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Application of physicochemically prepared activated carbon fiber for the removal of basic blue 3 from water

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ABSTRACT

In this study the adsorption of basic blue 3 (BB3) from aqueous solution onto activated carbon fiber (ACF) derived from Kenaf have been investigated. The adsorption studies include both equilibrium and kinetics. Langmuir, Freundlich and Temkin isotherm models were used to illustrate the experimental Equilibrium data and their constants. Obtained results revealed that equilibrium data fitted reasonably to the Langmuir isotherm model. According to Langmuir model, adsorption of BB3 on ACF was monolayer and the maximum adsorption capacity was 666.67 mg/g. The kinetic of adsorption was evaluated by pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. Results of Kinetic studies showed that the adsorption process follows the pseudo-second-order model. According to pseudo-second-order model the rate limiting step may be chemisorptions.

Keywords: Activated carbon fiber; Kenaf; Basic blue 3

1. Introduction

Dyes have been extensively used in many industries, such as textile, paper, leather, wood and ink. Considering its high consumption volume, Dyes discharge into the environment is worrying for both toxicological and aesthetical reasons so it is necessary to find appropriate dye removal techniques [1].

Among several chemical and physical methods, the adsorption onto activated carbons (ACs) has been found to be one of the effective methods to removal of dyes from aqueous solutions. ACs are capable for efficient adsorption of a broad range of pollutants and design of adsorption systems is simple [2].

Activated carbons are frequently used in granular and powdered form to remove synthetic organic chemicals from contaminated water. However, activated carbon fibers (ACF) and activated carbon cloth (ACC) have recently attracted attention as better adsorbents than granular activated carbon in liquid phase applications, since they usually present much higher adsorption rate and capacity [3].

Preparation of ACs is generally classified as physical and chemical activation methods. In general, physical activation using oxidizing gases such as CO_2 and steam was found to significantly develop pores in a wide range of diameters. Chemical activation with oxidizing chemicals such as KOH, or H_3PO_4, on the other hand, is used to form micropores which are expected to effectively produce surface functional groups [4]. Thus, a combined physicochemical activation process is a potential technique in preparing ACs for the removal of dyes from aqueous solutions.

The purpose of this work was investigation of the possibility of physicochemically prepared ACF as an adsorbent with high surface area for the removal of Basic blue 3 (BB3) from aqueous solution. The equilibrium and kinetic model of adsorption process were processed to understand the ability of the prepared ACF for BB3 removal.

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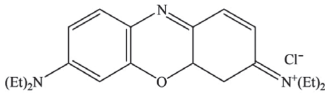
2. Materials and methods

2.1. Materials

Kenaf was obtained from a local market in the Iran. Other chemicals were analytical grades. The molecular structure and characteristic of BB3 is shown in Table 1 [5].

Table 1
Properties of BB3

Commercial name	Cationic blue X-GB
Structure	
Color index number	51004
Molecular weight (g/mol)	359.9
Molecular formula	$C_{20}H_{26}C_{1}N_{3}O$
l_{max} (nm) in H_2O solution (nm)	654

2.2. Preparation procedure and surface characteristics of activated carbon fiber

ACF was prepared from Kenaf by physicochemical activation method using carbonization at 300 °C under inert atmosphere with N_2 flow for 1 h, then impregnation with 30% w/v K_2HPO_4 solution and finally activation at 850 °C for 2 h under atmosphere of carbon dioxide (CO_2) with the rate of achieving the activation temperature equal to 2 °C/min.

The specific surface area of the prepared ACF was 1842 m^2/g , with total pore volume of 0.850 cm^3/g. Iodine number of ACF was 1114 mg/g and its pH_{PZC} was determined equal to 7.3 at which the ACF surface has net electrical neutrality.

