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Adsorption Kinetics of A Cationic Dye onto Indigenously Prepared Activated Kaza's Carbon

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ABSTRACT

Adsorption kinetics of cationic dye, rhodamine B onto indigenously prepared activated Kaza's carbon was studied. The kinetic process was investigated by applying the pseudo-first-order, pseudo-second-order, intraparticle diffusion, pore diffusion and Elovich models. The adsorption process offered excellent fit with pseudo-second-order model. Kinetic parameters such as rate constants and correlation coefficients, for each kinetic equation were calculated and discussed. Low SSE values of pore diffusion and Elovich equations indicate that pore diffusion plays a vital role in controlling the rate of the reaction.

Keywords: Adsorption, rhodamine-B, SSE.

INTRODUCTION

Textile and dyeing industrial effluents are highly colored and they show adverse effects on aquatic species. Out of many conventional removal processes such as coagulation, flocculation, and biological methods, adsorption has proved to be more versatile and efficient method [1]. In the present study, activated carbon indigenously prepared from agricultural waste, i.e., maize shell. Adsorption kinetics of rhodamine B onto prepared activated carbon was studied. The other relevant work also done[16-20].

MATERIALS AND METHODS

Maize shells are collected and double washed to remove clay and sand matter and then dried in sunlight for two days. The dried maize shells were crushed and carbonized in uniform nitrogen flow in a horizontal tube furnace electrically heated to 600^{0}C for four hours. It is cooled to room temperature. This carbon is sieved to have a particle size of 45mesh. It is chemically activated with 0.1N HNO_3 acid solution. Further it was washed with double-distilled water to remove the excess acid and dried at 150^{o}C for 12h. The Maize Shell Carbon (MZC) after activation was named after Kaza Somasekhara Rao, as Activated Maize Shell Carbon.

All chemicals used in this experiment are of analytical grade. A stock solution of rhodamine B (RB) of concentration 1000mg L^{-1} was prepared in double distilled water and adsorption experiment was carried out at room temperature 27±2^{o}C. 50ml of 30mg L^{-1} RB solution was shaken at constant agitation speed (160 rpm) with optimum dose (0.6g) of MZC for a specific period of contact time (range 5-50 min) in a thermostatic orbit incubator shaker. pH of solution was adjusted to 7 by adding 1N HCl or 1N NaOH solution. Dye solutions after equilibration were filtered through Whatmann No. 42 filter paper. Initial and equilibrium concentrations of dye solution were measured by spectrophotometric method using Elico UV visible spectrophotometer Model: SL 171 at wavelength 545nm. The percent removal of dye and amount adsorbed (in mg g^{-1}) are calculated using the following relationships

$$\text{Percent removal of dye} = 100(C_i-C_e)/C_i \quad \ldots\ldots\ldots\ldots..(1)$$

$$\text{Amount of dye adsorbed } (q_e) = (C_i-C_e)V/m\ldots\ldots\ldots(2)$$

where C_i and C_e are the initial and equilibrium concentrations (mg l^{-1}) of dye respectively; 'm' is the mass of MZC in grams and V is the volume of solution in litres.

Effect of agitation time on dye adsorption: The effect of agitation time on the percent removal of RB dye by MZC is shown in figure 1. The percent removal increases with time and attains equilibrium at 30 min. At this equilibrium time, the percent removal of dye is 99%. The change in the rate of removal of dye with time might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the dye uptake rate by adsorbent had decreased significantly due to the decrease in adsorption sites. Decreased removal rate, particularly, towards the end of experiment, indicates the possible monolayer of adsorbate on the outer surface and pores of the adsorbent leading to pore diffusion onto inner surface of adsorbent particles [2].

