ELSEVIER

Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent—Silkworm pupa

B. Noroozi [b], G.A. Sorial [a,*], H. Bahrami [b], M. Arami [b]

[a] *Department of Civil and Environmental Engineering, University of Cincinnati, P.O. Box 210071, Cincinnati, OH 45221-0071, United States*
[b] *Textile Engineering Department, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran*

Abstract

In this work the use of silkworm pupa, which is the waste of silk spinning industries has been investigated as an adsorbent for the removal of C.I. Basic Blue 41. The amino acid nature of the pupa provided a reasonable capability for dye removal. Equilibrium adsorption isotherms and kinetics were investigated. The adsorption equilibrium data were analyzed by using various adsorption isotherm models and the results have shown that adsorption behavior of the dye could be described reasonably well by either Langmuir or Freundlich models. The characteristic parameters for each isotherm have been determined. The monolayer adsorption capacity was determined to be 555 mg/g. Kinetic studies indicated that the adsorption follows pseudo-second-order kinetics with a rate constant of 0.0434 and 0.0572 g/min mg for initial dye concentration of 200 mg/l at 20 and 40 °C, respectively. Kinetic studies showed that film diffusion and intra-particle diffusion were simultaneously operating during the adsorption process. The rate constant for intra-particle diffusion was estimated to be 1.985 mg/g min$^{0.5}$.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Adsorption isotherm; Adsorption kinetics; Basic Blue 41; Silkworm pupa

1. Introduction

Chemical contamination of water by a wide range of pollutants is a serious environmental problem due to their potential human toxicity. The textile industry uses large volumes of water in wet processing operations and, thereby, generates substantial quantities of wastewater containing large amounts of dissolved dyestuffs and other products, such as dispersing agents, dye bath carriers, salts, emulsifiers, levelling agents and heavy metals [1,2].

Dyes are synthetic aromatic compounds which are embodied with various functional groups. Some dyes are reported to cause allergy, dermatitis, skin irritation, cancer, and mutations in humans. Thus, the removal of dyes from effluents before they are mixed up with unpolluted natural water bodies is important [3]. Today there are more than 10,000 dyes available commercially [4]. The annual production of dyes worldwide is around 7×10^5 t, 5–10% of which is discharged into waste streams by textile industries. The majority of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and genotoxic effects [5].

Textile wastewaters offer considerable resistance to biodegradation due to presence of the dyestuffs which have a complex chemical structure and are resistant to light, heat and oxidation agents. The colored dye effluents are considered to be highly toxic to the aquatic life and affect the symbiotic process by disturbing natural equilibrium by reducing photosynthetic activity due to the colorization of the water [6].

Biological treatment processes such as aerated lagoons and conventional activated sludge processes are frequently used to treat textile effluents. These processes are efficient in the removal of suspended solids but largely ineffective in removing dyes from wastewater [7]. Removal of dyes from effluents in an economic fashion remains a major problem for textile industries. The need of treating textile wastewaters by a tertiary treatment, mostly for residual dye removal is required [1].

Physico-chemical processes are generally used to treat dyes laden wastewater. These processes include flocculation, electro-flotation, precipitation, electro-kinetic coagulation, ion exchange, membrane filtration, electrochemical destruction,

---

* Corresponding author. Tel.: +1 513556 2987; fax: +1 513556 2599.
E-mail address: George.Sorial@uc.edu (G.A. Sorial).

Nomenclature

A	Tempkin isotherm constant (l/g)
b	related to the energy of adsorption in Langmuir isotherm (l/mg)
B	Tempkin isotherm constant
BB41	Basic Blue 41
Bt	mathematical function of F
C_e	equilibrium concentration of the adsorbate (mg/l)
C_i	initial concentration of the adsorbate (mg/l)
F	fraction of solute adsorbed at different times t
k_{ad2}	rate constant of pseudo-second-order model adsorption (g/min mg)
k_p	rate constant for intra-particle diffusion (mg/g min$^{0.5}$)
K	saturation constant in generalized isotherm equation (mg/l)
K_f	constant of Freundlich isotherm (mg/g)/(mg/l)^n
m	dry weight of adsorbent (g)
n	constant of Freundlich isotherm
n_b	cooperative binding constant in generalized isotherm equation
q_e	amount of solute adsorbed at equilibrium (mg/g)
q_{max}	maximum adsorption capacity of the adsorbent (mg/g)
q_t	amount of dye adsorbed at time t (mg/g)
Q_0	the adsorption capacity in Langmuir isotherm (mg/g)
R^2	square of the correlation coefficient
SEM	scanning electron microscopy
SWP	silkworm pupa
V	volume of solution used in the adsorption experiment (l)

irradiation and ozonation. However, all these processes are costly and cannot be used by small industries to treat the wide range of dye wastewater [8]. Adsorption is one of the most efficient methods of removing pollutants from wastewater, especially if the adsorbent is inexpensive and readily available. Adsorbents may be of mineral, organic or biological origin [9]. Almost all the work related to adsorption techniques for dye removal from industrial effluents was based on studies using activated carbon [10–12], however, activated carbon suffers from high-cost production and regeneration [7,13]. Hence, attempts