2.3. Batch equilibrium and kinetic studies

The equilibrium adsorption experiments have been done to assess the ability of prepared ACF to remove BB3 from aqueous solution and also to find isotherm constants. For this purpose 100 ml of BB3 solutions with different initial concentrations were prepared in erlenmeyer flasks (250 ml). Equal masses of 0.05 g of ACF were added to BB3 solutions and kept in an isothermal shaker (28 ± 1 °C, 170 rpm) to reach the equilibrium of the solid-solution mixture. The flasks were then removed from the shaker and samples were withdrawn by syringe and the concentration of BB3 was determined using a UV-vis spectrophotometer (Perkin-Elmer 550SE, Germany) at 654 nm. The adsorption capacity of the adsorbent at equilibrium, q_e (mg/g), was calculated by:

$$q_e = V\,\frac{C_0 - C_e}{w} \qquad (1)$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of BB3 at initial and equilibrium, respectively. V is the volume of the solution (l) and w is the mass of ACF (g) [5].

The kinetic experiments had a similar procedure with those of equilibrium tests with initial dye concentration of 20 mg/l and ACF masses of 0.015 g. At different time intervals the concentration of the residual pollutant in the solution was analyzed by the same procedure as batch equilibrium studies. The adsorption capacity of the adsorbent at time t, q_t (mg/g), was calculated by

$$q_t = V\,\frac{C_0 - C_t}{w} \qquad (2)$$

where C_t (mg/l) is the liquid-phase concentration of dye at time t [6].

2.4. Model fitting

2.4.1. Isotherm models

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [7]. It is important to establish the most appropriate correlation for the equilibrium curves. An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium [5]. The equilibrium isotherms of BB3 were analyzed using Langmuir, Freundlich and Temkin isotherm models.

The Langmuir adsorption isotherm is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent and once an adsorbate molecule occupies a site, no further adsorption takes place at that site. Theoretically, the sorbent has a finite capacity to adsorb the adsorbate. Therefore, a saturation value is reached beyond which no further sorption takes place. The monolayer capacity can be represented by the expression:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \qquad (3)$$

The linear form of the above equation is represented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \tag{4}$$

where C_e is the concentration of the BB3 solution (mg/l) at equilibrium, q_e the amount of BB3 adsorbed per unit weight of adsorbent (mg/g) and K_L is the constant related to the free energy of adsorption (l/mg). q_{max} (mg/g) is the maximum adsorption capacity. The values of q_{max} and K_L were calculated from the slope and intercept of the plot of C_e/q_e as a function of C_e. The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L:

$$R_L = \frac{1}{1 + K_L} C_0 \tag{5}$$

The value of R_L indicates the type of isotherm to be favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or irreversible $R_L = 0$ [8&9].

The Freundlich equation is an empirical equation employed to describe heterogeneous systems:

$$q_e = K_f C_e^{1/n_f} \tag{6}$$

where the K_f is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent ((mg/g^{-1})(l/mg)$^{1/n}$) and n_f is the heterogeneity factor. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. The linear form of Eq. (6), can be obtained by taking logarithm of both sides of it:

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \tag{7}$$

A plot of ln q_e versus ln C_e yields straight lines, which permits the determination of $1/n_f$ and K_f from the slope and intercept [10].

Another model, Temkin isotherm, was also used to fit the experimental data. Temkin isotherm which accounts for multilayer adsorption can be explained with the existence of a heterogeneous pore distribution. Unlike the Langmuir and Freundlich equations, the Temkin isotherm takes into account the interactions between adsorbent and BB3 to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [11]. The isotherm is as follows:

$$q_e = \frac{RT}{b} \ln\,(AC_e) \tag{8}$$

where A is the equilibrium binding constant corresponding to the maximum binding energy, b is the Temkin isotherm constant, T is the temperature (K), and R is the ideal gas constant (8.314 J/molK). A linear form of the Temkin isotherm can be expressed as:

$$q_e = B \ln A + B \ln C_e \tag{9}$$

where $B = RT/b$ [9].

2.4.2. Kinetic models

Three simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the pseudo-first-order equation as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

where q_e and q_t are the amounts of BB3 adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of adsorption.

The pseudo-second-order equation based on equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

where k_2 (g/mg·min) is the rate constant of second-order adsorption [7].

When the diffusion (internal surface and pore diffusion) of dye molecules inside the adsorbent is the rate-limiting step, then adsorption data can be presented by the following equation:

$$q_t = k_i t^{\frac{1}{2}} \tag{12}$$

where k_i (mg/g·min$^{\frac{1}{2}}$) is the intraparticle diffusion rate constant. The k_i values are found from the slopes of q_t versus $t^{\frac{1}{2}}$ plots [11].

