Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Rhodamine B onto O-Carboxymethylchitosan-N-Lauryl

Maria Claudia Tonelli Largura[a]; Aline Debrassi[a]; Helen Helena dos Santos[a]; Alyni Terreiro Marques[a]; Clóvis Antonio Rodrigues[a]
[a] Núcleo de Investigações Químico-Farmacêuticas (NIQFAR), Universidade do Vale do Itajaí (UNIVALI), Itajaí, Santa Catarina, Brazil

To cite this Article Largura, Maria Claudia Tonelli , Debrassi, Aline , Santos, Helen Helena dos , Marques, Alyni Terreiro and Rodrigues, Clóvis Antonio(2010) 'Adsorption of Rhodamine B onto O-Carboxymethylchitosan-N-Lauryl', Separation Science and Technology, 45: 10, 1490 — 1498

To link to this Article: DOI: 10.1080/01496391003698091

URL: http://dx.doi.org/10.1080/01496391003698091

Separation Science and Technology, 45: 1490–1498, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003698091

Adsorption of Rhodamine B onto O-Carboxymethylchitosan-N-Lauryl

Maria Claudia Tonelli Largura, Aline Debrassi, Helen Helena dos Santos, Alyni Terreiro Marques, and Clóvis Antonio Rodrigues
Núcleo de Investigações Químico-Farmacêuticas (NIQFAR), Universidade do Vale do Itajaí (UNIVALI), Itajaí, Santa Catarina, Brazil

The adsorption of a cationic dye (rhodamine B; RB) on O-carboximethyl-N-acetylated (L-CMCh) in aqueous solution was investigated. The effect of the process parameters such as the contact time, pH, and temperature are reported. Both temperature and pH influence dye adsorption. To determine the adsorption capacity, the equilibrium adsorption data were analyzed by the Langmuir, Langmuir-Freundlich, and Redlich-Peterson isotherm models. The results showed better agreement with the Langmuir-Freundlich model than the other models. The maximum adsorption capacity of RB for L-CMCh was determined as 38.5 mg g^{-1} at pH 8.5 and 25°C. The kinetic results follow a pseudo-second-order rate equation. The activation energy value for adsorption of RB on L-CMCh was found to be 52.0 kJ mol^{-1}. The negative values of Gibbs free energy and enthalpy show the adsorption to be spontaneous and exothermic. The negative value of the enthalpy for adsorption of RB onto L-CMCh shows the adsorption to be exothermic.

Keywords carboxymethylchitosan-N-acetylated; equilibrium adsorption; kinetic adsorption; rhodamine B

INTRODUCTION

Different kinds of synthetic dyestuffs arising from many sources, such as the textile, dyestuff, leather, rubber, plastic, cosmetics, and paper industries are present in wastewater effluents. Even small amounts of dyes in water may have a serious environmental impact, as many are toxic to aquatic creatures and humans. As synthetic dyestuffs have mostly aromatic structures and are biologically non-degradable, special techniques to remove them from wastewater are required (1,2).

Several methods for removing dye pollution from wastewater have been investigated, activated sludge (3), photodegradation (4), and ozonation (5). Of these, adsorption has been found to be one of the most successful treatment methods.

Various materials have been developed for this purpose —activated carbon (6,7) peat (8), alumina (9), cellulose-based wastes (10), formaldehyde and sulphuric acid treated sawduts (11), sepiolite (2), chitosan (1,10,12–15), mesoporus (16), algae-manufacturing waste (17), bottom ash and deoiled soya (18–21).

Despite the fact that activated carbon is one of the most effective adsorbents, its high cost poses a barrier to its application for the large-scale treatment of effluents, so interest is growing in the application of low-cost adsorbents (22,23). Biopolymers are a suitable option for this purpose due to their biodegradable characteristics and tolerable cost. Chitosan, a biopolymer obtained from the deacetylation of chitin, has been widely used as an adsorbent of dyes and metal ions, due to its amino and hydroxyl groups, which serve as coordination sites (12,24–26).

The aim of this investigation was to study the adsorption of the cationic dye Rhodamine B (RB), from aqueous solution at different pH values and temperatures onto a hydrophobic-modified chitosan derivative. The kinetics of adsorption was determined using pseudo-first-order, pseudo-second-order, and intraparticle diffusion, and the thermodynamic parameters were determined. The Langmuir, Langmuir-Freundlich, and Redlich-Peterson equations were applied to fit the equilibrium isotherms.

EXPERIMENTAL

Materials

The chitosan (Ch) was purchased from Purifarma, São Paulo, SP, Brazil. The degree of deacetylation was 79% and the average molecular weight was 565 kDa, determined by the viscosimetric method. The other reagents used were all analytical grade from Vetec Quimica Fina, Rio de Janeiro, Brazil, and all the solutions were prepared with distilled water.

Synthesis of O-Carboxymethylchitosan-N-Lauryl (L-CMCh)

O-carboxymethylchitosan (CMCh), with a carboxymethylation degree of 22%, was prepared in accordance

---

Received 27 November 2009; accepted 12 February 2010.

Address correspondence to Clóvis Antonio Rodrigues, Núcleo de Investigações Químico-Farmacêuticas (NIQFAR), Universidade do Vale do Itajaí (UNIVALI), Itajaí, 88302-202, Santa Catarina, Brazil. Tel.: 0055 (47) 341-7664; Fax: 0055 (47) 341-7600. E-mail: crodrigues@univali.br

with the methods described in the literature (27). The L-CMCh was synthesized by modification of the method described by Tien et al. (2003) (28) to synthesize N-acylated chitosan. 5 g of CMCh was dispersed in 600 ml of distilled water to total solubilization. The pH was adjusted to 7.0 by the addition of NaOH. Lauroyl chloride (20 mL) (Aldrich, Milan, Italy) was then added. After 6 h, the solution was neutralized (pH 7.0) and precipitated with acetone. The precipitate was collected by filtration, washed with methanol, and purified with acetone using a Soxhlet extractor. Finally, the product was dried under vacuum.

