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Adsorption Anionic Dye on Bacterial and Plant Cellulose: Thermodynamic and Kinetic Study

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ABSTRACT

Bacterial cellulose is extracellular cellulose synthesized by some bacteria. The thickness of the microfibrous structure of bacterial cellulose is much less than that of plant cellulose. One major dye class used on cellulosic polymers is that of direct dyes. The aim of this study was to determine of kinetic and thermodynamic adsorption of direct blue 71 dye with bacterial and plant cellulose. The effects contact time and temperature on adsorption of direct dye by bacterial and plant cellulose were also evaluated. Kinetic analyses were conducted using pseudo first- and second-order models. The regression results showed that the adsorption kinetic for both cellulosic polymers was more accurately represented by a pseudo second-order model. Changes in the free energy of adsorption ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$), as well as the activation energy (E_a) were determined. $\Delta H^{\#}$, $\Delta S^{\#}$ and E_a with pH control were -26kJ/mol, -228J/mol and 43kJ/mol for bacterial cellulose and -18.07 kJ/mol, -198J/mol and 30kJ/mol for cotton. The values of $\Delta H^{\#}$, $\Delta G^{\#}$ and E_a indicate that the adsorption of direct dye onto bacterial cellulose and cotton was a physisorption process.

Keywords: Bacterial cellulose, Cotton, Kinetic, Thermodynamic, adsorption

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INTRODUCTION

Cotton is an abundant natural fibre which consists of practically pure cellulose (about 88-96%) [1]. Cotton may be described chemically as poly (1, 4-β-D-anhydroglucopyranose) [2]. As biosynthesized cellulose, Bacterial cellulose (BC) is extracellular cellulose produced by bacteria of genus Acetobacter [3]. The primary structure of BC is similar to that of plant cellulose: an unbranched polymer of β -1, 4-linked glucopyranose residues. However, the fibrous structure of BC is different from that of plant cellulose. BC is composed of nanofibrils, which have a ribbon-like structure, and the thickness (0.1×10^{-6} m) is two orders of magnitude smaller than that of plant cellulose (10×10^{-6} m). In addition, the nanofibrils retain a fine network structure. Because of its characteristic microstructure, BC has various advantageous properties, such as high tensile strength, elasticity, large surface area, etc [4, 5]. Natural cellulose fibers carry a small negative charge due to the presence of some carboxylic acid groups from oxidation at the primary hydroxylic sites [6].

Direct dyes are widely used due to their low cost, excellent color range, good light fastness and ease of application to the material. These dyes are water soluble and contain one or more ionic groups most often sulfonic acid and/or amino groups. Direct dyes posses good affinity for cellulosic fibers. The main aim of this study was to investigate the potentiality of using BC and cotton fibers as sorbent for the adsorption of direct blue 71 dye from aqueous solution. The effects of temperature and contact time on BC and cotton fibers adsorptions were studied. Sorption thermodynamic and kinetic parameters were also calculated and discussed.

MATERIALS AND METHODS

Instruments and Chemicals

A thermostated shaker bath (Heto-Holten A/S Denmark, Type SBD-50 cold), operated at 100 rpm, was used to study the kinetic adsorption of direct blue 71dye onto BC and cotton. A pH meter (Mettler Delta 320, UK) was used to measure the pH values of the dye solutions. A Cary 100 Bio UVevisible spectrophotometer (VARINA-UK) was employed for absorbance measurements using quartz cells of path length1 cm. All the chemicals and reagents used in the present investigation were of analytical grade and mainly purchased from Sigma-Aldrich (USA) and Merck (Germany).

Cotton yarn preparation

The cotton yarn used was purchased from the Gorgan District, Iran. To remove the wax and impurities, the cotton yarn (100g) was added to boiling water (2L) to which had been added soap flakes (ca 7g) and sodium carbonate (3g). The mixture was then boiled for 1 h. The cotton was then removed, washed with hot water and cold water in order to avoid break down of the emulsion and precipitation of the impurities on the cotton, squeezed to remove excess liquor and air dried. Finally, it was treated with 1 M HCl (ca 2L) at room temperature for 30 min and then removed and washed with deionized water until the rinsed water was neutral. The cotton yarn was then dried at room temperature.