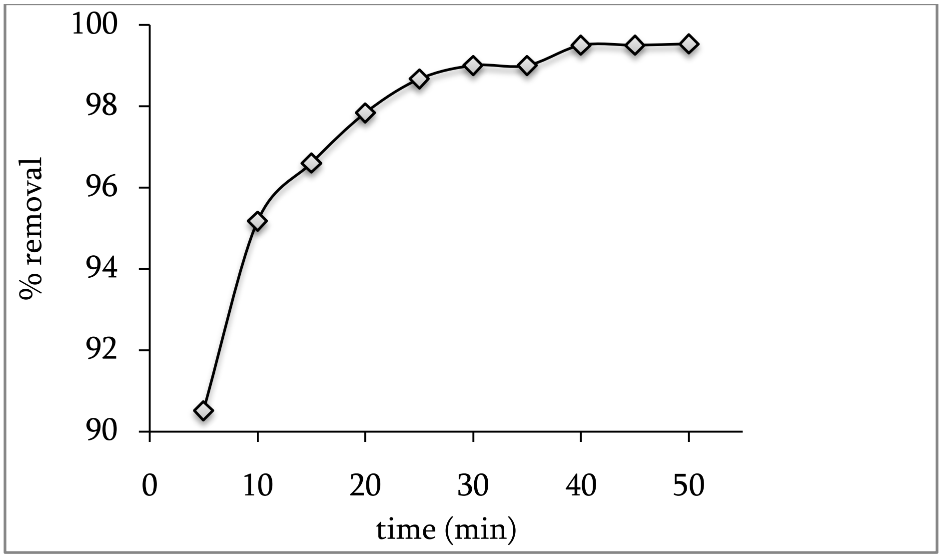

Figure 1. Effect of contact time on adsorption of RB dye onto MZC.

Adsorption kinetics: To study the adsorption kinetics, five kinetic models were used which include pseudo-first-order [3], pseudo-second-order [4], Weber and Morris intraparticle diffusion [5], Bangham's pore diffusion [6] and Elovich models [7]. The relevant equations and results are tabulated in table 1.

Table 1. Different kinetic models applied and their parameters

Model/Parameter	**Value of the parameter**
Pseudo-first-order	
$q_{e(expt.)}$ (mg g^{-1})	4.9500
$k_1 X10^{-1}$ (min^{-1})	1.5338
$q_{e(cal.)}$ (mg g^{-1})	1.0186
SSE	0.63079
R^2	0.9732
Pseudo-second-order	
$q_{e(expt.)}$ (mg g^{-1})	4.9500
$k_2 X10^{-1}$ (g $mg^{-1} min^{-1}$)	3.3904
$q_{e(cal.)}$ (mg g^{-1})	5.0403
SSE	0.00033
R^2	1.0000
Intraparticle diffusion	
$q_{e(expt.)}$ (mg g^{-1})	4.9500
$k_{ip} X10^{-1}$ (mg g^{-1} $min^{-0.5}$)	1.4310
$q_{e(cal.)}$ (mg g^{-1})	5.0358
SSE	0.00030
R^2	0.9326
Pore diffusion	
$q_{e(expt.)}$ (mg g^{-1})	4.9500
k_o ml (g $l^{-1})^{-1}$	9.0218
$q_{e(cal.)}$ (mg g^{-1})	4.9284
SSE	0.00002
R^2	0.9184
α	0.0412
Elovich equation	
$q_{e(expt.)}$ (mg g^{-1})	4.9500
β	5.3447
$q_{e(cal.)}$ (mg g^{-1})	4.9287
SSE	0.00002
R^2	0.9245
α	0.0573

Pseudo- first-order model: The Lagergren's rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. The linear form of pseudo-first-order rate expression of Lagergren is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \ldots\ldots\ldots\ldots.\ldots\ldots (3)$$

After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; the integrated form of Eq. (3) becomes

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

However, Eq. (4) is transformed into its linear form to use in the kinetic analysis of data

$$log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \ldots\ldots\ldots\ldots.\ldots\ldots (5)$$

where, q_e and q_t are the amounts of dye adsorbed on adsorbent (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order kinetics.