Determining the Degree of Acylation

The degree of N-acylation was determined by FT-IR from the band transmittance area at 2840 cm^{-1} (ascribed to the CH_2 group) of lauroyl groups incorporated in L-CMCh. To determine the degree of N-acylation of L-CMC, the band area at 2840 cm^{-1} was used, with a standard curve prepared with different concentrations of lauric acid. Powdered samples of L-CMCh and lauric acid were compressed with KBr to obtain a disk (100 mg) for FT-IR analysis. For each sample or standard curve point, at last three disks were used to obtain a statistical evaluation. The FT-IR spectra were recorded using a Bomen BM 100 spectrophotometer (Quebec, Canada).

Adsorption Study

Adsorption Isotherms

Adsorption isotherms were determined using batch methods. For the batch experiments, 0.020 g of Ch or L-CMCh was added to 20 mL of RB dye ([RB] = 1.0 to 50.0 mg L^{-1} or 50.0 to 500.00 mg L^{-1}) in a buffer solution CH_3COO/CH_3COONa (0.1 M) for the lower pH range (4.5; 5.5), and NaH_2PO_4/Na_2HPO_4 (0,1 M) for pH 6.5, 7.5, and 8.5. The solutions were stirred with thermostatting for 60 min. Afterwards, the samples were filtered and the dye concentration was determined using a Spectrovision UV-visible DB-1880S spectrophotometer (China), at the wavelength of 526 nm. The amount of dye adsorbed was calculated from difference of initial concentration and the equilibrium concentration of dye. In order to obtain the thermodynamic parameters, the same procedure was performed at solution temperatures of 25, 35, 45, and 55°C.

Kinetics Experiment

The kinetic study was carried out by stirring 0.020 g of L-CMCh or Ch into 20 mL of Rhodamine B at 25 mg L^{-1} in a buffer solution NaH_2PO_4/Na_2HPO_4 (0,1 M) pH 8.5. The flasks were stirred for variable times (15–360 min). Aliquots of solution were removed at regular intervals, and the amount of dye adsorbed was determined as described above. The kinetic experiments were carried out at solution temperatures of 25, 35, 45, and 55°C.

Effect of pH on Adsorption

The influence of dye solution pH on the adsorption process was investigated over a pH range of 4.5–8.5. The dye solutions were prepared in a buffer solution CH_3COO/CH_3COONa (0.1 M) for the lower pH range (4.5; 5.5), and NaH_2PO_4/Na_2HPO_4 (0,1 M) for pH 6.5, 7.5, and 8.5.

RESULTS AND DISCUSSION

Characterization of L-CMCh

O-carboxymetylchitosan-N-lauryl (L-CMCh), Fig. 1, was synthesized using lauroyl chloride and its chemical structure was characterized by FT-IR. The FT-IR spectrum of L-CMCh. Figure 2 shows the characteristics of O-carboxymethylchitosan at: 3455 cm^{-1} (ν_{as} OH), 1590 cm^{-1} (δ NH), and 1740 cm^{-1} (–C=O of –COOH). In addition, the L-CMCh spectrum showed new characteristic absorption peaks at 2950 cm^{-1} (ν_{as} CH_2), 2870 cm^{-1} (ν_s CH_2), 1450 cm^{-1} (δ CH_2), confirming the alkyl substitution in chitosan.

The degree of substitution of L-CMCh was 0.69 ± 0.04, as determined by an IR method (28).

Effect of Initial RB Concentration

The dye concentration plays an important role in the adsorption capacity of the adsorbent. The influence of the initial RB concentration is shown in Fig. 3. Clearly, the adsorption capacity of L-CMCh increases with the concentration range of the dye. Figure 3 shows that the amount of RB adsorbed to be 33 mg g^{-1} and 90 mg g^{-1} for the lower and higher concentration ranges, respectively. The increase in adsorption capacity with dye concentration is due to an increase in the driving force of the concentration gradient, as the dye concentration is increased (29).

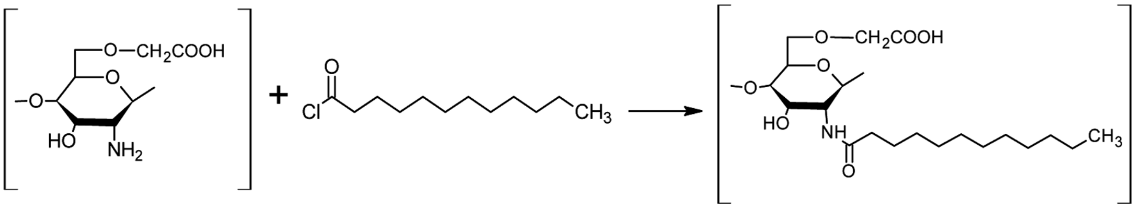


FIG. 1. Modification of chitosan with lauroyl chloride.

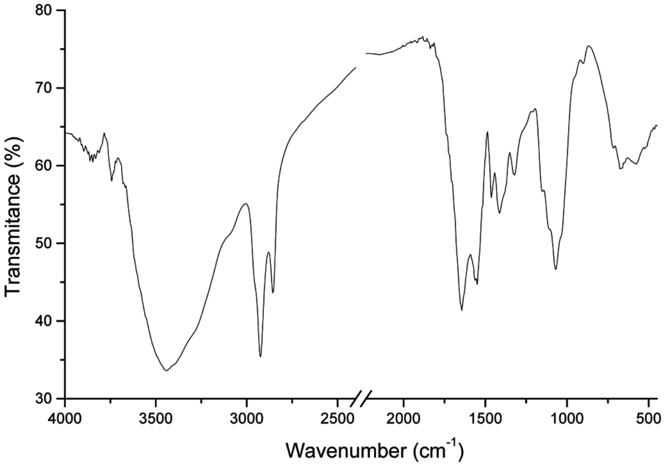


FIG. 2. FT-IR spectrum of O-Carboxymethylchitosan-N-Lauryl.

Effect of Adsorbent

The adsorption capacities of RB onto L-CMCh and Ch are shown in Fig. 4. The equilibrium adsorption shows that the maximum amount of RB adsorbed by Ch was 3.5 mg g^{-1}, while the other hand, the maximum amount of RB adsorbed by L-CMCh was 33 mg g^{-1}. The difference in the amount of dye adsorbed can be attributed to introduction of O-carboxyl and N-lauroyl groups in the chitosan chain. The introduction of carboxyl groups can greatly improve the ionic interaction with cationic dye, resulting in increased adsorption capacity. The introduction of a lauryl group to the chitosan molecule led to significant changes in the chitosan properties, especially an increase in hydrophobicity. In this case, the adsorption of dye is the result of a hydrophobic interation between the RB and alkyl groups present in L-CMCh.