3. Results and disscussion

3.1. Adsorption isotherms

In order to optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Adsorption equilibrium is established when the amount of dye being adsorbed onto the adsorbent is equal to the amount being desorbed. It is possible to depict the equilibrium adsorption isotherms by plotting the concentration of the dye in the solid phase versus that in the liquid phase. Adsorption isotherms of dye were determined on the basis of batch analysis using a series of dye solutions at varying concentration in contact with ACF pieces of fixed masses. Adsorption isotherm data of dye were fitted to well-known and widely applied isotherm models such as Langmuir, Freundlich and Temkin using the plots of (C_e/q_e) against q_e, ln q_e against ln C_e and q_e against ln C_e, respectively (Fig. 1).

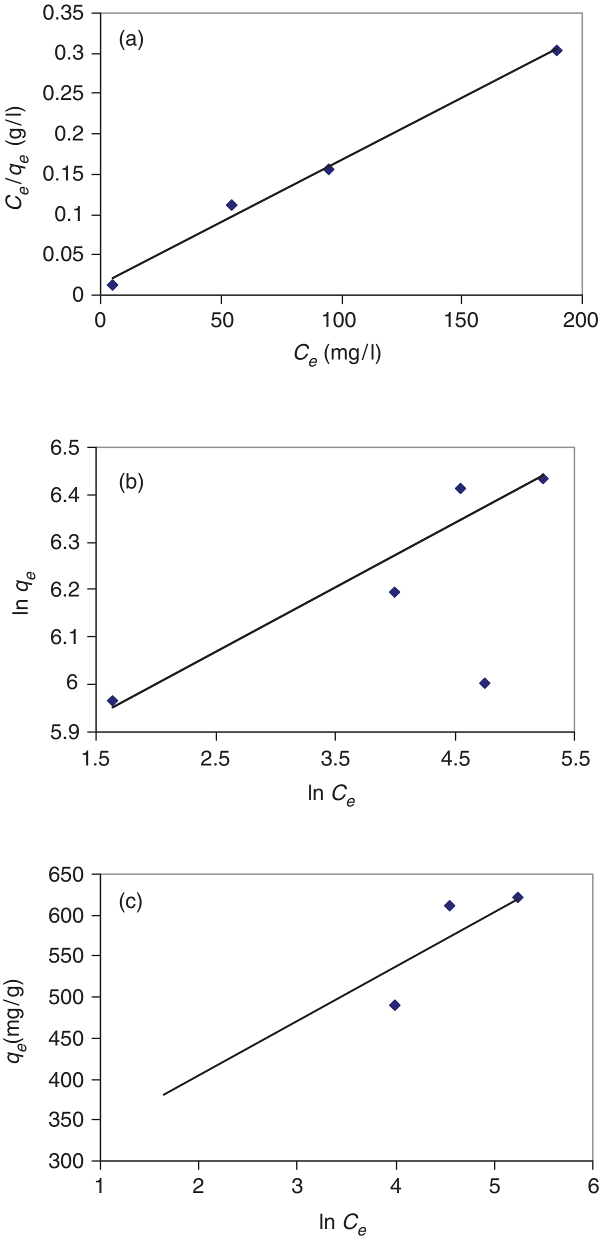


Fig. 1. Isotherm models for BB3 adsorption on ACF (T = 28 °C, m = 0.05 g, V = 100 ml, pH = 6, agitation rate = 170 rpm and t = 3 d); (a) Langmuir, (b) Freundlich and (c) Temkin.

The Langmuir isotherm parameters for the adsorption of dye onto ACF were determined using Fig. 1a. The q_{max} and K_L according to Langmuir isotherm were 666.67 mg/g and 0.115 l/mg, respectively with correlation coefficient of 0.9940 (Table 2). The value of R_L for adsorption of BB3 onto activated carbon was 0.017. These values indicate that the adsorption behavior of activated carbon is favorable for the BB3 ($0 < R_L < 1$).