Bacterial cellulose Preparation

AccetobacterXylinum ATCC 23768 was used for BC production. The microbe was provided from the medical sciences faculty tarbialmodares university, Tehran, Iran. The bacterium was grown in SH medium at 28ºC under static culture conditions. SH medium was composed of 2% (W/V) glucose, 0.5% (W/V) yeast extract, 0.5% peptone, 0.27% (W/V) Na_2HPO_4 and 0.115% (W/V) citric acid. Preinoculum for all experiments was prepared by transferring a single colony grown on SH agar medium into a 50 mL Erlenmeyer flask filled with liquid SH medium. After 7 days of cultivation at 28°C, the cellulose pellicle formed on the surface of the culture broth. Ten milliliters of the cell suspension was introduced into a 500 mL Erlenmeyer flask containing 100 mL of a fresh SH medium. The culture was carried out statically for 72 h and the cell suspension derived from the synthesized cellulose pellicle was used as the inoculums for further cultures [4,8].The cellulose sheets were removed after cultivation and rinsed with distilled water. They were cut into 0.05 gr and used for dye biosorbent.

Direct dye solution baths preparation

In the present investigation, direct blue 71 dye (obtained from Bimco International B.P.M Dye.Co in Iran) was used without further purification. Stock solutions of both dyes were prepared by dissolving 0.1 g of dye in 1000 ml of double distilled water. Standard curves were developed through the measurement of the dye solution absorbance by UV/visible spectrophotometer. The general characteristics and chemical structure of this dye is shown in Table 1 & Figure1.

Table 1. Properties of Direct Blue 71 dye

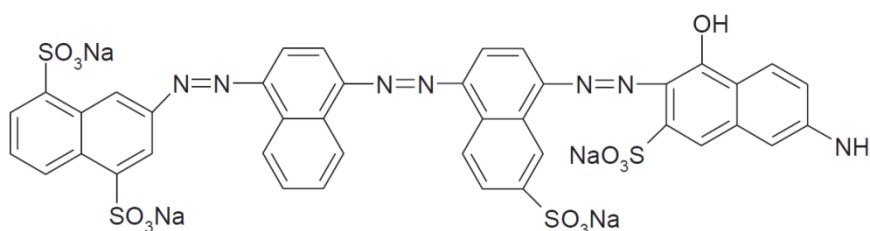| Name	CAS namber	C.I number	Formula	Molecular Weight	λ max
Direct Blue 71	4399-55-7	34140	$C_{40}H_{23}N_7O_{13}S_4\ Na_4$	1029.88	587

Figure 1. Chemical structureof Direct Blue 71 Dye

Kinetic experiments

For batch kinetic experiments, the pH of the dye solutions was adjusted to 3.0 with glacial acetic acid. The dye solution (25 mL) in each conical flask (100 mL) was shaken in a thermostatted shaker bath operated at 100 rpm. After 30 min, the BC and cotton (0.050 g), which had been pre-warmed in the thermostatted bath for 30 min, were immersed in the

dye solution. The BC and cotton samples were then rapidly withdrawn after different immersion times. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at λ_{max} 587nm versus dye concentration in standard dye solutions. The amount of dye adsorbed per gram of BC and cotton (mg/g BC or cotton) at any time (q_t) was calculated by a mass-balance relationship equation (1).

$$q_t = (C_0 - C_t)\frac{V}{W}$$

(1)

Where C_0 is the initial dye concentration (mg/L) and C_t is the dye concentration after dyeing time t (mg/L), V is the volume of dye solution (mL) and W is the weight of BC or cotton (g) used.