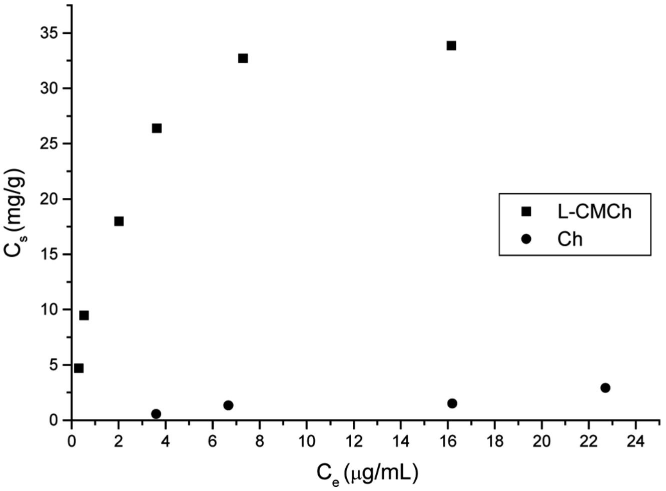


FIG. 4. Effect of type of adsorbent in RB adsorption. Range dye concentration (1.0–50.0 mg L^{-1}), sample dose 0.020 g/25 mL, pH 8.5 temperature 25°C and equilibrium time 60 min.

Effect Temperature on Adsorption

The effect of temperature on the adsorption rate of RB on L-CMCh was investigated at 25, 35, 45, and 55°C. Figure 5 shows the results of the equilibrium adsorption experiment carried out at different temperatures. The adsorption of RB by L-CMCh decreased from 33 mg g^{-1} to 27 mg g^{-1}, as the temperature of the solution decreased, indicating the exothermic nature of the process. This decrease in adsorption may be the result of an increase of the desorption step in the adsorption mechanism. A similar observation was reported previously for adsorption of methylene blue on active carbon (30), adsorption of malachite green on chitosan beads (15), eosin Y by

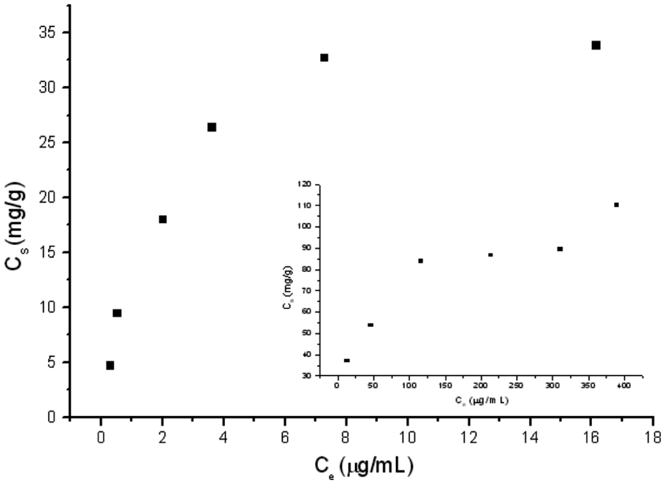


FIG. 3. Effect of concentration range on adsorption of RB dye onto L-CMCh. Range dye concentration 1.0–50.0 mg L^{-1}, sample dose 0.020 g/25 mL, pH 8.5, temperature 25°C and equilibrium time 60 min. Insert: range concentration dye 50.0–500.00 mg L^{-1}.

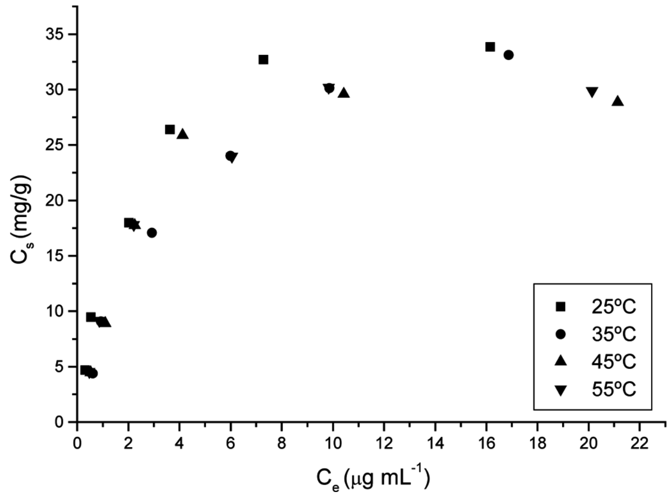


FIG. 5. Adsorption isotherm of RB dye onto L-CMCh at different temperature. Range dye concentration (1.0–50.0 mg L^{-1}), sample dose 0.020 g/25 mL, pH 8.5 and equilibrium time 60 min.

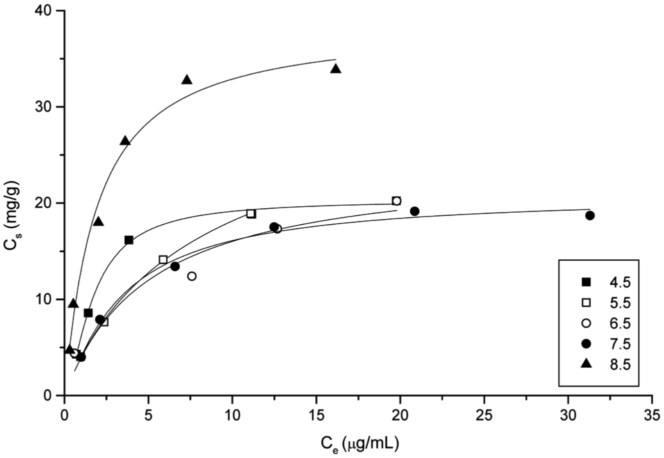


FIG. 6. Adsorption isotherm of RB dye onto L-CMCh at different pH values. Dye concentration range (1.0–50.0 mg L^{-1}), sample dose 0.020 g/25 mL, pH 8.5, temperature 25°C and equilibrium time 60 min. The full lines represent the fits of experimental data to the Langmuir-Freundlich isotherm (non-linear plot).

chitosan hydrobeads (13), and congo red onto chitosan hydrobeads (14).