The Freundlich isotherm constants for the adsorption of BB3 onto ACF were obtained using Fig. 1b. Values of K_f and n_f were determined equal to 307.11 and 7.396 respectively with R^2 of 0.9274. The parameter K_f is related to the distribution coefficient, and consequently to the degree of BB3 affinity and mobility to the ACF. The value of $n_{f,}$ which is greater than unity, indicates that BB3 is favorably adsorbed by activated carbon. The results obtained from analyzing the experimental isotherm adsorption data with Temkin isotherm (Fig. 1c) are shown in Table 2, too.

From Table 2, the correlation coefficient for the Langmuir isotherm is significantly higher than the other isotherms. The order of R^2 was Temkin < Freundlich < Langmuir. Therefore, the Langmuir isotherm has the best fitting to the BB3 adsorption data. This model is obtained under the ideal assumption of a totally homogenous adsorption surface. It is then assumed that once an adsorbate molecule occupies a site, no further adsorption can take place at that site. As a result, a saturation value is reached and no further adsorption can take place [5].

3.2. Kinetic studies

Kinetic models are used to determine the rate of the adsorption process. Pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used to investigate the adsorption process of BB3 on ACF

Table 2
Langmuir, Freundlich and Temkin isotherms constants for BB3 adsorption on ACF (T = 28 °C, m = 0.05 g, V = 100 ml, pH = 6, agitation rate = 170 rpm and t = 3 d)

Isotherm	Parameters	Values
Langmuir	q_{max} (mg/g)	666.67
	K_L (l/mg)	0.115
	R^2	0.9940
	R_L	0.017
Freundlich	K_f ((mg/g)·(l/mg)$^{1/n}$)	307.11
	n_f	7.396
	R^2	0.9274
Temkin	A(l/mg)	58.00
	B	66.72
	R^2	0.9015

using the plots of ln $(q_e - q_t)$ against t, t/q_t against t and q_t against $t^{\frac{1}{2}}$, respectively (Fig. 2). The pseudo-first-order rate constants for this study were calculated using plot of Fig. 2a. The values of k_1 and calculated q_e were determined as 0.03 and 76.46, respectively with R^2 equal to 0.9743 (Table 3).

The pseudo-second-order model parameters for the adsorption of BB3 onto ACF were also obtained. According to Fig. 2 b, BB3 adsorption on ACF fitted reasonably with pseudo-second-order model with R^2 of 0.9895. The calculated q_e values (Table 3), indicating the applicability of this model to describe the adsorption process of BB3 onto the ACF [7]. The possibility of fitting intraparticle diffusion model to the adsorption of BB3 onto ACF was investigated, too. The k_i value was calculated and is shown in Table 3.