Pseudo- second-order model: The pseudo-second-order chemisorption kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Rearranging and integrating within the boundary conditions t=0 to t=t and q_t=0 to q_t=q_e, gives the linearised form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

which is integrated rate law for a pseudo-second-order reaction. Rearranging it again, Eq. (7) reduces to

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where, q_e and q_t have the same meaning as mentioned previously and k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant of pseudo-second-order adsorption. Eq. (9) does not have the problem of assigning an effective q_e. If the pseudo-second-order kinetic equation is applicable, the plot of t/q_t against t of Eq. (9) should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot.

Intraparticle diffusion: Rate of sorption is frequently used to analyze nature of the 'rate-controlling step', and the use of the intraparticle diffusion model has been greatly explored in this regard which is represented by the following Weber and Morris equation.

$$q_t = k_{ip} t^{1/2} + C \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

where, C is the intercept, related to the thickness of the boundary layer and k_{ip} is the intraparticle diffusion rate constant. According to this model, if adsorption of a solute is controlled by the intraparticle diffusion process, a plot of q_t versus $t^{1/2}$ gives a straight line.

Pore diffusion model (Bangham's model): Bangham's equation (Eq. (11)) has been used to describe pore diffusion during adsorption process.

$$loglog\left(\frac{C_i}{C_i - q_t m}\right) = log\left(\frac{k_o}{2.303V}\right) + \propto log\, t \ldots\ldots\ldots.\ldots\ldots\ldots (11)$$

where, C_i is the initial concentration of the adsorbate in solution (mg L^{-1}), V is the volume of the solution (mL), m is the weight of adsorbent (g L^{-1}), q_t (mg g^{-1}) is the amount of adsorbate retained at time t, and α

(less than 1) and k_0 are the constants. As such log log[$C_i/(C_i-q_tm)$] was plotted against log(t) gives straight line if the sorption process involves pore diffusion.

Elovich equation: The Elovich equation is given as follows;

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \dots\dots\dots\dots\dots\dots (12)$$

The integration of the rate equation with the same boundary conditions as the pseudo first- and second-order equations becomes the Elovich equation.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta t) = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \dots\dots\dots\dots\dots\dots (13)$$

where α (mg g^{-1} min^{-1}) is the initial sorption rate, and the parameter β (g mg^{-1}) is related to the extent of surface coverage and activation energy for chemisorption. The kinetic results will be linear on a q_t versus ln(t) plot, if the results follow an Elovich equation.

Fitness of the kinetic models: The best-fit among the kinetic models was assessed by the squared sum of errors (SSE) values. It is assumed that the model which gives the lowest SSE values is the best model for the particular system [8]. The SSE values were calculated by the equation,

$$SSE = \sum \frac{(q_{e(expt.)} - q_{e(cal.)})^2}{q^2_{e(expt.)}} \dots\dots\dots\dots\dots\dots (14)$$

where $q_{e(expt.)}$ and $q_{e(cal.)}$ were experimental sorption capacity of dye (mg g^{-1}) at equilibrium time and the corresponding value that is obtained from the kinetic models.

RESULTS AND DISCUSSION

Figures 2 and 3 represent the plots of linearized form of pseudo-first-order kinetic model and pseudo-second-order for RB dye adsorption onto MZC. The pseudo-first-order rate constant (k_1) and $q_{e(cal.)}$ values were determined from the slope and the intercept (from Eq. (5)) of corresponding plot and are listed in table 1. For pseudo-second-order kinetics, the values of $q_{e(cal.)}$ and k_2 were determined from the slope and intercept of the corresponding plot obtained from Eq. (9) and are compiled in table 1.