have been made to utilize natural as well as waste materials as alternative adsorbents. Natural materials, biosorbents, and waste materials from industry and agriculture represent potentially more economical alternative adsorbents [14]. Since the cost is an important parameter in most developing countries, efforts have been made to explore the possibility of using various low cost adsorbents such as sphagnum peat, sulphonated coal, fly ash, lignite, wood sawdust, boiler bottom ash, rice husk, plant portions, chitin and chitosan and clay materials. Most of the adsorbents explored for decolorization studies are cheap, require little or no processing, are easily available and are biodegradable or easily disposed by incineration thereby providing energy [15]. Table 1 shows some adsorbents, which have been used for dyes removal. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost, simple design and easy operation, less energy intensiveness, non-toxic, and superior removal of organic waste constituents as compared to the conventional biological treatment processes [16]. An adsorption process produces an effluent that is free of harmful substances such as carcinogenic aromatic amines which are produced by microbial degradation or by photodegradation using UV light [5].

Adsorption of dyes is mainly dependent on the dye's properties and structure and to an equal extent on the surface chemistry of the adsorbent. For any batch adsorption process, the main parameters to be considered are pH, temperature, particle size and time. Hence, it is necessary to investigate extensively the relationship between adsorption efficiency and the parameters affecting it.

In the present work adsorption of Basic Blue 41 (BB41) dye by silkworm pupa (SWP), a natural adsorbent, has been investigated and the obtained experimental data were correlated by four adsorption isotherm models namely, Langmuir, Freundlich, Tempkin, and a generalized isotherm model. The effect of temperature and initial pH of dye solution has been studied. Kinetic experiments have been also conducted to determine the rate of BB41 adsorption by SWP.

2. Materials and methods

2.1. Dye stuff

The dye BB41 was purchased from Sigma–Aldrich, Milwaukee, WI. This dye is a monoazo-basic dye with C.I. no.: 11105, $\lambda_{max} = 610$ nm, color of bright blue hue and molecular weight of 483 g/mol. It is particularly suitable for dyeing of

Table 1
Natural adsorbents used for dyes removal

Adsorbate	Adsorbent
Acid dyes	Cationized sawdust [17], compost sorbent [18], maize waste [19], orange peel [20], peat [21], polysaccharides [22], red mud [23], shale oil ash [24]
Cationic dyes	Bagass flyash [8], blast furnace sludge [3], clinoptilolite and amberlite [7], compost sorbent [18], dried activated sludge [25], fly ash [26], giant duckweed [27], linseed Cake [28], maize waste [19], natural zeolite [13], peat [29], shale oil ash [24]
Direct dyes	Chitosan [30], coal based sorbent [31], compost sorbent [18], fly ash [26]
Disperse dyes	Polysaccharides [22]
Reactive dyes	Chitin [32], eggshell membrane [33], eucalyptus bark [34], maize waste [19], polysaccharides [22]

acrylic substrates and can also be applied to some polyamide and polyester types, viscose, cotton, and wool. It is also effective as a stainer for the identification of avian leukocytes and blood and bone-marrow cells [35]. Stock aqueous solution of the dye was prepared in deionized water in the concentration range of 1000 mg/l.

2.2. Preparation of adsorbent

SWP wastes obtained from silk spinning process of Pileh va Abrisham Shomal Co., Rasht, Iran, were washed with distilled water, dried, and ground. The powdered pupa was sieved (50–100 mesh) and used as an adsorbent. The adsorbent before any experimental run was dried in the oven at 110 °C overnight. The general analysis of SWP showed that it contains about 58% protein, 24% minerals, 8% fat, 5% water and 5% ash. Scanning electron microscopy (SEM) was used for determining the structural and morphological characteristics of the adsorbent.

2.3. Methods

2.3.1. Impact of initial pH and temperature
To study the effect of initial pH on the dye removal by SWP, the pH was adjusted by adding a few drops of dilute NaOH or H_2SO_4 before each experiment. Experimental conditions consisted of 0.2 g SWP; 50 ml of 200 mg/l dye solution, temperature equal to 30 °C and contact time of 2 h. It should be noted that for these experiments no pH buffer was used and the pH rise by the end of the experiment was less than 0.5 units. The effect of temperature (at 20, 40 and 50 °C) on the adsorption of BB41 by SWP was explored at pH 7.0, 4 g/l SWP and initial dye concentration of 200 mg/l for 1 h.

2.3.2. Equilibrium studies
Batch studies were carried out at 22 ± 1 °C. A weighed quantity of adsorbent was placed in a bottle (125 ml) with a lid containing 100 ml of a dye solution. Three initial concentrations of 100, 250, and 400 mg/l were considered. Masses of SWP ranged from 10 to 180 mg/bottle, 12–240 mg/bottle and 15–280 mg/bottle for initial dye concentration of 100, 250 and 400 mg/l, respectively. The pH of the adsorbent–adsorbate system was buffered to 7 by adding potassium dihydrogen phosphate and sodium hydroxide. The bottles were rotated for 2 weeks using a horizontal shaker operated at 150 rpm. To eliminate any change in the nature of dye solution during the experiment, two bottles for each concentration with no adsorbent added were run in the shaker. A Cintra 10 UV–vis spectrophotometer was used to determine the maximum absorption wavelength of the dye. After equilibration, the solutions were filtered and analyzed by high performance liquid chromatography (HPLC Agilent 1100 Series) with a diode array detector. Analysis was performed on Supelco column (15 cm × 4.6 mm, 5 μm). The mobile phase composed of 50% acetonitrile and 50% water at 30 °C with a flow rate of 0.8 ml/min and post-time of 4 min. The equilibrium concentration of each solution was determined by interpolation within the obtained calibration curve by the HPLC at the maximum absorption wavelength of the dye, i.e., 610 nm.