Effect pH Value on Adsorption

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of the dye. The influence of pH on the adsorption of RB by L-CMCh was studied, to gain further insight into the adsorption process. The adsorption of RB was studied in a pH range of 4.5–8.5.

Figure 6 and Table 1 show the effect of pH on the adsorption of RB onto L-CMCh. The plots indicate that the adsorption of RB by both adsorbents increased with an increase in the pH of the solution. RB is a cationic dye and in acid solution, cationic L-CMCh repulses the cationic dye, thereby reducing the adsorption of RB onto L-CMCh. However, as the pH is increased the adsorption increases. This can be explained by the electrostatic interaction that exists between the negatively charged surface of the adsorbent due to the $-NH_2$ free groups in Ch and $-COO^-$ and $-NH_2$ in L-CMCh, and RB, a cationic dye. On the other hand, the appreciable amount of RB adsorption on L-CMCh throughout the pH range suggests a strong involvement of different adsorption mechanisms, principally the hydrophobic interaction between the aromatic residues of the dye and lauryl groups of adsorbent. A similar observation has been reported for the adsorption of methylene blue onto yellow passion fruit peel (31), malachite green onto chitosan beads (15), and methyl violet and methylene blue onto sepiolite (2).

Adsorption Isotherm

The adsorption isotherm indicates how the dye molecules are distributed between the liquid phase and solid phase when the adsorption process reaches equilibrium. Three different adsorption isotherms were tested to find the most suitable one: the Langmuir, the Langmuir-Freundlich and the Redlich-Peterson.

The experimental values of the isotherms were used in this non-linear form of Langmuir equation (1). This equation is valid for monolayer adsorption. The model contains a limited number of sites and predicts a homogeneous distribution of adsorption energies (32).

$$C_s = (K_L q_m C_{eq})/(1 + KC_{eq}) \quad (1)$$

TABLE 1
Isotherm constants for the adsorption of RB on L-CMCh at different pH values and temperatures

	Langmuir			Langmuir-Freundlich				Redlich-Peterson			
	K_L (mL g^{-1})	q_m (mg g^{-1})	r^2	K_{LF} (mL g^{-1})	q_m (mg g^{-1})	c	r^2	K_{RP} (mL g^{-1})	a_{RP} (L mg^{-1})	c	r^2
pH											
4.5	0.446	22.98	0.976	0.439	20.34	1.56	0.998	0.185	42.06	1.21	0.990
5.5	0.146	30.56	0.999	0.135	33.94	0.930	0.999	0.202	23.79	0.912	0.999
6.5	0.196	24.17	0.946	–	–	–	–	–	–	–	–
7.5	0.254	22.04	0.989	0.243	20.92	1.14	0.991	0.143	32.61	1.11	0.993
8.5	0.507	39.38	0.985	0.516	38.58	1.05	0.986	0.296	54.77	1.12	0.988
T (°C)	(pH 8.5)										
25	0.507	39.38	0.985	0.516	38.58	1.05	0.986	0.296	54.77	1.12	0.988
35	0.246	41.38	0.994	0.245	41.94	0.982	0.994	0.259	39.99	0.988	0.994
45	0.337	39.80	0.966	0.359	31.84	1.63	0.994	0.0285	305.6	1.83	0.999
55	0.365	37.32	0.986	0.374	36.60	1.02	0.986	0.487	30.73	0.921	0.986

where: C_s = amount of dye adsorbed ($mg\,g^{-1}$); C_{eq} = equilibrium concentration of dye in solution ($mg\,L^{-1}$); K_L = adsorption constant of Langmuir ($L\,mg^{-1}$); q_m = maximum amount of dye adsorbed onto 1 g of adsorbent.

The Langmuir and Freundlich models may be combined to give the composite Langmuir-Freundlich equation (2)

$$C_s = (K_{LF} q_m C_{eq}^c)/(1 + KC_{eq}^c) \tag{2}$$

where: K_{LF} = adsorption constant of Langmuir-Freundlich ($L\,mg^{-1}$); c = heterogeneity parameter. As the equation has three fitting constants, it describes the adsorption much better. For independent non-interacting adsorption sites corresponding to the Langmuir model, c is 1. When $c > 1$, positive cooperativity is assumed, while when $0 < c < 1$, negative adsorption cooperativity is expected.

The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equations. The Redlich-Peterson isotherm incorporates the three parameters, and can be applied either in homogeneous or heterogeneous systems, Eq. (3)

$$C_s = (K_{RP} a_{RP} C_{eq})/(1 + KC_{eq}^c) \tag{3}$$

where: K_{RP} = Redlich-Perterson adsorption constant ($L\,mg^{-1}$); c = heterogeneity parameter, which lies between 0 and 1; a_{RP} affinity coefficient ($L\,mg^{-1}$). If c is equal to 1, Eq. (3) reduces to the Langmuir isotherm equation, while when the term KC_{eq}^c is much >1, the Redlich-Peterson isotherm equation can be approximated by a Freundlich type equation (32). Values of c were found to be higher than 1 for some conditions, which means that the Redlich-Peterson model is not a suitable one to explain this adsorption process (33).

Non-linear regression was used to determine the most fitted isotherm, and the method of least squares was used to fit the parameters of the isotherm. Table 1 summarizes the isotherm constant determined for the three different equilibrium isotherms tested, as well as the non-linear correlation coefficients under different conditions. On the basis of the correlation coefficient, the Langmuir-Freundlich adsorption isotherm model was found to provide the best prediction for the adsorption of RB onto L-CMCh. The plot for the non-linear Langmuir-Freundlich isotherm is shown in Fig. 5. Table 1 shows that the q_m of RB adsorbed onto L-CMCh decreases as the temperature increases. A similar finding was previously reported for the adsorption of acid dyes onto chitosan (34), adsorption of congo red by chitosan hydrobeads (14), and malachite green on chitosan beads (15).

