×10^{-2}	0.95	2.36×10^{-3}	0.72
9.1	3.85×10^{-2}	0.93	0.99×10^{-3}	0.99
Average	3.15×10^{-2}		1.13×10^{-3}	

second-order kinetic models of BB 41 adsorption onto PAC, CAC, and AC at 25˚C for natural pH of BB 41 are given in Figs. 5–7. The values of the adsorption rate constants calculated for different initial concentrations of BB 41 at different temperatures are shown in Tables 3–5. Kinetic data were adequately fitted by the pseudo-first-order kinetic model. For PAC, k_1 has values of 0.0292, 0.0334, and 0.0368 min^{-1}; and k_2 has values of 0.00231, 0.00457, and 0.00315 $\mathrm{g\,mg^{-1}\,min^{-1}}$ at 25, 30, and 35˚C, respectively. For CAC, k_1 values are 0.032, 0.0282, and 0.0254 min^{-1}; and k_2 values are 0.00132, 0.00084, and 0.00064 $\mathrm{g\,mg^{-1}\,min^{-1}}$ at 25, 30, and 35˚C, respectively. AC has values of 0.0258, 0.0263, and 0.0315 min^{-1} for k_1 and values of 0.00427, 0.00098, and 0.00113 $\mathrm{g\,mg^{-1}\,min^{-1}}$ for k_2 at these temperatures, respectively.

The adsorption rate data of BB 41 onto PAC, CAC, and AC at different concentrations was found to follow first-order kinetics with higher values of r^2. There have been many studies in which a first-order kinetics were reported for the adsorption of basic dyes onto some different adsorbents [35,37,41,42].

4. Conclusions

The BET surface area of PAC, AC, and CAC samples obtained were 52.6, 741, and 1,325 $\mathrm{m^2\,g^{-1}}$, respectively. Applying chemical treatment by use of KOH addition resulted in AC samples having 25 times larger surface area than that of PAC samples, and about 2 times higher surface area than the commercial AC samples. Thermal treatment with KOH resulted in enhancement in the porosity characteristics particularly in micropores, and the surface area of the CAC samples. Surface analysis results have shown that PAC is not sufficient on its own to enhance the surface area and the micropore volumes, but chemical treatment with KOH was a very effective way of increasing the micropores and the surface area of the coal particles.

The values of the Langmuir adsorption isotherm constant corresponding to the maximum surface coverage of dye Q_0 at 25, 30, and 35˚C were found as 96.4, 52.1, and 54.7 $\mathrm{mg\,g^{-1}}$ for PAC adsorbent; 420.2, 427.4, and 460.8 $\mathrm{mg\,g^{-1}}$ for CAC; and 262.5, 283.3, and 293.3 $\mathrm{mg\,g^{-1}}$ for AC, respectively. The adsorption capacity of the adsorbent was greatly related to the surface area. The highest BB 41 dye adsorption capacities were obtained with the KOH-treated AC sample.

Adsorption capacity increased with increase in temperature for BB 41 onto CAC and AC, so the adsorption process was endothermic, this was attributed to increased surface coverage at higher temperature, expansion, and creation of reactive and active sites, which is the usual behavior of chemisorption. For BB 41 adsorption onto PAC, the decrease in sorption effectiveness caused by increased temperature indicated the exothermic nature of the sorption process that is related to physisorption. Physical adsorption decreases with increasing temperature, and chemical adsorption increases as the temperature increases.

Kinetic data adequately fit the pseudo-first-order kinetic model. This study shows that CAC is an effective adsorbent for the removal of BB 41 dye from aqueous solutions. The adsorption capacity of the studied adsorbents was found to decrease in the order CAC > AC > PAC. The amount of dye adsorbed was found to be dependent on temperature, adsorbent type, contact time, and initial dye concentration. CAC was the most effective adsorbent for BB 41 adsorption under all conditions in this study. The present study shows that AC prepared from coal by CAC could be effectively used for the adsorptive removal of BB 41 from aqueous solutions.