2.3.3. Kinetic studies
Kinetic experiments were carried out by stirring a known amount of the adsorbent with 500 ml of the solution containing the dye on a magnetic stirrer equipped with temperature controller. At pre-determined time intervals, portions of the mixture were drawn by a syringe and then centrifuged. The dye concentration was then determined. This procedure has been done at two temperatures, 20 and 40 °C.

3. Results and discussion

3.1. SEM studies

SEM is one of the most widely used surface diagnostic tools. SEM photographs for SWP shown in Fig. 1a and b reveal surface texture and low porosity. It is also seen from Fig. 1a and b that SWP has heterogeneous surface with insignificant macropores structures. Microscopy studies were conducted after adsorption (see Fig. 1c and d) indicates that no significant changes in the surface structure of the SWP were observed and also reveals that there is a tight binding between the dye and the adsorbent.

3.2. Adsorption isotherm studies

Fig. 2 represents the adsorption of BB41 on the SWP at 22 °C. Equilibrium surface loading, q_e, was calculated from the mass balance equation around the isotherm bottle:

$$q_e = \frac{V(C_i - C_e)}{m} \tag{1}$$

where V is the volume of solution used in the adsorption experiment (l), C_i and C_e are the initial and equilibrium concentrations of the adsorbate (mg/l), respectively, and m is the dry weight of adsorbent (g).

The obtained experimental equilibrium adsorption data (Fig. 2) were then compared with the adsorption isotherm models. Four models were used: Langmuir [36], Freundlich [37], Tempkin [38] and a generalized adsorption isotherm [39].

The linearized Langmuir model is given by:

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

where C_e is the concentration of adsorbate (mg/l) at equilibrium, q_e the amount of solute adsorbed at equilibrium (mg/g), constant Q_0 signifies the adsorption capacity (mg/g) and b (l/mg) is related to the energy of adsorption.

The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model and can be written as:

$$\log \frac{x}{m} = \log q_e = \log K_f + \frac{\log C_e}{n} \tag{3}$$

where x is the amount of adsorbate (mg), m the weight of the adsorbent used (g), q_e or x/m the amount of adsorbate at equi-
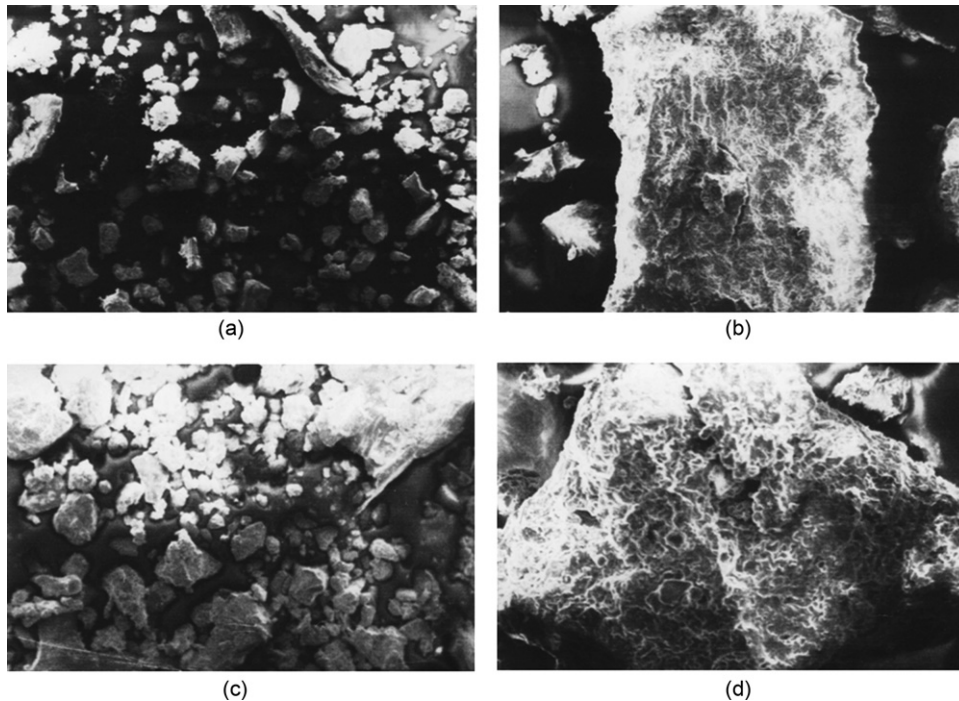
Fig. 1. SEM photographs of the SWP powder before adsorption (a [30×],b [200×]) and after adsorption (c [30×],d [250×]).

librium (mg/g), C_e the adsorbate concentration in the solution (mg/l) at equilibrium and K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. In general, as the K_f value increases, the adsorption capacity of the adsorbent, for the given adsorbate, increases. n values between 1 and 10 show beneficial adsorption. If n is close to 1, the surface heterogeneity could be assumed to be less significant and as n approaches 10 the impact of surface heterogeneity becomes more significant [19].