RESULTS AND DISCUSSION

Temperature and contact time effects

The effect of temperature on the sorption of dye on BC and cotton were investigated. It was found that a higher dyeing temperature resulted in higher initial dye adsorption rate on BC and cotton before equilibrium as shown in Figures 2(a&b). Near the equilibrium time, the dye adsorbed by the BC and cotton decreased with increasing temperature, indicating an exothermic process. As can be observed from Figure 2(a&b), the time required to reach equilibrium was shorter at higher dyeing temperatures, i.e., 120, 60 and 5 min at 30, 45 and 60°C, respectively. The dyeing condition of pH 3.0, initial dye concentration of 100 mg/L and MLR of 1:500 was subsequently used to study the adsorption kinetics of direct blue 71 dye on BC and cotton.
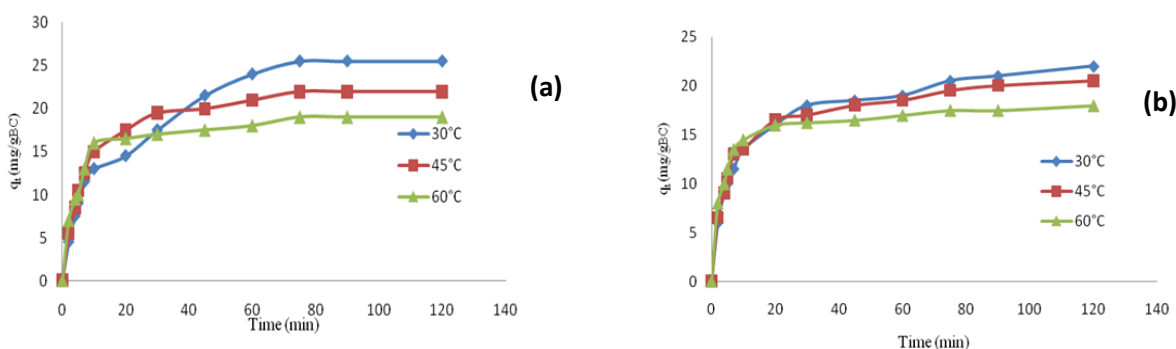

Figure 2(a&b). Temperature and contact time effects of dye on BC and cottonat an initial dye concentration 100 mg/L, MLR 1:500 and pH 3.0, amount of BC and cotton 0.05g.

Kinetics analyze

In order to analyze the adsorption kinetics of direct blue 71dye on BC and cotton, the pseudo first- and second-order kinetic models were used to analyze the experimental data. A simple kinetic analysis of adsorption is the Lagergren equation. The Lagergren equation, a pseudo first-order equation, describes the kinetics of the adsorption process as follows [9]:

$$(2)$$

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t)$$

Where k_1 is the rate constant of pseudo first-order adsorption(s^{-1}), and q_e and q_t are the amounts of dye adsorbed per gram of BC and cotton (mg/g BC or Cotton) at equilibrium and at time t. In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over only the initial stage of the adsorption [10]. After definite integration by applying the initial conditions q_t=0 at t = 0 and q_t= q_t at t = t, Eq. (2) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

A straight line of$\ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model to fit the experimental data. The first-order rate constant k_1 and equilibrium adsorption density q_e were calculated from the slope and intercept of this line Figure 3(a&b).

The pseudo second-order kinetic model [10] is based on adsorption equilibrium capacity and can be expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \qquad (4)$$

Where k_2 (g BC or cotton/mg min) is the rate constant for pseudo second-order adsorption. Integrating Eq. (4) and applying the initial conditions give:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (5)$$

or equivalently,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (6)$$

and

$$h_i = k_2 q_e^2 \qquad (7)$$

Where h_i [11]. is the initial dye adsorption rate (mg/g BC or cotton min). If pseudo second-order kinetics are applicable, the plot of (t/q_t) versus t would show a linear relationship. The slope and intercept of (t/q_t) versus t were used to calculate the pseudo

second order rate constant k_2 and q_e. It is likely that the behavior over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step [10]. Kinetic data obtained from dye adsorption in the present study, was analyzed using the pseudo first-order kinetic model proposed by Lagergren [12] according to Eq. (3). The results are listed in Table 2. Based on the correlation coefficients obtained, the adsorption of dye on BC and cottonare not likely to be a first-order reaction.

