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Sorption Dynamics of Acid Blue 92 and Direct Red 28 onto Activated Carbon Derived From Sterculia Quadrifida Seed Shell Waste

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ABSTRACT

Activated carbon was prepared from *Sterculia quadrifida* seed shell waste by Phosphoric acid activation. The adsorption of Acid Blue 92 and Direct Red 28 on this Phosphoric acid treated activated carbon was investigated to assess the possible use of this adsorbent for the processing of dyeing industry wastewater. The influence of various factors such as initial dye concentration, temperature and Particle size on the adsorption capacity has been studied. Kinetic data have been studied using Pseudo-first order, Elovich model and Pseudo-second order equations for understanding the reaction mechanism.

Introduction

The concentration and effective utilization of activated carbon generated from natural plant material have attracted worldwide attention in a view of the large disposal problem without detriment to environment [1,2,3]. High production and use of dyes generates coloured wastewater and pollute the environment. Textile, paper and food industries, tanneries, electroplating factories discharge coloured wastewater [4]. The methods of colour removal from industrial effluents include coagulation, floatation, biological treatment, hyper filtration, adsorption and oxidation. Among these options, adsorption is most preferred method and activated carbon is most effective adsorbent widely employed to treat wastewater containing different classes of dyes, recognizing the economical drawback of commercial activated carbon.

Many investigators have the feasibility of using inexpensive alternative materials like Jatropha Curcus seed shell, Delomix regia seed shell, Ipomea Carnia stem [5] Fly-ash [6] Wollastonite [7] Olive stones [8], almond shells [9], apricot and peach stones [10], maize cob [11], linseed straw [12], saw dust [13], rice hulls [14], cashew nut hull, cashew nut sheath [15], coconut shells and husks [16], eucalyptus bark [17], linseed cake, tea waste ash [18]. Beside these other source of activated carbon is sulfonated coal [19], tyre coal dust [20], activated bauxite, cement kiln dust[21], Share oil ash [22] and ground sunflower stalk [23], Feronia limonia swingle shell [24], Moringa oleifera fruit shell waste [25] etc., as the carbonaceous precursors for the removal of dyes from waste water.

In the present investigation the adsorption of Acid Blue 92 and Direct Red 28 on activated carbon prepared from *Sterculia quadrifida* seed shell waste by carbonization with phosphoric acid activation process. The kinetic adsorption data obtained were correlated to characterize the prepared carbon sample for the adsorption of Acid Blue 92 and Direct Red 28. Three simplified kinetic models including Pseudo first order equations, Pseudo second order equations and Elovich equations were used to describe the adsorption process [26]

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Experimental

Adsorbent

Sterculia quadrifida seed shells were collected from various places in Erode city, Tamil Nadu, India. They were cut into small pieces, dried in sunlight until all the moisture was evaporated. The dried Material was used for the preparation of activated carbons using physical and chemical activation methods. The materials to be carbonized were soaked with phosphoric acid for a period of 24 hours. After impregnation, the product was washed with large volume of water to remove the free acid, and then it was dried at 160 °C for 2 hours by using air oven finally activated at 800 °C and powdered.

The Nitrogen adsorption-desorption isotherms of activated carbons were measured using a gas sorption analyzer (NOVA 1000, Quanta Chrome corporation) in order to determine the surface area and the total pore volume. The surface area was calculated using the BET equation.

Batch adsorption studies

The batch adsorption studies were performed at 30 °C. A predetermined amount of adsorbent is mixed with known initial concentration of Acid Blue 92 and Direct Red 28 solution and agitated for desired time. The adsorbent and the adsorbate were separated by filtration and the filtrate was analyzed for residual Acid Blue 92 and Direct Red 28 concentration spectrophotometrically. The amount of Acid Blue 92 and Direct Red 28 adsorbed in mg/L at time t was computed by using the following equation.

$$q_{t=}\frac{C_0-C_t}{m_s}\times v \qquad (1)$$

Where, C_o and C_t are the Acid Blue 92 and Direct Red 28 concentration in mg/L initially and at given time t, respectively, V is the volume of the Acid Blue 92 and Direct Red 28 solution in ml and m_s is the weight of the activated carbon. The percentage of removed Acid Blue 92 and Direct Red 28 ions (R %) in solution was calculated using equation.

$$\%Removal = \frac{C_o - C_t}{m_s} \times 100 \quad (2)$$

The initial concentration of Acid Blue 92 and Direct Red 28, pH and temperature was investigated by varying any one parameters and keeping the other parameters constant.