Tempkin and Pyzhev [38] considered the effects of indirect adsorbate–adsorbate interactions on adsorption isotherms. They noted that the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage due to adsorbate–adsorbate interactions. The Tempkin isotherm can be expressed in its linear form as:

$$q_e = B \ln A + B \ln C_e \tag{4}$$

where B and A are the Tempkin constants and can be determined by a plot of q_e versus $\ln C_e$.

A linear form of the generalized isotherm equation [39] is given by:

$$\log \left[\frac{q_{max}}{q_e} - 1 \right] = \log K - n_b \log C_e \tag{5}$$

where K is the saturation constant (mg/l); n_b the cooperative binding constant; q_{max} the maximum adsorption capacity of the adsorbent (mg/g) (obtained from Langmuir model); q_e (mg/g) and C_e (mg/l) are the equilibrium dye concentrations in the solid and liquid phases, respectively. A plot of the equilibrium data in form of $\log((q_{max}/q_e)-1)$ versus $\log C_e$ gives K and n_b constants.

Parameters related to each isotherm were determined by using linear regression analysis and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is provided in Table 2. A
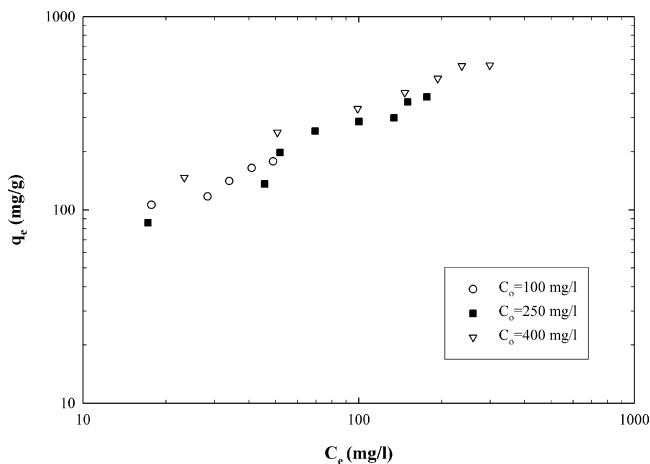

Fig. 2. Adsorption isotherm of BB41 on SWP at 22 °C.

Table 2
Regression parameters for the different isotherm equations

Model equations	R^2	Parameters	
Langmuir isotherm	0.904	Q_0 (mg/g) 555.5	b (l/mg) 0.01138
Freundlich isotherm	0.946	K_f (mg/g)/(mg/l)^n 16.15	n 1.586
Tempkin isotherm	0.904	A (l/g) 0.0778	B 160.5
Generalized isotherm	0.894	K (mg/l) 157.25	n_b 1.161

comparison of the experimental isotherms with the adsorption isotherm models showed that the generalized equation represented the poorest fit of experimental data as compared to the other isotherm equations ($R^2 = 0.894$). It has been found that the best fitted isotherm equation was Freundlich with $R^2 = 0.946$. The n parameter of the Freundlich equation reveals that the adsorption sites have narrow energy distribution since its value was close to 1 ($n = 1.586$). The correlation coefficient of Tempkin isotherm equation ($R^2 = 0.904$) is lower than that obtained for the Freundlich equation. Although the Langmuir equation describes adsorption on strongly homogeneous surfaces, which is not the case for natural adsorbents because they exhibit a chemical heterogeneity as represented by the different functional groups, however, the n parameter of the Freundlich adsorption equation reveals adsorption sites with low energetically heterogeneity of this natural adsorbent [19]. Based on this reason it can be seen from the obtained data that Langmuir equation can be fitted with a desirable $R^2 = 0.904$ with a monolayer capacity of 555 mg/g. The obtained monolayer capacity was significantly higher than other reported natural adsorbents. Davila et al. [19] obtained a value of 75 mg/g for maize waste at 25 °C and Liversidge et al. [28] obtained a value of 363 mg/g for peat at 30 °C. This could indicate the superiority of SWP in removing BB41 as compared to other adsorbents.