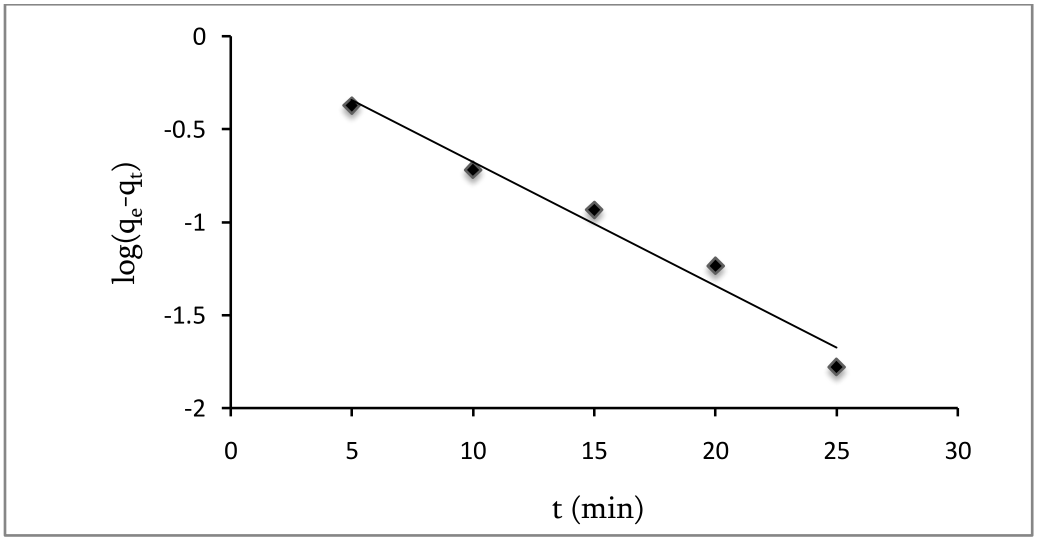

Figure 2. Pseudo-first-order kinetics for adsorption of RB onto MZC

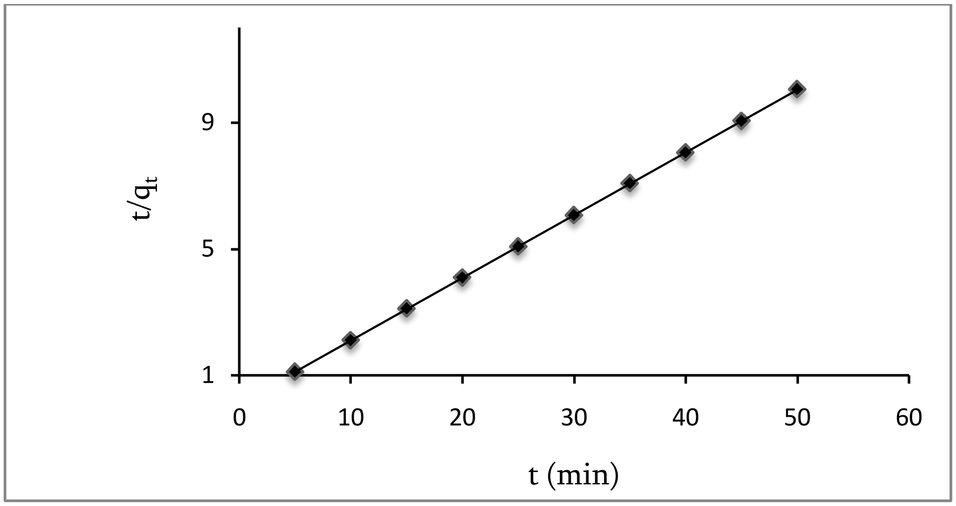

Figure 3. Pseudo-second-order kinetics for adsorption of RB onto MZC

In case of adsorption of RB dye onto MZC, the correlation co-efficient (R^2) value for pseudo-second-order adsorption model has high value 0.9998 than pseudo-first order. The lower SSE value for pseudo-second-order model also indicated that the adsorption kinetics of dye onto MZC can be better described by pseudo-second-order model. Similar phenomenon has been observed in the literature for the adsorption of dyes onto various adsorbents [9]. The pseudo-second-order model is based onto the sorption capacity on the solid phase. Contrary to other well established models, it predicts the behavior over the whole range of studies and it is in agreement with the chemisorption mechanism being the rate controlling step [10, 11].