The pseudo second-order kinetic model was also used to test the experimental data using Eq. (6), and plots of (t/q_t) against t for the adsorption of dye on BC and cotton are given in Figure 4(a&b). The slopes and intercepts of these plots were used to calculate the adsorption capacity $(q_{e,cal})$ and the rate constant (k_2). The experimental data showed a good compliance with the pseudo second-order equation and the correlation coefficients for the linear plots were higher than 0.99 for all the experimental data. Also, the calculated $q_{e,cal}$ values agreed very well with the experimental data. Figure 4(a&b) shows the comparison of experimental and calculated q_e values. These results suggested that the experimental data for the adsorption kinetics of dye on BC and cotton were fitted by the pseudo second-order kinetic model.
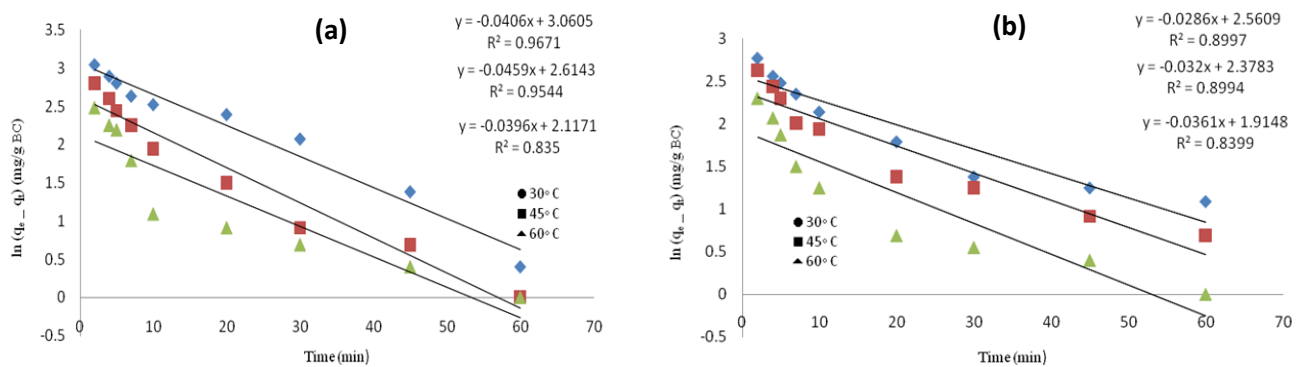

Figure 3(a&b).Plot of the pseudo first-order equation at different temperatures for the adsorption of dye on BC and cotton.
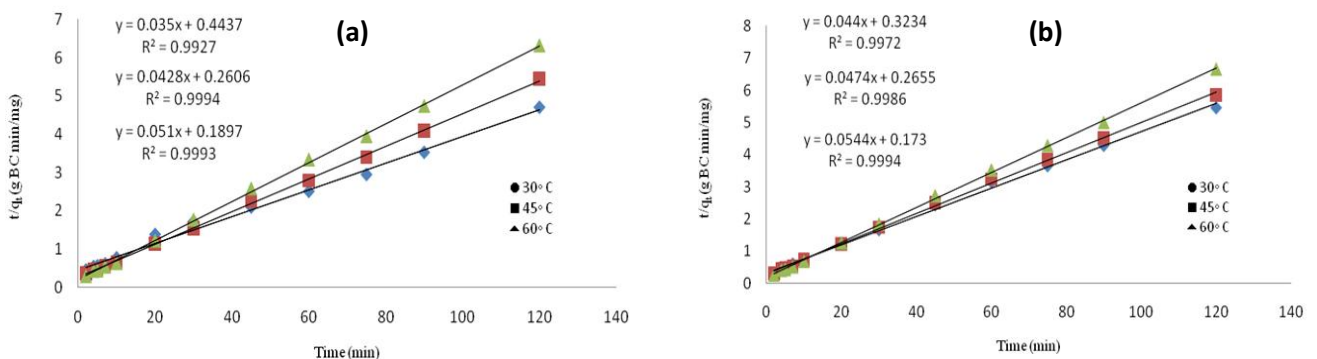

Figure 4(a&b).Plot of the pseudo second-order equation at different temperatures for the adsorption of dye on BC and cotton.

Table 2. Comparison of the pseudo first- and second-order adsorption rate constants of dyeing onto BC and cotton at an initial dye concentration 100 mg/L, MLR 1:500 and pH 3.0

Good	Temp (ºC)	$q_{e,exp}$ (mg /g)	Pseudo first-order model			Pseudo second-order model			
			K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg min)	$q_{e,cal}$ (mg/g)	h_i (mg/g min)	R^2
BC	30	25.15	$4. \times 10^{-2}$	0.9671	21.33	2.71×10^{-3}	28. 55	2.20	0.9927
	45	22.01	4.5×10^{-2}	0.9544	13.65	$7. \times 10^{-3}$	23.31	3.83	0.9994
	60	19	3.9×10^{-2}	0.835	8.30	13.05×10^{-3}	19.65	4.97	0.9993
cotton	30	22	3.86×10^{-2}	0.8997	12.94	5.99×10^{-3}	22.72	3.42	0.9927
	45	20.5	3.61×10^{-2}	0.8994	7.7	8.46×10^{-3}	21.09	3.86	0.9986
	60	18	3.2×10^{-2}	0.8399	6.78	17.11×10^{-3}	18.38	4.26	0.9994

Activation parameters

From the rate constant k_2 (Table 2), the activation energy (E_a) for the adsorption of direct blue 71 dye on BC and cotton were determined using the Arrhenius equation (9) [13]:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (9)$$

Where E_a, R and A refer to the Arrhenius activation energy, the gas constant and the Arrhenius factor, respectively.