Fig. 3 shows the effect of the initial pH of the dye solution on the amount of adsorption of BB41 by SWP. Significant dye adsorption occurred between pH 4 and 9. At pH higher than 11 the dye was not stable and hence no investigations were conducted. At a pH less than 4 there was very small amount of removal of dye by the adsorbent. These results could be due to the chemisorption occurring between the dye and SWP. As it is known, chemisorption is a type of adsorption occurring with a single layer. The BB41 dye is cationic with $-NH_3^+$ groups in its structure. The amino acid groups in the structure of SWP are both positively and negatively charged when they are in ionic solutions due to the acidity of aqueous solutions of BB41. A chemical affinity then forms between the negative charges of SWP and the positive charges in the structure of the dye. As a
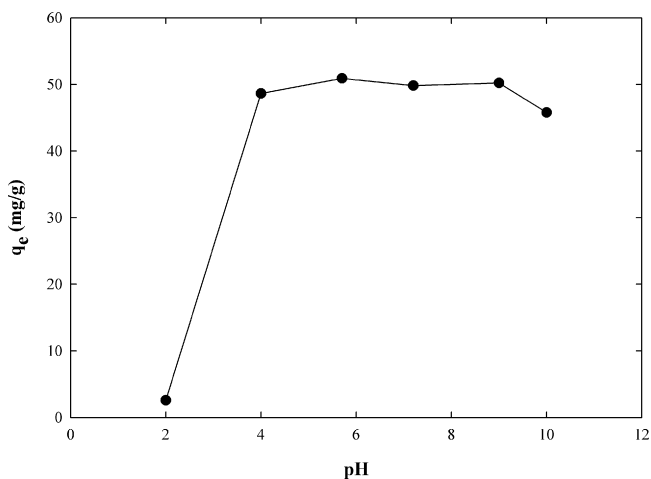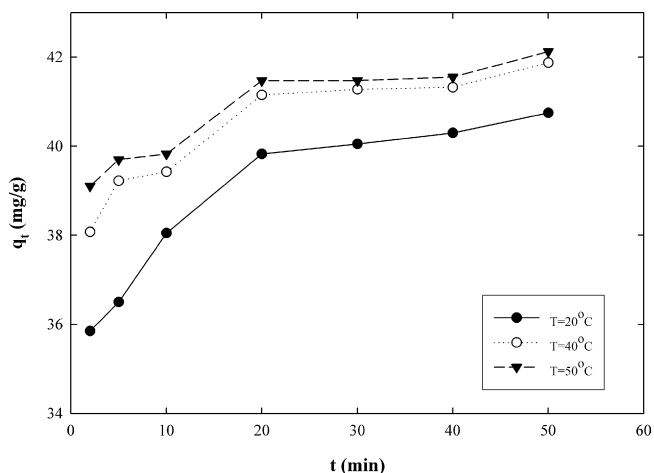

Fig. 4. Effect of temperature on the adsorption of BB41 by SWP (initial dye concentration: 200 mg/l; SWP: 4 g/l; pH 7).

result of this chemical affinity, the resistance of the boundary layer surrounding the adsorbent weakens [9]. In a media with acidic pH the pre-dominant charge of the adsorbent is positive, hence, there will be repulsion between species with the same charge, i.e., the dye molecule and the surface of the adsorbent. This will provide low removal of the dye from solution.

Fig. 4 shows the effect of temperature on the adsorption of BB41 by SWP from aqueous solution. As can be seen there is a small effect between 40 and 50 °C but a significant effect between 20 and 40 °C. This can be attributed to the endothermic nature of adsorption. According to the nature of the adsorbent and the type of dye used, the process of dye adsorption can be discussed similar to dyeing process where intermolecular interactions between the functional groups of the dye and the surface chemistry of the substrate may play an important role.

3.3. Kinetic studies

Batch experiments were conducted to explore the rate of BB41 adsorption by SWP at pH 7.0, SWP of 4 g/l and initial dye concentrations of 100 and 200 mg/l. The kinetic adsorption data can be processed to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. The process of dye removal from aqueous phase by a certain adsorbent may be represented by pseudo-first-order kinetics (reversible or irreversible) or pseudo-second-order kinetics [31,40].

The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_{ad2}q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_{ad2} (g/min mg) is the rate constant of pseudo-second-order model adsorption. $k_{ad2}q_e^2$ considered as the initial adsorption rate (mg/g min). If pseudo-second-order kinetics is applicable, a plot of t/q_t versus t should provide a linear relationship. The calculated regression coefficients for reversible pseudo-first-order model ($R^2 = 0.823$ at 20 °C and $R^2 = 0.810$ at 40 °C for $C_0 = 200$ mg/l; $R^2 = 0.870$ for $C_0 = 100$ mg/l at 20 °C) and irreversible pseudo-first-order model ($R^2 = 0.859$ at 20 °C and $R^2 = 0.846$ at 40 °C for $C_0 = 200$ mg/l; $R^2 = 0.849$ for
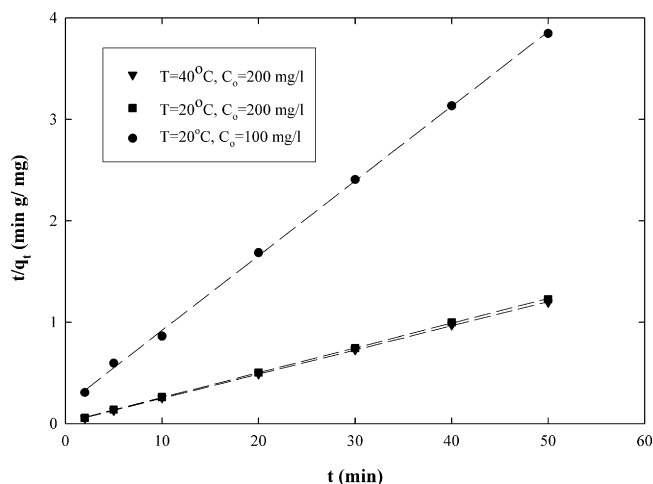

Fig. 3. Effect of initial pH on the adsorption of BB41 by SWP (initial dye concentration: 200 mg/l; temperature: 30 °C; time: 2 h; SWP: 4 g/l).

Fig. 5. Pseudo-second-order kinetic model for the adsorption of BB41 by SWP (SWP: 4 g/l; pH 7).