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Nomenclature

b	—	Langmuir model constant ($\mathrm{l\,mg^{-1}}$)
C	—	concentration of BB 41 in solution at time t ($\mathrm{mg\,l^{-1}}$)
C_0	—	initial concentration of BB 41 in solution ($\mathrm{mg\,l^{-1}}$)
C_e	—	concentration of BB 41 in solution at equilibrium ($\mathrm{mg\,l^{-1}}$)
K_f	—	Freundlich isotherm constant
k_1	—	pseudo-first-order adsorption rate constant ($\mathrm{min^{-1}}$)
k_2	—	pseudo-second-order adsorption rate constant ($\mathrm{g\,mg^{-1}\,min^{-1}}$)
n	—	exponent in Freundlich isotherm model
q	—	concentration of BB 41 adsorbed in the adsorbent at time t ($\mathrm{mg\,g^{-1}}$)
q_e	—	equilibrium concentration of BB 41 adsorbed in the adsorbent ($\mathrm{mg\,g^{-1}}$)
r^2	—	square of the correlation coefficient
Q_0	—	Langmuir constant corresponding to monolayer sorption capacity ($\mathrm{mg\,g^{-1}}$)
t	—	time (min)
T	—	temperature (˚C)
V	—	volume of solution (l)
W	—	amount of adsorbent (g)
λ_max	—	maximum wavelength (nm)

References

[1] V.M. Correia, T. Stephenson, S.J. Judd, Characterisation of textile wastewaters: A review, Environ. Technol. 15 (1994) 917–929.

[2] A. Khaled, A. El Nemr, A. El Sikaily, O. Abdelwahab, Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon, Desalination 238 (2009) 210–232.

[3] P.C. Vandervivere, R. Binachi, W. Verstrate, Treatment of watewater from textile, wet processing industry: Review of emerging Technologies, J. Chem. Technol. Biotechnol. 72 (1998) 289–302.

[4] V.K. Gupta, S. Suhas, Application of low-cost adsorbents for dye removal—A review, J. Environ. Manage. 90 (2009) 2313–2342.

[5] Ö. Gök, A.S. Özcan, A. Özcan, Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite, Appl. Surf. Sci. 256 (2010) 5439–5443.

[6] G. Sun, X. Xu, Sunflower stalks as adsorbents for color removal from textile wastewater, Ind. Eng. Chem. Res. 36(3) (1997) 808–812.

[7] M.M. Nassar, Y.H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, Chem. Eng. J. 66 (1997) 223–226.

[8] C. Namasivayam, D.J.S.E. Arasi, Removal of congo red from wastewater by adsorption onto waste red mud, Chemosphere 34 (1997) 401–417.

[9] K. Kadirvelu, M. Palanival, R. Kaplana, S. Rajeswari, Activated carbon from an agricultural by-product for the treatment of dyeing industry wastewater, Bioresour. Technol. 74 (2000) 263–265.

[10] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—A comparative study, Dyes Pigm. 51 (2001) 25–40.

[11] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions, Waste Manage. 21 (2001) 105–110.

[12] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigm. 54 (2002) 47–58.

[13] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Comparison of optimised isotherm models for basic dye adsorption by kudzu, Bioresour. Technol. 88 (2003) 143–152.

[14] M. Doğan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, Chemosphere 50 (2003) 517–528.

[15] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of Acid Yellow 36, Dyes Pigm. 56 (2003) 239–249.

[16] M. Alkan, Ö. Demirbaş, M. Doğan, Removal of acid yellow 49 from aqueous solution by adsorption, Fresenius Environ. Bull. 13 (2004) 1112–1121.

[17] F. Kargi, S. Ozmıhcı, Comparison of adsorption performances of powdered activated sludge and powdered activated carbon for removal of turquoise blue dyestuff, Process Biochem. 40 (2005) 2539–2544.

[18] A.A. Attia, W.E. Rashwan, S.A. Khedr, Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, Dyes Pigm. 69 (2006) 128–136.

[19] K.V. Kumar, S. Sivanesan, Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon, J. Hazard. Mater. 134 (2006) 237–244.