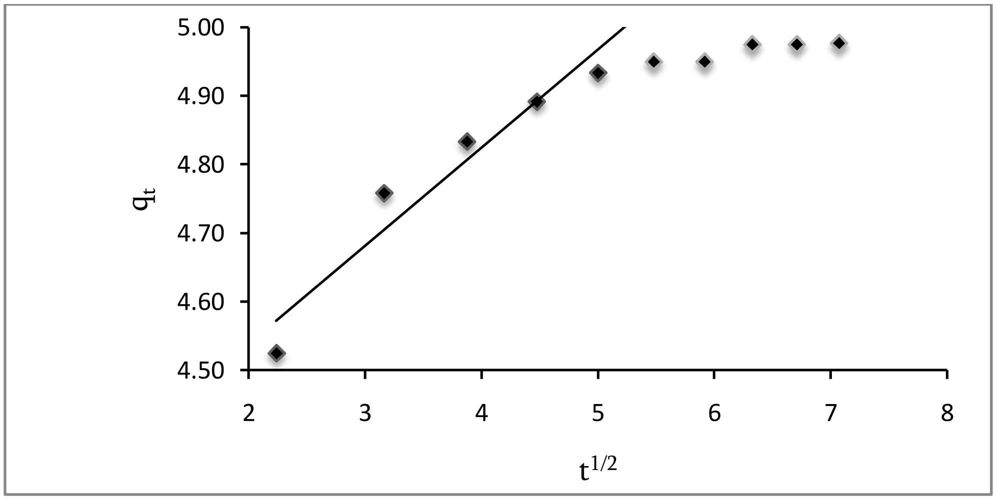

Figure 4. Intraparticle diffusion kinetic model for adsorption of RB onto MZC

Weber and Morris plot of q_t versus $t^{1/2}$ (from Eq. (10)) was shown in figure 4 and the corresponding results are tabulated in table 1. It is evident from the plot that there are two separate stages; first linear portion (Stage I) and second curved path followed by a plateau (Stage II). In Stage I, nearly 50% of dye was rapidly up taken by MZC within few minutes. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface. In Stage II, very slow diffusion of adsorbate from surface site into the inner pores is observed. Thus initial portion of dye adsorption by carbon adsorbent might be governed by the initial intraparticle transport of dye, controlled by surface diffusion process and later part is controlled by pore diffusion. Similar dual nature with initial linear and then plateau were found in the literature [12]. Though intraparticle diffusion renders straight line with correlation co-efficient (0.9326), the intercept of the line fails to pass through the origin. It might be due to difference in the rate of mass transfer in the initial and final stages of adsorption [13] and indicates some degree of boundary layer control which implies that intraparticle diffusion is not only the rate controlling step [14]. The data were further used to learn about the slow step occurring in the present adsorption system using pore diffusion model.