Fig. 6. Intra-particle diffusion plot for BB41/SWP system (SWP: 1 g/l; initial dye concentration: 110 mg/l; temperature: $30 \pm 0.2\,^\circ$C; pH 7; time: 2 h).

$C_0 = 100$ mg/l at $20\,^\circ$C) were below 0.9. On the other hand, the pseudo-second-order model ($R^2 = 0.999$ at 20 and $40\,^\circ$C for $C_0 = 100$ and 200 mg/l) revealed to be the best in representing adsorption of BB41 by SWP.

Fig. 5 shows the plot of the pseudo-second-order model for two initial concentrations (100 and 200 mg/l) of BB41. For the 200 mg/l initial concentration two temperatures were considered. From Fig. 5, it is seen that the plots for the 200 mg/l initial concentration at the two temperatures studied almost coincide. However, the rate constants, k_{ad2}, were 0.0434 and 0.0572 g/min mg at 20 and $40\,^\circ$C, respectively, which is consistent with Arrhenius form of equation. The calculated rate constant, k_{ad2}, for initial concentration of 100 mg/l at $20\,^\circ$C was 0.0299 g/min mg. The initial adsorption rate, $k_{ad2}q_e^2$, for $C_0 = 200$ mg/l at $20\,^\circ$C is 73.0 mg/g min while for $C_0 = 100$ mg/l the initial rate was only 5.5 mg/g min. This could be due to the greater concentration gradient between the solid and liquid phase at the higher dye concentration.

3.4. Intra-particle diffusion studies

Adsorption is a multi-step process involving transport of solute molecules from the aqueous phase to the surface of the solid particles and, then, diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process, and is therefore, rate determining. Webber and Morris [41] provided the rate, q_t, for intra-particle diffusion by:

$$q_t = k_p t^{0.5} \tag{7}$$

where q_t is the amount of dye adsorbed (mg/g) at time t, and k_p (mg/g min$^{0.5}$) is the rate constant for intra-particle diffusion. The plot of q_t against $t^{0.5}$ may present a multi-linearity correlation, which indicates that two or more steps occur during adsorption process. The first sharper portion is the external mass transfer (film diffusion) or instantaneous adsorption stage. The second portion is the gradual adsorption stage where the intra-particle diffusion can be rate controlling. The third portion is the final equilibrium stage where the intra-particle diffusion starts to slow
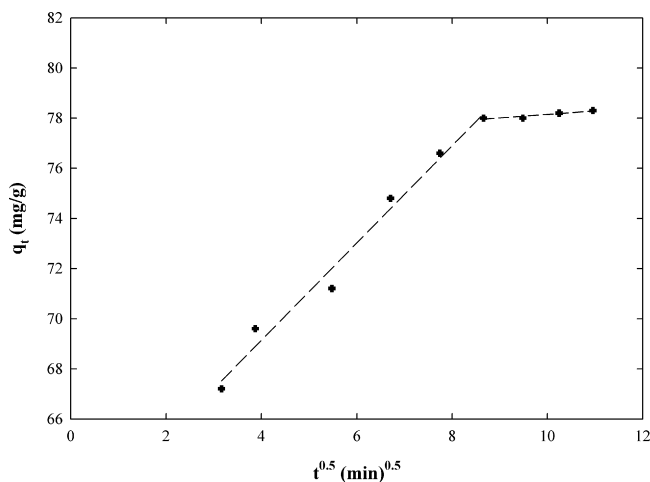
down due to the extremely low solute concentration in solution [42].

The fraction of dye uptake against $t^{0.5}$ is shown in Fig. 6 for the studied adsorbate–adsorbent system. The linear portions between $t = 5$ and 75 min could be due to intra-particle diffusion effects. The slope of this linear portion, $k_{p1} = 1.985$ mg/g min$^{0.5}$, can be defined as a rate parameter and characteristic of the rate of adsorption in the region where intra-particle diffusion is occurring. Initially, within a short time period, it is postulated that the dye was transported to the external surface of the adsorbent through film diffusion and its rate have been very fast. After saturation of the surface, the dye molecule entered into the SWP particle by intra-particle diffusion through pore and interior surface diffusion until equilibrium is attained which is represented by the second straight line in Fig. 6 with $k_{p2} = 0.205$ mg/g min$^{0.5}$. Since the q_t versus $t^{0.5}$ plot does not go through the origin it may be concluded that both film diffusion and intra-particle diffusion were simultaneously operating during the process of the adsorption of BB41 by SWP [31,43]. In order to determine the actual rate-controlling step involved in the dye adsorption process, the adsorption data can be further analyzed using Eq. (8) [44]:

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \tag{8}$$

where F is the fraction of solute adsorbed at different times t and Bt is a mathematical function of F and F can be expressed as:

$$F = \frac{q_t}{q_e} \tag{9}$$

where q_t and q_e represent the amount adsorbed (mg/g) at any time t and at infinite time. Substituting Eq. (9) into Eq. (8), the kinetic expression becomes:

$$Bt = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{10}$$

Thus, the value of Bt can be calculated for each value of F using Eq. (10). The calculated Bt values were plotted against time as shown in Fig. 7. The linearity of this plot will provide useful information for distinguishing between film diffusion and
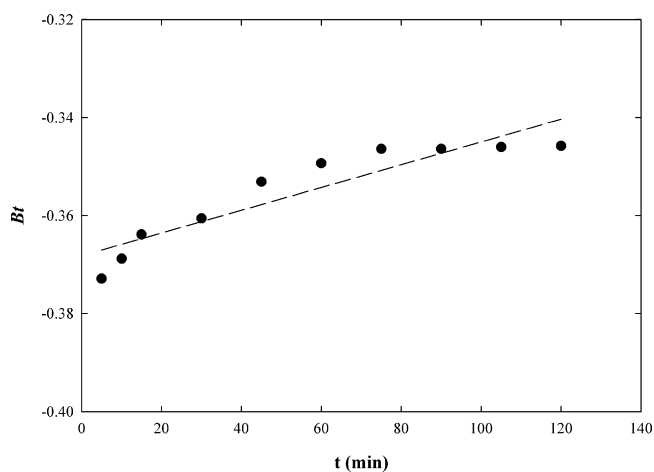
Fig. 7. Correlationship of Bt vs. *t* for BB41/SWP system (SWP: 1 g/l; initial dye concentration: 110 mg/l; temperature: $30 \pm 0.2\,°C$; pH 7; time: 2 h).

intra-particle diffusion rates of adsorption. If a plot of Bt versus *t* is a straight line passing through the origin, then adsorption will be governed by a particle-diffusion mechanism, otherwise governed by film diffusion [13]. From Fig. 7, it is observed that the plot has not a desirable linear form ($R^2 = 0.85$); indicating that film diffusion mainly governs the rate-limiting process. It is speculated that it could be due to the electrostatic interaction between the adsorbent surface and the cationic dye.

4. Conclusion

Equilibrium and kinetic studies were studied for the adsorption of BB41, a cationic dye, from its aqueous solutions by SWP. The equilibrium data have been analyzed against Freundlich, Langmuir, Tempkin models, and a generalized isotherm equation. The characteristic parameters for each isotherm have been determined. The results showed that the experimental data were best correlated by the Langmuir and Freundlich adsorption isotherms. This adsorbent has high adsorption capacity with a monolayer adsorption capacity of 555 mg/g. The adsorption was dependent on the pH of the solution because of the ionization of amino acid groups existing on the surface of the adsorbent. Significant dye adsorption occurred between pH 4 and 9. A good agreement of the experimental kinetic data with the pseudo-second-order model at two different temperatures (20 and 40 °C) was obtained. The calculated rate constant, k_{ad2}, for $C_0 = 200$ mg/l was 0.0434 and 0.0572 g/min mg at 20 and 40 °C, respectively. The rate constant for $C_0 = 100$ mg/l at 20 °C showed the lowest amount ($k_{ad2} = 0.0299$ g/min mg). Intra-particle diffusion study showed that both film diffusion and intra-particle diffusion were simultaneously operating during the process of the adsorption of BB41 by SWP and the rate constant for intra-particle diffusion was estimated to be 1.985 mg/g min$^{0.5}$.

Acknowledgements

References

[1] S.A. Figueiredoa, J.M. Loureirob, R.A. Boaventurab, Natural waste materials containing chitin as adsorbents for textile dyestuffs: batch and continuous studies, Water Res. 39 (2005) 4142–4152.

[2] C. Sourja, D. Sirshendu, D. Sunando, K.B. Jayanta, Adsorption study for the removal of a basic dye: experimental and modeling, Chemosphere 58 (2005) 1079–1086.

[3] A. Bhatnagar, A.K. Jain, A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, J. Colloid Interf. Sci. 281 (2005) 49–55.

[4] R. Gong, M. Li, C. Yang, Y. Suna, J. Chenb, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. B 121 (2005) 247–250.

[5] C. Sudipta, C. Sandipan, P.C. Bishnu, R.D. Akhil, K.G. Arun, Adsorption of a model anionic dye, eosin Y, from aqueous solution by chitosan hydrobeads, J. Colloid Interf. Sci. 288 (2005) 30–35.

[6] K. Ravikumar, S. Ramalingam, S. Krishnan, K. Balu, Application of response surface methodology to optimize the process variables for reactive red and acid brown dye removal using a novel adsorbent, Dyes Pigments 70 (2006) 18–26.

[7] Y. Julide, K. Turkan, D. Gulsen, D. Timur, Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, J. Colloid Interf. Sci. 294 (2006) 255–264.

[8] D.M. Indra, C.S. Vimal, K.A. Nitin, M.M. Indra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colloid Surf. A 264 (2005) 17–28.

[9] U. Ilhan, Kinetics of the adsorption of reactive dyes by chitosan, Dyes Pigments 70 (2006) 76–83.

[10] A. Thomas, R.Y.-L. Yeh, Color removal from dye wastewaters by adsorption using powdered activated carbon: mass transfer studies, J. Chem. Technol. Biotechnol. 63 (1995) 48–54.

[11] K.K.H. Choy, G. McKay, J.F. Porter, Sorption of acid dyes from effluents using activated carbon, Resour. Conserv. Recy. 27 (1999) 57–71.

[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 Pigments 54 (2002) 47–58.

[13] S. Wang, H. Li, L. Xu, Application of zeolite MCM-22 for basic dye removal from wastewater, J. Colloid Interf. Sci. 295 (2006) 71–78.