Kinetic Models

In order to investigate the mechanism of adsorption and potential controlling steps such as mass transport, several kinetic models were tested including the Pseudo first order kinetic model, the Elovich model and the Pseudo second order kinetic model for a batch contact time process, where the rate of sorption of dye on to the given adsorbent is proportional to the amount of dye sorbed from the solution phase.

Pseudo First Order Kinetic Model

A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by Lagergren.

$$\frac{dq_t}{dt} = k_L (q_e - q_t) \quad (3)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_L}{2.303} t \quad (4)$$

Where k_1 is the pseudo first order rate constant. A plot of log (q_e-q_t) Vs time enables calculation of the rate constant k_1 and q_e from the slope and intercept of the plot.

Elovich Model

The Elovich or Roginsky–Zeldovich equation is generally expressed as follows

$$\frac{dq_t}{dt} = \alpha \exp(\beta q_t)$$

(5)

On integrating this equation for the boundary conditions,

$$q_t = \frac{1}{\beta} 1n(\alpha\beta) + \frac{1}{\beta} \ln t \quad (6)$$

Where the initial dye adsorption rate (mg/g) and desorption constant (g/mg) respectively are obtained from the slope and intercept of linear plot of q_t vs ln t.

Pseudo Second Order Kinetic Model

To describe the dye adsorption, the modified pseudo second order kinetic equation is expressed as

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (7)$$

Where, k_2 is the pseudo second order rate constant. A plot of t/q_t Vs t enables calculation of the rate constant k_2 which in turn is used to calculate the initial sorption rate h as follows

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

Result and Discussion

Adsorption kinetics

Effect of concentration

The batch adsorption experiments were carried out by using three different concentrations of dye viz. 20, 40 & 60 mg/L at P^H 6.5 at reaction temperature of 30 °C were selected for the adsorbent. Figure 1 & 2 clearly reveals the extend of adsorption of Acid Blue 92 and Direct Red 28 on the adsorbent increases linearly with increase in concentration of the adsorbent and then remains constant.

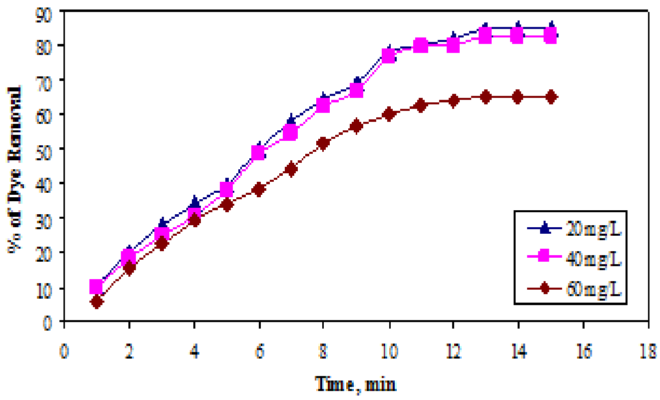

Figure 1. Effect of Initial Dye Concentration on Acid Blue 92 Adsorption

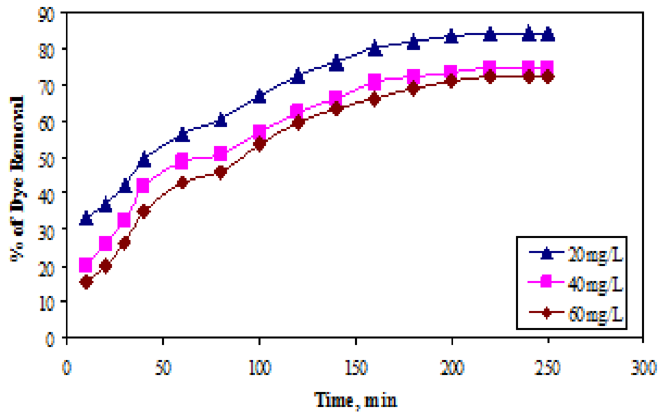

Figure 2. Effect of Initial Dye Concentration on Direct Red 28 Adsorption

Effect of initial concentration on kinetic rate parameters for Acid Blue 92 Adsorption

Acid Blue 92 dyes were carried out by using various concentrations of 20, 40 & 60 mg/L at P^H 6.5 at reaction temperature of 30 °C. The rate constant and the rate parameters at different initial dye concentration presented in the Table 1showed that the rate constants increase with increase in initial dye concentration.