The q_m value of RB on L-CMCh at 25°C and pH 8.5, was much higher in comparison to the other adsorbents reported, such as fly ash 4.37 $mg\,g^{-1}$ (35), coal ash 2.47 $mg\,g^{-1}$ (36), surfactant-modified coconut coir pith 14,9 mg/g (37) zeolite 12.9 $mg\,g^{-1}$ (38), Jalshakti® 15.5 $mg\,g^{-1}$ (39), and dried biomass of actived sludge 7.2 $mg\,g^{-1}$ (2), polyurethane foam 3.2 mg/g (40), baker's yeast 25.0 mg/g (41), *Rhizopus oryzae* biomass 39.1 mg/g (42).

Adsorption Kinetics

The contact time between the adsorbent and the dye is of significant importance in the treatment of wastewater by adsorption. Achievement of equilibrium within a short space of time may indicate that an adsorbent might be effective in wastewater treatment plant.

Figure 7 presents the adsorption kinetic curves of RB on L-CMCh. On increasing the contact time, the amount of dye absorbed increases rapidly over several minutes, reaching its maximum value at about 120 min. The adsorption curves of the RB with contact time are single and smooth, with continuous leading saturation. These curves indicate the possible monolayer coverage of RB on the L-CMCh surface. Zubieta et al. (16) have reported a 5 h equilibrium adsorption time for RB adsorption on mesoporous material. Similarly, a contact time of only 15 min was required to achieve the equilibrium adsorption of RB onto dried biomass of activated sludge (2).

The kinetics of the adsorption process was studied at 25°C, 35°C, 45°C, and 55°C. The kinetics of dye adsorption on the L-CMCh was determined with different kinetic models, such as the pseudo-first-order, the pseudo-second-order, and intraparticle diffusion.

The pseudo-first-order equation, the so-called Lagergren equation, is one of the most commonly used for the adsorption of solute from solution. The model is represented as follows:

$$\mathrm{Ln}\,(q_{eq} - q_t) = \mathrm{Ln}\,q_{eq} - K_1 t \tag{4}$$

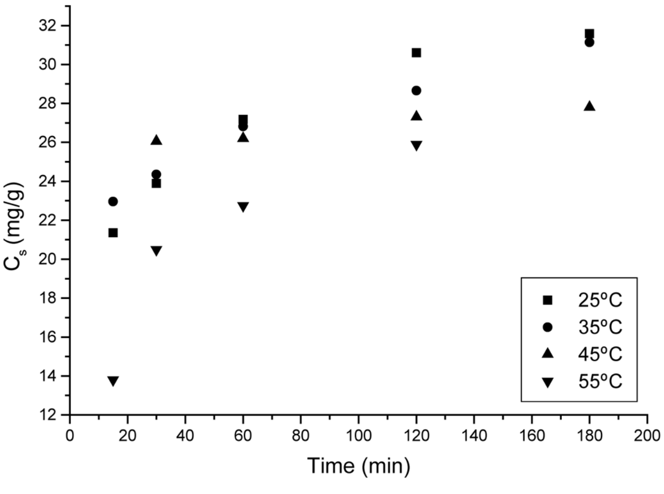


FIG. 7. Effect of contact time on the adsorption of RB dye onto L-CMCh at different temperatures. Dye concentration 25 $mg\,L^{-1}$ sample dose 0.020 g/25 mL, pH 8.5, and equilibrium time 60 min.

were, K_1 is the rate constant of pseudo-first-order adsorption (mim^{-1}) and q_{eq} and q_t denote the amounts of dye adsorbed at equilibrium and at time t ($\mu g\,g^{-1}$), respectively.

The pseudo-second-order equation based on the adsorption equilibrium capacity can be expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}} \tag{5}$$

where, K_2 is the rate constant of pseudo-second-order adsorption ($\mu g\,g^{-1}\,\text{min}^{-1}$).

The intraparticle diffusion model was tested to identify the diffusion mechanism. According to the model:

$$q_t = K_P\, t^{1/2} + C \tag{6}$$

were, K_P is the intraparticle diffusion constant ($\mu g\,g^{-1}\,\text{mim}^{-0.5}$) and C ($\mu g\,g^{-1}$) is the intercept of the straight line (30).

The straight line plots of three models for adsorption of RB by L-CMCh are shown in Fig. 8. The parameters and correlation coefficient were calculated from these plots, under different temperature values. The results are shown in Table 3.

As shown in Table 2, the pseudo-second-order equation fitted well with the experimental data. The correlation coefficient (r^2) is between 0.990–0.999. On the other hand, the r^2 values for first-order and intraparticle diffusion equations were found to be slightly lower. The results show that the adsorption of dyes by L-CMCh obeys the pseudo-second-order kinetic model.

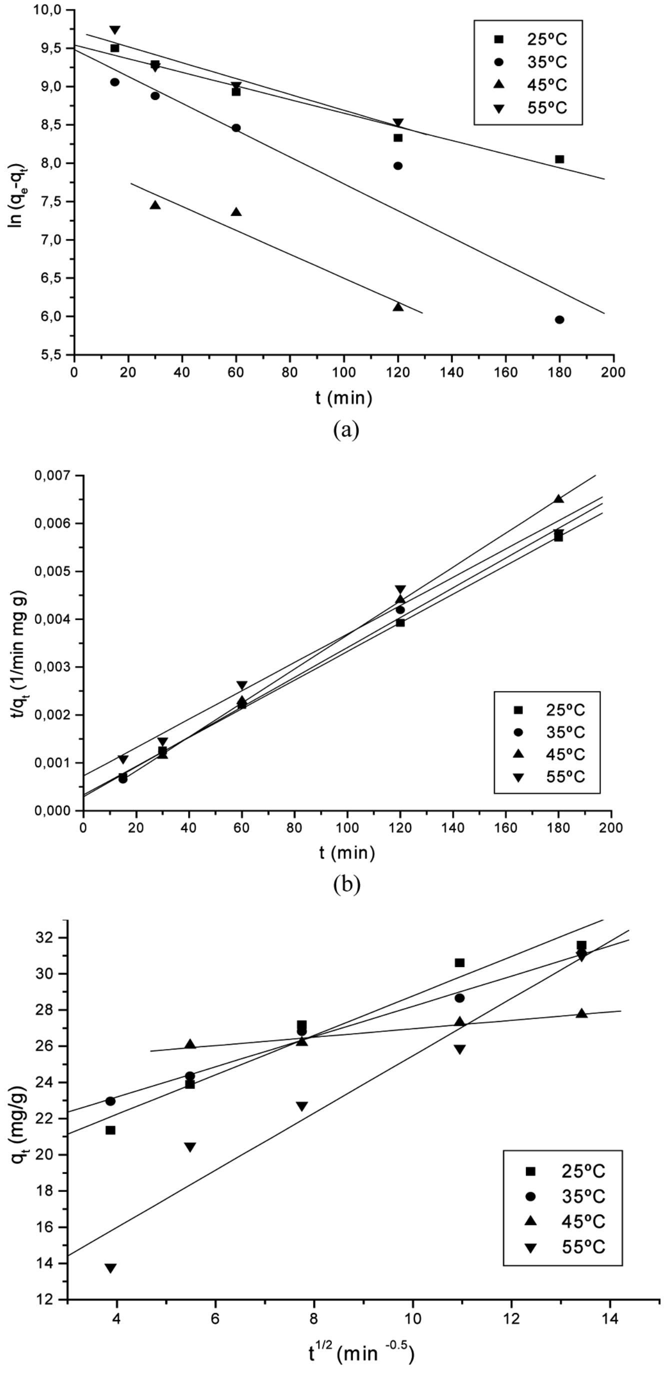
According to the intraparticle diffusion model, the uptake plot should be linear if intraparticle diffusion is involved in the adsorption process, and if these lines pass through the point of origin. When the plots do not pass through the origin, it can be concluded that intraparticle diffusion is not the only rate controlling step for the adsorption of RB onto L-CMCh.