The Arrhenius plot of ln k against 1/T for the adsorption of dye on BC and cotton are shown in Figure 5(a&b) and the activation energy value is listed in Table 3. The Arrhenius activation energy (E_a) was calculated from the slope of plot of ln k versus 1/T. The enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy ($\Delta G^{\#}$) of activation were also calculated using the Eyring equation (10) [13] as follows:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \qquad (10)$$

Where k_b and h refer to Boltzmann's constant and Planck's constant, respectively. The enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) were calculated from the slope and intercept plot of ln (k/T) versus 1/T in figure 6(a&b), while the free energy of activation ($\Delta G^{\#}$) was obtained from Eq. (11):

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (11)$$

The calculated values are listed in Table 3. The $\Delta G^{\#}$ values were negative at all tested temperatures (30-60ºC) verifying that the sorption of direct dye onto BC and cotton were spontaneous and thermodynamically favorable. In other words, more negative $\Delta G^{\#}$ implies a

greater driving force of adsorption, resulting in increased adsorption capacity. As temperature increased from 30 to 60 ºC, $\Delta G^{\#}$ decreased negative, suggesting that adsorption capacity decreased at high temperatures. The negative $\Delta H^{\#}$ values indicate that adsorption of direct dye onto BC and cotton is an exothermic process, which is supported by the decrease in adsorption of direct dye as temperature increase. Furthermore, the negative $\Delta S^{\#}$ indicates that the degrees of freedom decreased at the solid-liquid interface during adsorption of direct dye onto BC and cotton. Physisorption and chemisorptions can be classified, to a certain extent, by the magnitude of enthalpy change. Bonding strengths of < 84kJ/mol are typically considered as those of physisorption bonds. Chemisorptions bond strengths can be 84-420 kJ/mol. Generally, $\Delta G^{\#}$ for physisorption is less than that for Chemisorptions. The former is between -20 and 0 kJ/mol and the latter is between -80 and -400 kJ/mol [14]. Additionally, Nollet et al. [15] demonstrated that the physisorption process normally had activation energy of 5-40 kJ/mol, while Chemisorption had a relatively higher activation 40-800 kJ/mol. Therefore, the values of $\Delta H^{\#}$, $\Delta G^{\#}$ and E_a all suggest that sorption of direct blue 71dye onto BC and cotton by a physisorption process.
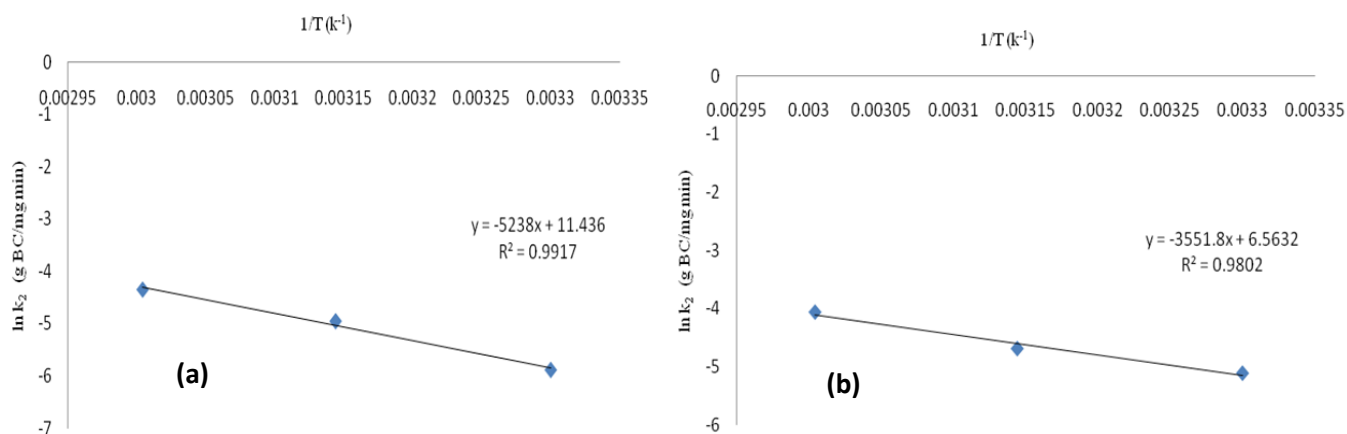