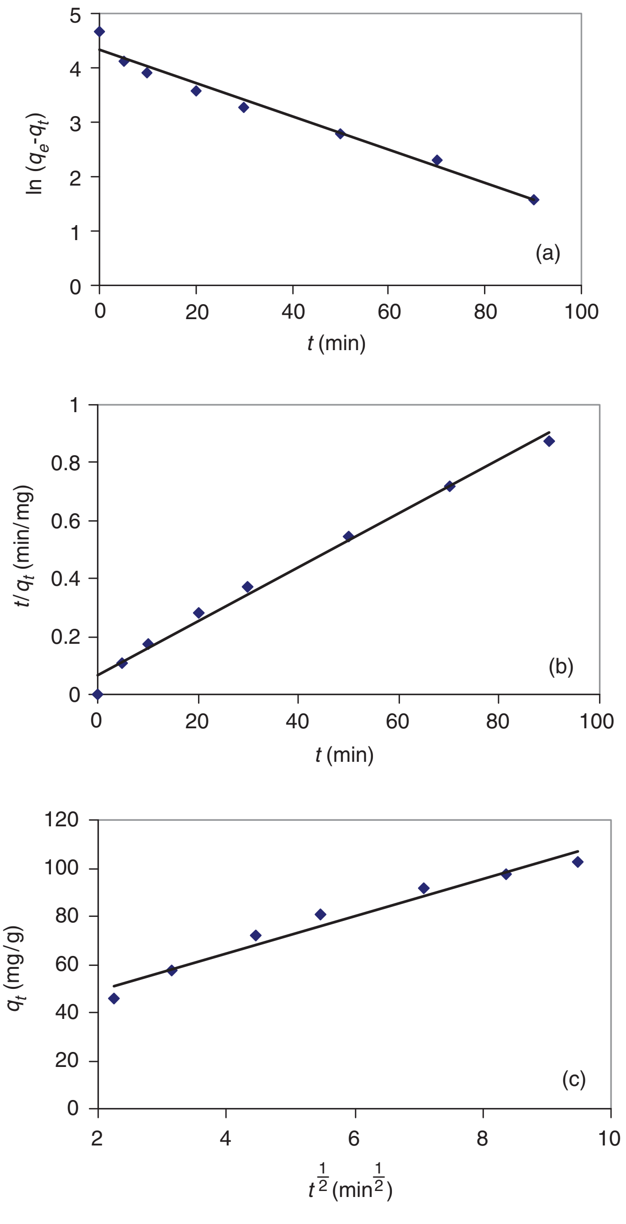


Fig. 2. Adsorption kinetics of BB3 on ACF (C_0 = 20mg/l, T = 28 °C, m = 0.015 g, V = 100 ml, pH = 6 and agitation rate = 170 rpm); (a) pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion.

Table 3
The constants of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models for BB3 adsorption on the ACF (C_0 = 20 mg/l, T = 28 °C, m = 0.015 g, V = 100 ml, pH = 6 and agitation rate = 170 rpm)

Kinetic models	Parameters	Values
Pseudo-first-order	K_1 (1/min)	0.03
	R^2	0.9743
	q_e (mg/g)	76.46
Pseudo-second-order	K_2 (g/mg min)	0.0013
	R^2	0.9895
	q_e (mg/g)	107.53
Intraparticle diffusion	k_i (mg/g·min$^{1/2}$)	10.07
	R^2	0.9137

From Table 3, the R^2 for the pseudo second-order kinetic model is significantly higher than the other isotherms. The order of correlation coefficient was intraparticle diffusion < pseudo-first-order < pseudo-second-order. Therefore, the adsorption process can be most satisfactorily described by the pseudo-second-order kinetic model for dye adsorption onto the activated carbon. This is on the hypothesis that the rate limiting step may be chemisorptions which is related to valence forces through sharing or exchange of electrons between adsorbent and adsorbate [7].

4. Conclusion

Experimental results indicate that ACF prepared from Kenaf could remove BB3 from aqueous solution. Langmuir model better fits the experimental data so the adsorption takes place in monolayer. The adsorption reaction can be satisfactorily described by the pseudo-second-order kinetic model.

Symbols

A	—	a constant of Temkin isotherm related to adsorption heat
AC	—	activated carbons
ACF	—	Activated Carbon Fiber
ACC	—	Activated Carbon cloth
B	—	maximum binding energy, the equilibrium binding constant in Temkin isotherm (l/mg)
C_0	—	initial concentration of pollutants in solution (mg/l or mol/l)

C_e — equilibrium concentration of pollutants in solution (mg/l or mol/l)
C_t — concentration of adsorbate in the solution at time t (mg/l)
k_1 — the rate constant of pollutant adsorption in pseudo-first-order kinetic model (1/min)
k_2 — the rate constant of adsorption in pseudo-second-order kinetic model (g/mg·min)
k_i — the rate constant of adsorption in intraparticle diffusion kinetic model (mg/g·min$^{1/2}$)
K_f — adsorption capacity of the adsorbent ((mg/g).(l/mg)$^{1/n}$), a constant of Freundlich isotherm
K_L — Langmuir constant, which indicates the intensity of adsorption (l/mg)
m — mass of ACF (g)
n_f — constant of Freundlich isotherm
q_{max} — maximum adsorption capacity on unit mass of adsorbent (mg/g), a constant of Langmuir isotherm
q_e — equilibrium amount of adsorbed pollutant per unit mass of adsorbent (mg/g or mol/g)
q_t — amount of pollutant adsorbed at time t per unit mass of adsorbent (mg/g)
R — the universal constant of gases (kJ/mol·K)
R^2 — linear regression coefficient
R_L — dimensionless separation factor for Langmuir isotherm
T — adsorption temperature (K or °C)
t — time (min or h)
V — volume of the solution (l)

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