[20] Y. Yasin, M.Z. Hussein, F.H. Ahmad, Adsorption of methylene blue onto treated activated carbon, The Malaysian J. Anal. Sci. 11 (2007) 400–406.

[21] J. Yener, T. Kopac, G. Dogu, T. Dogu, Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, J. Colloid Interface Sci. 294 (2006) 255–264.

[22] J. Yener, T. Kopac, G. Dogu, T. Dogu, Batch Adsorber rate analysis of methylene blue on amberlite and clinoptilolite, Sep. Sci. Technol. 41 (2006) 1857–1879.

[23] J. Yener, T. Kopac, G. Dogu, T. Dogu, Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon, Chem. Eng. J. 144 (2008) 400–406.

[24] Ö. Demirbaş, M. Alkan, Adsorption kinetics of a cationic dye from wastewater, Desalin. Water Treat. 53(13) (2015) 3623–3631.

[25] Ö. Demirbaş, Y. Turhan, M. Alkan, Thermodynamics and kinetics of adsorption of a cationic dye onto sepiolite, Desalin. Water Treat. 54(3) (2015) 707–714.

[26] M. Wawrzkiewicz, M. Wiśniewska, V.M. Gun'ko, V.I. Zarko, Adsorptive removal of acid, reactive and direct dyes from aqueous solutions and wastewater using mixed silica–alumina oxide, Powder Technol. 278 (2015) 306–315.

[27] F. Kooli, L. Yan, R. Al-Faze, A. Al-Sehimi, Removal enhancement of basic blue 41 by brick waste from an aqueous solution, Arab. J. Chem. 8 (2015) 333–342.

[28] T. Kopac, A. Toprak, Preparation of activated carbons from Zonguldak region coals by physical and chemical activations for hydrogen sorption, Int. J. Hydrogen Energy 32 (2007) 5005–5014.

[29] W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by $ZnCl_2$ activation, Chemosphere 45 (2001) 51–58.

[30] L. Wang, J. Zhang, R. Zhao, C. Li, Y. Li, C. Zhang, Adsorption of basic dyes on activated carbon prepared from Polygonum orientale Linn: Equilibrium, kinetic and thermodynamic studies, Desalination 254 (2010) 68–74.

[31] V. Gómez, M.S. Larrechi, M.P. Callao, Kinetic and adsorption study of acid dye removal using activated carbon, Chemosphere 69 (2007) 1151–1158.

[32] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage. 91 (2010) 1032–1038.

[33] S.K. Alpat, Ö. Özbayrak, Ş. Alpat, H. Akçay, The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite, J. Hazard. Mater. 151 (2008) 213–220.

[34] M. Doğan, H. Abak, M. Alkan, Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters, J. Hazard. Mater. 164 (2009) 172–181.

[35] D. Mohan, K.P. Singh, G. Singh, K. Kumar, Removal of dyes from wastewater using flyash, a low-cost adsorbent, Ind. Eng. Chem. Res. 41 (2002) 3688–3695.

[36] M. Doğan, M. Alkan, A. Türkyılmaz, Y. Özdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, J. Hazard. Mater. B109 (2004) 141–148.

[37] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder, Dyes Pigm. 65 (2005) 51–59.

[38] M. Doğan, M.H. Karaoğlu, M. Alkan, Adsorption kinetics of maxilon yellow 4GL and maxilon red GRL dyes on kaolinite, J. Hazard. Mater. 165 (2009) 1142–1151.

[39] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Adsorption of congo red by three Australian kaolins, Appl. Clay Sci. 43(3–4) (2009) 465–472.

[40] R. Jain, M. Shrivastava, Adsorptive studies of hazardous dye Tropaeoline 000 from an aqueous phase on to coconut-husk, J. Hazard. Mater. 158 (2008) 549–556.

[41] R. Gong, M. Lı, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. 121 (2005) 247–250.

[42] Y.C. Sharma, U.S.N. Upadhyay, F. Gode, Adsorptive removal of a basic dye from water and wastewater by activated carbon, J. Appl Sci. Environ. Sanita. 4(1) (2009) 21–28.