From the analysis the data reveals that the influence of the initial concentration of Acid Blue 92 was little persuade on the Pseudo first order rate constant. In the case of Elovich model the obtained data reveals that the initial sorption rate (α) was increases for 20 mg/L, 40 mg/L and 60 mg/L simultaneously. Then the (β) desorption constant was decreases with the increase in concentration.

In the case of Pseudo second order the amount of dye adsorbed at equilibrium q_e increase simultaneously for 20 mg/L, 40 mg/L and 60 mg/L concentrations. Then the rate constant k_2 was decreases for all the three concentrations. The initial adsorption rate (h) gradually decreases.

When increasing the initial dye concentration for 20 mg/L, 40 mg/L and 60 mg/L the Acid Blue 92 the linear regression co-efficient (R^2) was very closer or equal to 1 for Pseudo second order kinetic model, where as the Pseudo first order and Elovich kinetic models the R^2 values was comparatively low than the Pseudo second order. Hence the relatively higher R^2 values indicate that the model successfully describes the kinetics of Acid Blue 92 and Direct Red 28 adsorption Figure. 3 ,4 & 5.

Table 1. Kinetic Model Values for the Adsorption of Acid Blue 92 onto SQAC

Conc. mg/L	Pseudo First Order		Elovich			Pseudo Second Order			
	k_L, min^{-1}	R^2	β, g/ min	α, mg/g/ min	R^2	q_e, mg/g	k_2, g/mg/	h, g/ mg/ min	R^2
20	0.010	0.985	0.193	0.593	0.983	24.227	0.007	3.941	0.990
40	0.018	0.974	0.112	0.417	0.987	42.069	0.001	0.912	0.999
60	0.019	0.986	0.082	2.541	0.990	56.253	0.0003	0.869	0.999

Table 2. Kinetic Model Values for the Adsorption of Direct Red 28 onto SQAC

Conc. mg/L	Pseudo First Order		Elovich			Pseudo Second Order			
	k_L, min^{-1}	R^2	β, g/ min	α, mg/g/ min	R^2	q_e, mg/g	k_2, g/mg/	h, g/ mg/ min	R^2
20	0.007	0.972	0.333	3.109	0.941	18.707	0.004	1.544	0.992
40	0.020	0.888	0.112	0.403	0.941	45.931	0.001	1.172	0.988
60	0.020	0.906	0.085	3.227	0.960	59.520	0.0002	0.820	0.990

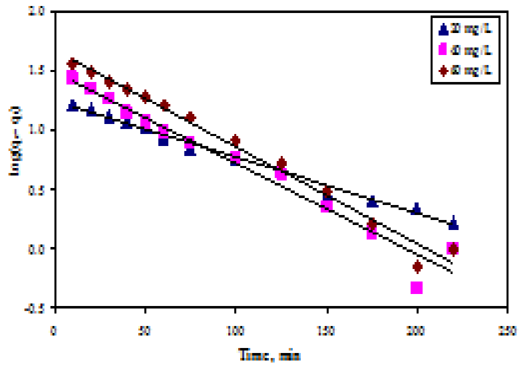

Figure 3. Effect of Initial Dye Concentration on Pseudo First Order Plot for Acid Blue 92 Adsorption

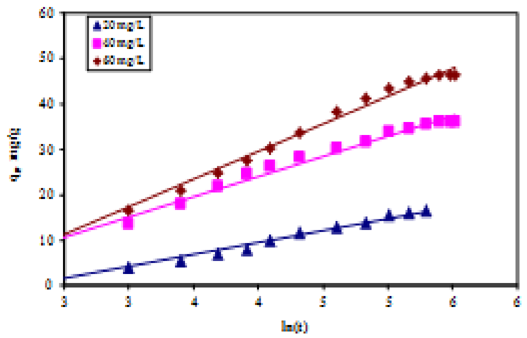

Figure 4. Effect of Initial Dye Concentration on Elovich plot for Acid Blue 92 Adsorption

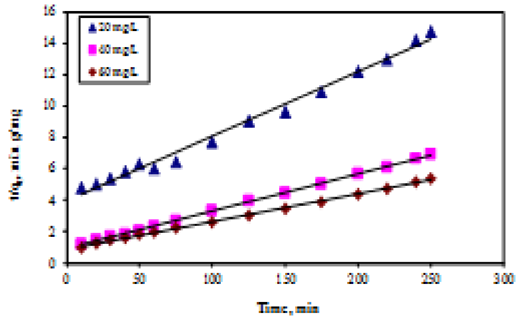

Figure 5. Effect of Initial Dye Concentration on Pseudo Second Order Plot for Acid Blue 92 Adsorption

Effect of initial concentration on kinetic rate parameters for Direct Red 28 Adsorption

Direct Red 28 dyes were carried out by using various concentrations of 20, 40 & 60 mg/L at P^H 6.5 at reaction temperature of 30 °C. The rate constant and the rate parameters at different initial dye concentration presented in the Table 2 showed that the rate constants increase with increase in initial dye concentration.