[14] J. Pavel, Š. Veronika, Effects of surfactants on the adsorptive removal of basic dyes from water using an organomineral sorbent-iron humate, J. Colloid Interf. Sci. 291 (2005) 19–27.

[15] R. Sanghi, B. Bhattacharya, Review on decolorisation of aqueous dye solutions by low cost adsorbents, Color. Technol. 118 (2002) 256–269.

[16] A.K.A. Rathi, S.A. Puranik, Treatment of wastewater pollutants from direct dyes, Am. Dyest. Rep. (1999) 42–50.

[17] M. Naouab, R. Guthier, H. Guthier, M. Rammah, Cationized sawdust as ion exchanger for anionic residual dyes, J. Appl. Polym. Sci. 82 (2001) 31–37.

[18] L.S. Tsui, W.R. Roy, M.A. Cole, Removal of dissolved textile dyes from wastewater by compost sorbent, Color. Technol. 119 (2003) 14–18.

[19] M.M. Davila-Jimenez, M.P. Elizalde-Gonzalez, A.A. Pelaez-Cid, Adsorption interaction between natural adsorbents and textile dyes in aqueous solution, Colloids Surf. A 254 (2005) 107–114.

[20] 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.

[21] K.R. Ramakrishna, T. Viraraghavan, Dye removal using peat, Am. Dyest. Rep. (1996) 28–34.

[22] F. Delval, G. Crini, N. Morin, J. Vebrel, S. Bertini, G. Torri, The sorption of several types of dye on crosslinked polysaccharides derivatives, Dyes Pigments 53 (2002) 79–92.

[23] C. Namasivayam, R.T. Yamuna, D.J.S.E. Arasi, Removal of acid violet from wastewater by adsorption on waste red mud, Environ. Geol. 41 (2001) 269–273.

[24] Z. Al-Godah, Adsorption of dyes using shale oil ash, Water Res. 34 (2000) 4295–4303.

[25] G. Osman, K. Aysenur, M. Fatih, A. Burhan, Sorption of basic dyes from aqueous solution by activated sludge, J. Hazard. Mater. B 108 (2004) 183–188.

[26] V.V. Basava, S.R. Mohan, Adsorption studies on treatment of textile dyeing industrial effluent by fly ash, Chem. Eng. J. 116 (2006) 77–84.

[27] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (spirodela polyrrhiza), Environ. Pollut. 125 (2003) 385–392.

[28] R.M. Liversidge, G.J. Lloyd, D.A.J. Wase, C.F. Forster, Removal of Basic Blue 41 from aqueous solution by linseed cake, Process. Biochem. 32 (1997) 473–477.

[29] S.J. Allen, G. Mckay, J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, J. Colloid Interf. Sci. 280 (2004) 322–333.

[30] K.D. Bhavani, P.K. Dutta, Physico-chemical adsorption properties on chitosan for dyehouse effluent, Am. Dyest. Rep. (1999) 53–58.

[31] S.V. Mohan, N.C. Rao, J. Kartikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, J. Hazard. Mater. B 90 (2002) 189–204.

[32] G. Mckay, H.S. Blair, J.R. Gardner, The adsorption of dyes onto chitin in fixed bed columns and batch adsorbers, J. Appl. Polym. Sci. 29 (1984) 1499–1514.

[33] B. Koumanova, P. Peeva, S.J. Allen, K.A. Galagher, M.G. Healy, Biosorption from aqueous solutions by eggshell membranes and *Rhizopus oryzae*:

[34] L.C. Morais, O.M. Freitas, E.P. Goncalves, L.T. Vasconcelos, C.G. Gonzalez, Reactive dyes removal from wastewater by adsorption on eucalyptus bark: variables that define the process, Water Res. 33 (1999) 979–988.

[35] M. Roulia, A.A. Vassiliadis, Interactions between C.I. Basic Blue 41 and aluminosilicate sorbents, J. Colloid Interf. Sci. 291 (2005) 37–44.

[36] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[37] H.M.F. Freundlich, Uber die adsorption in losungen, Zeitschrift fur Physikalische Chemie 57 (1906) 385–471.

[38] M.J. Tempkin, V. Pyzhev, Acta Physiol. Chem. USSR 12 (1940) 217–222.

[39] F. Kargi, S. Ozmıhcı, Biosorption performance of powdered activated sludge for removal of different dyestuffs, Enzyme Microb. Technol. 32 (2004) 267–271.

[40] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[41] W.J. Weber, J.C. Morris, Preliminary appraisal of advanced waste treatment processes, Water Pollut. Res. 2 (1963) 231–241.

[42] Q. Sun, L. Yang, The adsorption of basic dyes from aqueous solution on modified peat-resin particle, Water Res. 37 (2003) 1535–1544.

[43] A. Ozcan, E.M. Oncu, A.S. Ozcan, Adsorption of Acid Blue 193 from aqueous solutions onto DEDMA-sepiolite, J. Hazard. Mater. B 129 (2006) 244–252.

[44] G.E. Boyd, A.W. Adamson, L.S. Meyers, The exchange adsorption of ions from aqueous solution by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69 (1947) 2836–2848.

equilibrium and kinetic studies, J. Chem. Technol. Biotechnol. 77 (2002) 539–545.