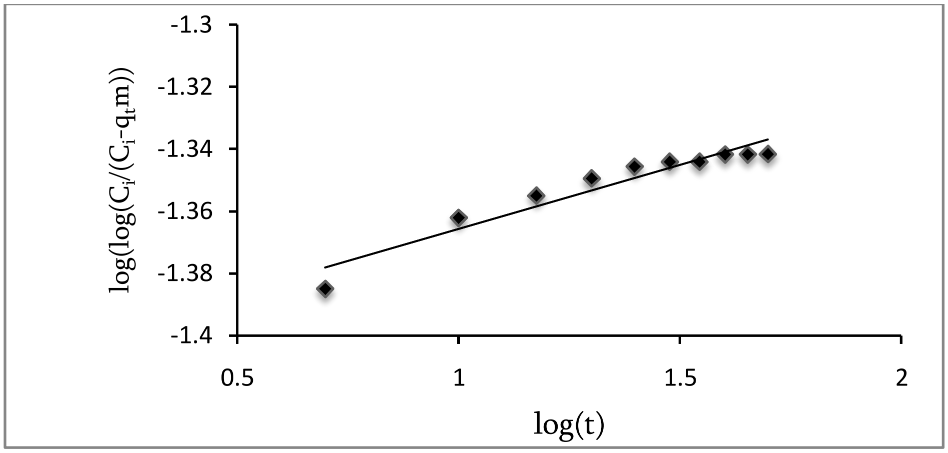

Figure 5. Bangham's pore diffusion kinetic model for adsorption of RB onto MZC

Bangham's plot of log(t) versus log[log(C_i/(C_i-q_tm)] (from Eq. 11) was shown in figure 5 and the corresponding results were tabulated in table 1. The Bangham's plot was found to be linear for each adsorbent with good correlation co-efficient (0.9184) and low SSE value (0.00002). It indicates that kinetics may be confirmed to Bangham's equation and therefore the adsorption of dye onto MZC might be pore diffusion controlled.

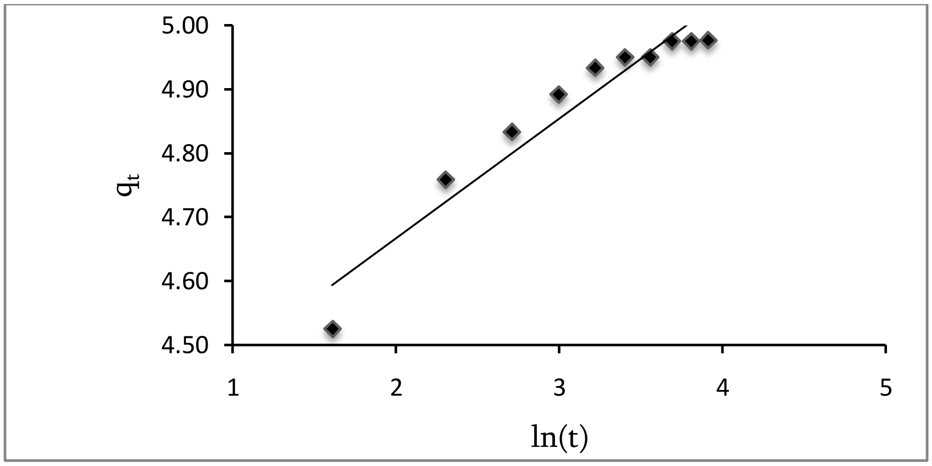

Figure 6. Elovich kinetic model for adsorption of RB onto MZC

Elovich plot of q_t versus ln(t) (from Eq. (13)) was shown in figure 6 and the corresponding results were compiled in tables 1. In this case, the R^2 value is 0.9245. This suggests that diffusion accounted for Elovich kinetics pattern; confirmation to this equation alone might be taken as evidence that the rate-determining step is diffusion in nature and that this equation should apply at conditions where rate of desorption can be neglected [15].

APPLICATIONS

The removal of RB dye adsorption on to MZC is useful in removal of color in textile/dyeing effluents. The prepared Activated Kaza's Carbon from Bio Waste material is cheap and useful. This Kinetic data is useful to know adsorption process.

CONCLUSIONS

For adsorption of RB onto MZC, the fitting of the kinetic data demonstrate that the dynamics of sorption could be better described by pseudo-second-order model indicating a chemisorptive rate-limiting. Though the plot of intraparticle diffusion renders straight line with good correlation coefficient, it failed to pass through origin. This suggests that the process is 'complex' with more than one mechanism limiting the rate of sorption. The good fitting of the kinetic data, to Bangham's and Elovich equations indicate that pore diffusion plays a vital role in controlling the rate of reaction.

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