The pseudo-second-order rate constant listed in Table 3 has been used to obtain the activation energy of RB adsorption on L-CMCh using the Arrhenius equation (7)

$$\text{Ln}K_2 = \text{Ln}\,K_o - \frac{Ea}{RT} \tag{7}$$

were, K_2 is the rate constant of the pseudo-second-order ($\mu g\,g^{-1}\,\text{min}^{-1}$); K_o is the Arrhenius factor, which is the temperature independent factor; R is the gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$); T is the absolute temperature (K) of the solution; and Ea is the activation energy ($J\,mol^{-1}$).

The plot of Ln K_2 versus 1/T shown in Fig. 9, for adsorption of RB onto L-CMCh, was applied to obtain the Ea from the slope, which was found to be $52.0\,kJ\,mol^{-1}$ for RB adsorption. The Ea value is used to identify the dominant type of adsorption, the diffusion controlled process has an activation energy of between $25–30\,J\,mol^{-1}$. The magnitude of E_a also reflects the type



(a)

(b)

(c)

FIG. 8. (a) Pseudo-first-order kinetics for adsorption of RB onto L-CMCh at different temperatures; (b) Pseudo-second-order kinetics for adsorption of RB using L-CMCh at different temperatures; (c) Intraparticle diffusion model kinetics for adsorption of RB using L-CMCh at different temperatures. Dye concentration $25\,mg\,L^{-1}$ sample dose 0.020 g/25 mL, pH 8.5.

TABLE 2
Kinetic fitting results for the absorption of RB on L-CMCh at different temperatures

	Pseudo-first-order			Peudo-second-order			Intraparticle diffusion		
T (°C)	q_e ($\mu g\,g^{-1}$)	K_1 (min^{-1})	r^2	q_e ($\mu g\,g^{-1}$)	k_2 ($\mu g\,g^{-1}\,min^{-1}$)	r^2	k_p ($\mu g\,g^{-1}\,min^{-1/2}$)	C ($\mu g\,g^{-1}$)	r^2
25°C	1.39×10^4	8.89×10^{-3}	−0.984	3.34×10^4	2.68×10^{-6}	0.999	1.09×10^3	1.79×10^4	0.981
35°C	1.31×10^4	1.75×10^{-2}	−0.958	3.20×10^4	3.33×10^{-6}	0.998	8.36×10^2	1.98×10^4	0.996
45°C	3.16×10^3	1.56×10^{-2}	−0.963	2.82×10^4	1.01×10^{-5}	0.999	2.32×10^2	2.46×10^4	0.978
55°C	1.66×10^4	1.04×10^{-2}	−0.955	3.38×10^4	1.20×10^{-6}	0.993	1.58×10^3	9.66×10^3	0.967

TABLE 3
Thermodynamic parameters for adsorption of dyes by adsorbent

Temperature (K)	ΔH^0 ($kJ\,mol^{-1}$)	ΔS^0 ($J\,mol^{-1}\,K^{-1}$)	ΔG^0 ($kJ\,mol^{-1}$)	E_a ($kJ\,mol^{-1}$)
298	−19.3	4.17	−20.4	52.0
308			−20.9	
318			−20.4	

of adsorption, i.e., physical or chemical. The E_a value ranges from 4 to $40\,kJ\,mol^{-1}$ for physisorption, while the range was from 40 to $95.5\,kJ\,mol^{-1}$ for chemisorption. The activation energy obtained for adsorption of RB by L-CMCh of $52.0\,kJ\,mol^{-1}$ suggests that the adsorption was not diffusion controlled, and that it was governed by interactions of a chemical nature. Similar E_a values have been reported for the study of malachite green adsorption by chitosan (15).

Thermodynamic Parameters of Adsorption

The thermodynamic parameters, including the Gibbs free energy change (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), were determined using the following equations and represented as van't Hoff equations

$$\mathrm{Ln}\,K_D = \frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT} \tag{8}$$

$$\Delta G^0 = -RT\,\mathrm{Ln}\,K_D \tag{9}$$

$$K_D = \frac{C_s}{C_{eq}} \tag{10}$$

were, K_D is the equilibrium constant; C_{eq} is the dye equilibrium concentration; Cs the amount of dye absorbed;

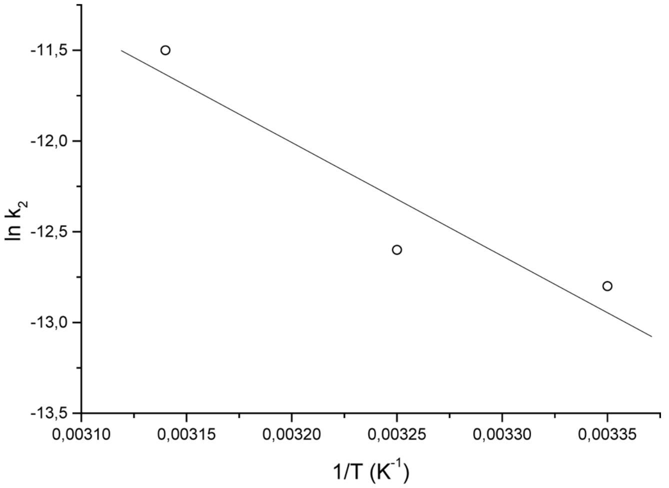


FIG. 9. Arrhenius plot for adsorption of RB onto L-CMCh.

