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RESEARCH ARTICLE

KINETICS OF ADSORPTION OF BASIC VIOLET 14 DYE FROM AQUEOUS SOLUTION ONTO ACTIVATED CARBON PREPARED FROM DELONIX REGIA PODS (FLAME TREE)

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Abstract

Adsorption of Basic Violet 14 dye (BV14) onto Activated Carbon prepared from Delonix regia pods activated with Zinc chloride (DRZAC). Batch mode adsorption experiments were conducted. The characteristics of the DRZAC were determined by BET analysis and pH_{ZPC}. The maximum removal efficiency of BV14 dye is 85% at pH 8. Under the chosen conditions, Experimental data obtained were fitted with linearised forms of Legergren and Ho kinetic models. The Sum of Error Squares Percentage (SSE %) for first order and second order kinetics were 4.98 & 3.23 respectively. Thus this adsorption followed second order kinetics. The results in this study indicated that DRZAC could be employed as an adsorbent for the removal of Basic Violet 14 dye from an aqueous solution.

Keywords: Adsorption; *Delonix regia $ZnCl_2$ activated carbon*; Basic Blue 9 dye; Kinetics.

Introduction

Dyes are synthetic chemical compounds having complex aromatic structures, which make them more stable and difficult to biodegradable. Dyes are extensively used to colour the products in the textile, cosmetic, plastic, food, and pharmaceutical industries. The major problem in the recent years concerning in the dyes and textile industry wastewaters is colored effluent. The colored wastewater contains number of toxic and organic compounds, which are destructive to all aquatic organisms (Ramakrishna, K.R., et al., 1997). Most of the dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack (Albanis, T.A., et al., 2000). The presence of these dyes is a great threat to animal health and desirable to remove colouring material from effluents before their discharge in environment not only for aesthetic reasons, but it is important to regions where water resources are scarce or sensitive.

The dye containing wastewater discharged from the industries can affect photosynthetic activity in aquatic life by impeding light penetration. Moreover, most of the dyes are toxic, carcinogenic and harmful to human health. Even at low concentration (1 mg/L), dyes could be highly noticeable, and could cause an aesthetic pollution and disturbance to the ecosystem and water sources (Vimonses, V., et al., 2010). Therefore, there is an increasing demand of efficient and economical technologies for removing dyes from water environment in the world. Activated carbon is the most popular adsorbent and has been used with great successes for many years in potable water treatments, in the pre treatment of water for its use in industry and in the safe disposal of different industrial effluents (Markovska, L., et al., 2001). Attention is being laid on the use of this commodity as pollution controlled media particularly in the removal of organics from liquid phase (Parkash, S., et al., 1974).

The uses of activated charcoals are widely used to remove pollutants from wastewaters by adsorption processes. Conversely, commercially available activated charcoal is expensive. In the past years, special attention on the preparation of activated carbon from several agricultural by-products has been given due to the growing interest in low cost activated charcoal from renewable agricultural resources. Many researchers have produced activated Charcoal from natural resource such as, bagasse (Tsai,W.T., et al., 2001) , cassava peel (Rajeshwarisivaraj, S., et al., 2001), date pits (Girgis, B.S., et al., 2002), coir pith (Kavita, D., et al., 2007), wood apple shell (Doke, K.M., et al ., 2012), jute fiber (Senthilkumaar S., et al., 2005), palm-tree cobs (Avom, J., et al., 1997), plum kernels (Wu, F.C., et al., 1999), rice husks (Yalcin, N., et al., 2000), olive stones (El-Sheikh, A.H., et al., 2004).

The advantage of using inexpensive natural resource as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture. Adsorption of dyes on activated charcoal was found as a superior technique for water reuse from industrial wastewater in terms of initial cost and not affected by toxic substances. The achievement of an activated charcoal treatment process depends on the type of charcoal and the characteristics of the industrial wastewater in addition to the operating conditions. Activated charcoal is relatively modern form of porous carbon materials with a number of significant advantages over the more traditional powder materials. These include high surface area and adsorption capacity as well as adsorption power from the gas and liquid phase (Carrott, P.J.M., et al., 2001).

The present study aims to evaluate the efficiency of activated carbon produced from *Delonix Regia* pods in the removal of Basis Violet 14 dye.

Material and Methods

Materials

All the chemicals used for this experiments are of analytical grade. Activated Carbon was prepared from *Delonix Regia* pods. BV14 dye purchased from Merck Company.