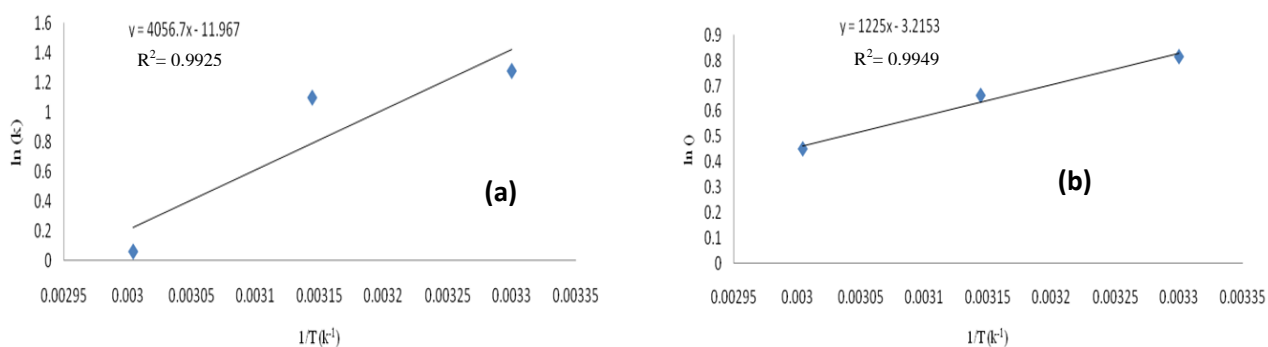Figure 5(a&b). Arrhenius plot for the sorption of direct dye on BC and cotton

Figure 6(a&b).Eyring plot for the sorption of direct dye on BC and cotton

Table 3. Activation parameters for the biosorption of direct dye on BC and cotton at an initial dye concentration 100mg/L, MLR 1:500 and pH 3.0

Good	Temp (ºC)	K_2(g BC/mg min)	E_a(kJ/mol)	R^2	$\Delta H^{\#}$(kJ/mol)	$\Delta S^{\#}$(kJ/mol k)	$\Delta G^{\#}$(kJ/mol)	R^2
BC	30	2.8×10^{-3}	43	0.9920	-26	-228	-16.20	0.9925
	45	7×10^{-3}					-15.71	
	60	13.04×10^{-3}					-11.89	
cotton	30	5.99×10^{-3}	30	0.9802	-18.07	-198	-14.3	0.9949
	45	8.46×10^{-3}					-11.05	
	60	17.11×10^{-3}					-8.11	

CONCLUSION

BC fibers are very pure, 10nm in diameter and about 0.5micron long. The molecular formula of bacterial cellulose is similar to that of plant cellulose. Its fibers are very stiff and it has high tensile strength, high porosity, and nanofibrillar structure. BC nanofibrials are much thinner than fibers of plant cellulose, much more reactive hydroxyl groups on the surface of BC can be functionalized.

Good wet fastness properties of direct dyes on cellulosic material are generally believed to be due to the unique linear structure which allows them to aggregate within the cellulose structure once they have penetrated the fiber. This survey showed that BC higher adsorption capacity for direct dye compared to that cotton and BC with highly water holding capacity as a biosorbent could be employed for the removal of dye from aqueous solution. This study investigated the sorption kinetics of direct blue 71 dye on BC and cotton. The dye adsorption rates onto BC and cotton decreased at higher dyeing temperatures which indicated the process was exothermic. The adsorption kinetics of dye on BC and cotton was found to follow the pseudo second-order kinetic model. The activation energy for the sorption process on BC and cotton were found to be 43kJ/mol and 30kJ/mol. The values of Gibbs free energy $\Delta G^{\#}$ showed that reaction was spontaneous. Also the values of $\Delta H^{\#}$, $\Delta G^{\#}$ and E_a all suggested that the sorption of direct dye onto BC and cotton was by physisorption.

ACKNOWLEDGMENT

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