From the analysis the data reveals that the influence of the initial concentration of Direct Red 28 was little persuade on the Pseudo first order rate constant. In the case of Elovich model the obtained data reveals that the initial sorption rate (α) was increases for 20 mg/L, 40 mg/L and 60 mg/L simultaneously. Then the (β) desorption constant was decreases with the increase in concentration.

In the case of Pseudo second order the amount of dye adsorbed at equilibrium q_e increase simultaneously for 20 mg/L, 40 mg/L and 60 mg/L concentrations. Then the rate constant k_2 was decreases for all the three concentrations. The initial adsorption rate (h) gradually decreases.

When increasing the initial dye concentration for 20 mg/L, 40 mg/L and 60 mg/L the Acid Blue 92 and Direct Red 28 the linear regression co-efficient (R^2) was very closer or equal to 1 for Pseudo second order kinetic model, where as the Pseudo first order and Elovich kinetic models the R^2 values was comparatively low than the Pseudo second order. Hence the relatively higher R^2 values indicate that the model successfully describes the kinetics of Direct Red 28 adsorption Figure. 6, 7 & 8.

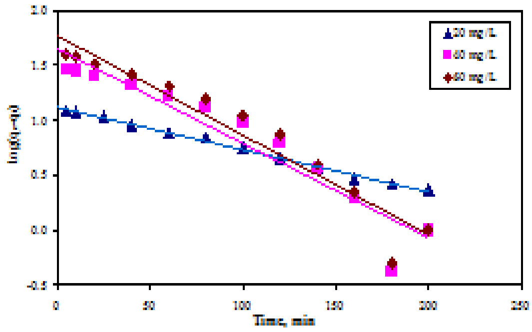

Figure 6. Effect of Initial Dye Concentration on Pseudo First Order Plot for Direct Red 28 Adsorption

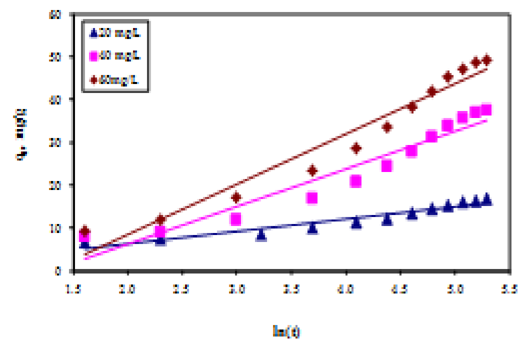

Figure 7. Effect of Initial Dye Concentration on Elovich plot forDirect Red 28 Adsorption

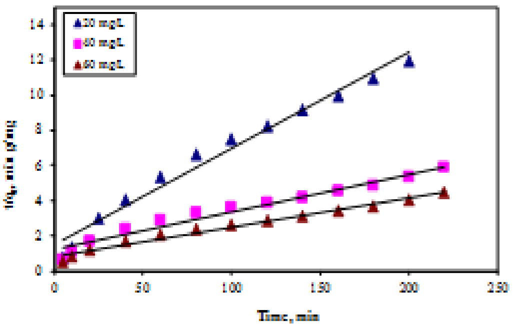

Figure 8. Effect of Initial Dye Concentration on Pseudo Second Order Plot for Direct Red 28 Adsorption

Conclusions

In the present study adsorption of Acid Blue 92 and Direct Red 28 on activated *Sterculia quadrifida* seed shell waste carbon have been investigated. The data obtained through supports that the *Sterculia quadrifida* seed shell waste carbon is an effective low cost adsorbent for the removal of Acid Blue 92 and Direct Red 28 from aqueous solution.

The Pseudo second order provides a best fit description for the adsorption of the Acid Blue 92 and Direct Red 28 on to *Sterculia quadrifida* relative to Elovich and Pseudo first order equations. The Pseudo second order was consider the most appropriate due to high correlation co-efficient when compared to Pseudo first order and Elovich equations.

This is in accordance with the correlation coefficients (R^2) as a goodness of fit criterion.

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