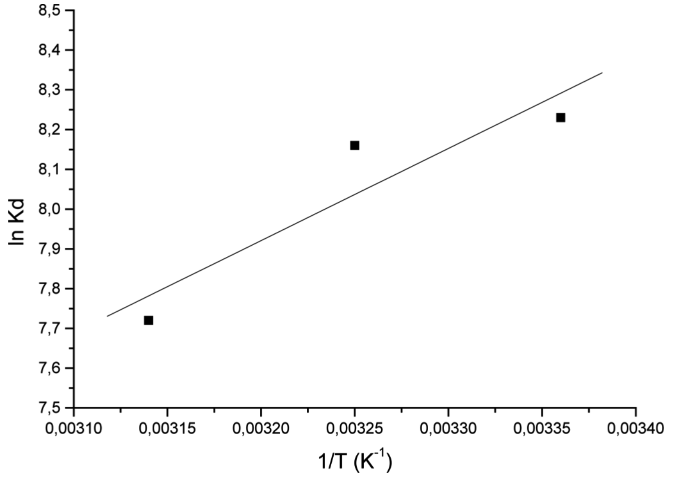


FIG. 10. van't Hoff plot for adsoption of RB onto L-CMCh.

R is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$); T is the absolute solution temperature (K).

From a plot of $\mathrm{LnK_D}$ versus 1/T, Fig. 10 has a slope of $\Delta H/R$ and intercept $\Delta S/R$. The results are shown in Table 3.

The results of the ΔG^o for adsorption of RB by L-CMCh, shown in Table 3, demonstrate that the adsorption of dye is spontaneous and that the system does not gain energy from any external source. The negative value of the enthalpy (ΔH^0) for adsorption of RB shows the adsorption to be exothermic, and the positive value entropy (ΔS^0) indicates an increase in the degree of freedom or increased disorder of the adsorption process. Similar results were also found for reactive dye adsorption onto chitosan (12).

CONCLUSION

The effect of dye adsorption onto L-CMCh at equilibrium is better described by the Langmuir-Freundlich model. The maximum adsorption capacities, at pH 8.5, were $38.5\,\mathrm{mg\,g^{-1}}$. Measurements of its kinetics imply that dye adsorption obeys the pseudo-second-order process. From the thermodynamic study, the E_a value obtained for RB L-CMCh is $52.0\,\mathrm{kJ\,mol^{-1}}$. Therefore, the type of adsorption between RB and L-CMCh can be considered as chemical adsorption. The negative value of the ΔH^o for adsorption of RB shows the adsorption to be exothermic.

ACKNOWLEDGEMENTS

This work was supported by grants from CNPq, ProBIC/ProPPEC/UNIVALI.

REFERENCES

1. Wang, L.; Wang, A. (2007) Adsorption characteristics of Congo Red onto the chitosan/montmorillonite nanocomposite. *J. Hazard. Mater.*, 147: 9795.
2. Dogan, M.; Özdemir, Y.; Alkan, M. (2007) Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes Pigm.*, 75 (3): 701.
3. Ju, D.J.; Byun, I.G.; Park, J.J.; Lee, C.H.; Ahn, G.H.; Park, T.J. (2008) Biosorption of a reactive bye (Rhodamine-B) from an aqueous solution using dried biomass of activated sludge. *Bioresour. Technol.*, 99: 7971.
4. Bergamini, R.B.M.; Azevedo, E.B.; Araújo, L.R.R. (2009) Heterogeneous photocatalytic degradation of reactive dyes in aqueous TiO_2 suspensions: Decolorization kinetics. *Chem. Engin. J.*, 149: 215.
5. Erol, F.; Özbelge, A.T. (2008) Catalytic ozonation with non-polar bonded alumina phases for treatment of aqueous dye solutions in a semi-batch reactor. *Chem. Engin. J.*, 139: 272.
6. Mohanty, K.; Naidu, J.T.; Meikap, B.C.; Biswas, M.N. (2006) Removal of crystal violet from wastewater by activated carbons prepared from rice husk. *Ind. Eng. Chem. Res.*, 45 (14): 5165.
7. Shaobin, W.; Zhu, Z.H. (2007) Effects of acidic treatment of activated carbons on dye adsorption. *Dyes Pigm.*, 75: 306.
8. Allen, S.J.; McKay, G.; Porter, J.F. (2004) Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *J. Colloid Interface Sci.*, 280 (2): 322.
9. Kannan, C.; Sundaram, T.; Palvannan, T. (2008) Environmentally stable adsorbent of tetrahedral silica and non-tetrahedral alumina for removal and recovery of malachite green dye from aqueous solution. *J. Hazard. Mater.*, 157 (1): 137.
10. Annadurai, G.; Juang, R.S.; Lee, D.J. (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J. Hazard. Mater.*, 92 (3): 263.
11. Garg, V.K.; Gupta, R.; Anu, B.Y.; Kumar, R. (2003) Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresour. Technol.*, 89 (2): 121.
12. Annadurai, G.; Ling, L.Y.; Lee, J.F. (2008) Adsorption of reactive dye from an aqueous solution by chitosan: Isotherm, kinetic and thermodynamic analysis. *J. Hazard. Mat.*, 152: 337.
13. Chatterjee, S.; Chatterjee, S.; Chatterjee, B.P.; Das, A.R.; Guha, A.K. (2005) Adsorption of a model anionic dye, eosin Y, from aqueous solution by chitosan hydrobeads. *J. Coll. Interf. Sci.*, 288: 30.
14. Chatterjee, S.; Chatterjee, S.; Chatterjee, B.P.; Guha, A.K. (2007) Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads. *Colloids Surf., A*, 299 (1): 146.
15. Bekçi, Z.; Özveri, C.; Seki, Y.; Yurdakoç, K. (2007) Sorption of malachite green on chitosan bead. *J. Hazard. Mater.*, 154 (1–3): 254.
16. Zubieta, C.; Sierra, M.B.; Morini, M.A.; Schulz, P.C.; Albertengo, L.; Rodríguez, M.S. (2007) The adsorption of dyes used in the textile industry on mesoporous materials. *Colloid Polym. Sci.*, 286 (4): 377.
17. Tsai, W.T.; Chen, H.R. (2010) Removal of malachite green from aqueous solution using low-cost chlorella-based biomass. *J. Hazard. Mater.*, 175: 844.
18. Mittal, A.; Gupta, V.K.; Malviya, A.; Mittal, J. (2008) Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (metanil yellow) by adsorption over waste materials (bottom ash and de-oiled soya). *J. Hazard. Mater.*, 151: 821.
19. Gupta, V.K.; Mittal, A.; Malviya, A.; Mittal, J. (2009) Adsorption of carmoisine A from wastewater using waste materials – bottom ash and deoiled soya. *J. Colloid Interf. Sci.*, 335: 24.
20. Mittal, A.; Kaur, D.; Malviya, A.; Mittal, J.; Gupta, V.K. (2009) Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents. *J. Colloid Interf. Sci.*, 337: 345.
21. Mittal, A.; Mittal, J.; Malviya, A.; Gupta, V.K. (2009) Adsorptive removal of hazardous anionic dye "Congo red" from wastewater using waste materials and recovery by desorption. *J. Colloid Interf. Sci.*, 340: 16.
22. Gupta, V.K.; Carrott, P.J.M.; Carrott, M.M.L.; Suhas, I.A. (2009) Low-cost adsorbents: Growing approach to wastewater treatment – a review. *Environ. Sci. Technol.*, 39: 783.
23. Gupta, V.K.; Suhas, I.A. (2009) Application of low-cost adsorbents for dye removal – a review. *J. Environ. Manage.*, 90: 2313.
24. Wong, Y.C.; Szeto, Y.S.; Cheung, W.H.; Mckay, G. (2008) Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan. *Process Biochem.*, 14 (1): 11.
25. Crini, G.; Badot, P.M. (2008) Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Prog. Polym. Sci.*, 33: 399.
26. Crini, G.; Gimbert, F.; Robert, C.; Martel, B.; Adam, O.; Morin-Crini, N.; Giorgi, F.D.; Badot, P.M. (2008) The removal of basic blue 3 from aqueous solutions by chitosan-based adsorbent: Batch studies. *J. Hazard. Mater.*, 153 (1–2): 96.
27. Chen, X.; Park, H. (2003) Chemical characteristics of O-carboxymethylchitosans related to the preparation conditions. *Carbohydr. Polym.*, 53 (4): 355.

28. Tien, C.L.; Lacroix, M.; Ispas-Szabo, P.; Mateescu, M.A. (2003) N-acylated chitosan: Hydrophobic matrices for controlled drug release. *J. Control. Rel.*, 93: 1.
29. Ju, D.J.; Byun, I.G.; Park, J.J.; Lee, C.H.; Ahn, G.H.; Park, T.J. (2006) Biosorption characteristics of reactive dye onto dried activated sludge. *Wat. Practic. Technol.*, 1 (3): 1.
30. Tan, I.A.W.; Ahmad, A.L.; Hameed, B.H. (2008) Adsorption of basic dye using activated carbon prepared from oil palm shell: Batch and fixed bed studies. *Desalinatio*, 225: 13.
31. Pavan, F.A.; Mazzocato, A.C.; Gushikem, Y. (2008) Removal of methylene blue from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. *Bioresour. Technol.*, 99: 3162.
32. Liu, Y.; Liu, Y.J. (2008) Biosorption isotherms, kinetics and thermodynamics. *Sep. Purif. Technol.*, 61: 229.
33. Redlich, O.; Peterson, D.L. (1959) A useful adsorption isotherm. *J. Phys. Chem.*, 63: 1024.
34. Wong, Y.C.; Szeto, Y.S.; Cheung, W.H.; Mckay, G. (2008) Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan. *Process Biochem.*, 14 (1): 11.
35. Shaobin, W.; Boyjoo, Y.; Choueib, A. (2005) A comparative study of dye removal using fly ash treated by different methods. *Chemosphere*, 60: 1401.
36. Shaobin, W.; Soudi, M.; Zhu, Z.H.; Li, L. (2006) Coal ash conversion into effective adsorbents for removal of heavy metals and dyes from wastewater. *J. Haz. Mat.*, B133: 243.
37. Sureshkumar, M.V.; Namasivayam, C. (2008) Adsorption behavior of Direct Red 12B and Rhodamine B from water onto surfactant-modified coconut coir pith. *Colloid Surf. A: Physicochem. Eng. Aspects*, 317: 277.
38. Shaobin, W.; Zhu, Z.H. (2006) Characterization and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution. *J. Haz. Mat.*, B136: 946.
39. Dhodapkar, R.; Rao, N.N.; Pande, S.P.; Nandy, T.; Devotta, S. (2007) Adsorption of cationic dyes on Jalshakti®, super absorbent polymer and photocatalytic regeneration of the adsorbent. *React. Funct. Polym.*, 67: 540.
40. Baldez, E.E.; Robaina, N.F.; Cassella, R.J. (2009) Study of rhodamine B retention by polyurethane foam from aqueous medium in presence of sodium dodecylsulfate. *Sep. Sc. Technol.*, 44: 3128.
41. Yu, J.X.; Li, B.H.; Sun, X.M.; Jun, Y.; Chi, R.A. (2009) Adsorption of methylene blue and rhodamine B on baker's yeast and photocatalytic regeneration of the biosorbent. *Biochem. Eng. J.*, 45: 145.
42. Das, S.K.; Bhowal, J.; Das, A.R.; Guha, A.K. (2006) Adsorption behavior of rhodamine B on *Rhizopus oryzae* biomass. *Langmuir*, 22: 7265.