Preparation of Stock solution

BV14 dye was used without further purification. The dye stock solution was prepared by dissolving appropriate amount of accurately weighed dye in double distilled water to a concentration of 500 mg/L. The experimental solutions were prepared by proper dilution.

Preparation of Adsorbent:

Delonix Regia pods were collected from Kumbakonam region, Thanjavur District. *Delonix Regia* pods were repeatedly washed with distilled water to remove dirt, dust and impurities. The washed shells materials were then dried in sunlight for a month. The dried shells were chopped into small chips. Chemical activation of the *Delonix Regia* pods was carried out with $ZnCl_2$ solution. 20g of dried *Delonix Regia* pods were well mixed with 20ml desired concentration (20%,40%) of $ZnCl_2$ 1:1 w/v aqueous solution. The slurry was kept in an air oven at 100^{o}C for 24 hours. The resulting product was then subjected to carbonization and activation process in a muffle furnace at 400^{o}C for 1 hour. Then the sample was cooled and subsequently washed with 0.05M HCl and then with deionized water for several times. It was ground and sieved. The particle size ranged between 110 mm & 90 mm were taken and kept in a desiccator for further use.

Physico-chemical Characterization of DRZAC

The properties of DRZAC were given in Table 1. The total surface areas were calculated using the BET equation (Brunauer, S.P. et al., 1938).

Batch Adsorption procedure:

Batch adsorption studies were carried out in 250 mL iodine flasks with 50 mL of the working BV14 dye solution of different concentrations ranging from 100 mg/L to 200 mg/L. Known amount of adsorbent was added to the solution. The flasks were agitated at a constant speed of 180 rpm. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. The concentration of BV14 dye in the supernatant solution after and before adsorption was determined using colorimeter (Elico, Japan) at 660 nm. The amount of dye adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

$$q_e = (C_i\text{-}C_e)/V/W$$

Where C_i and C_e are adsobate concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage

Structure of Basic Violet 14 dye

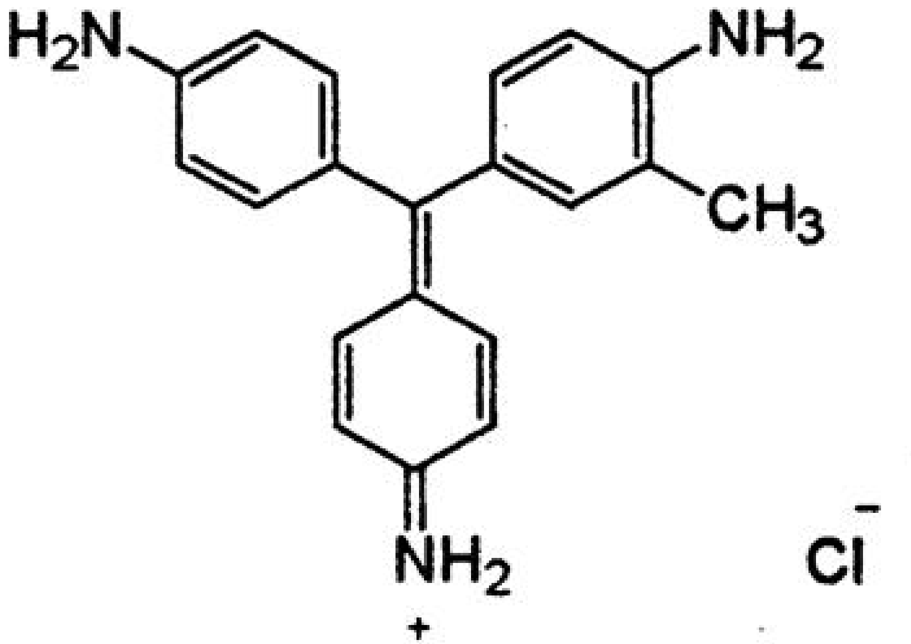

Table:1 Physico-chemical characteristics of DRZAC

S.No.	Properties	DRZAC Values
	PHzpc	6.0
	Particle size, mm	90-110
	Surface area (BET), m^2/g	916.1234
	Pore volume, cm^3/g	0.3986
	Pore size (Pore width), nm	2.7174
	Bulk density, g/Ml	0.52
	Fixed Carbon, %	71.11
	Moisture content, %	4.36

of removal of dye was calculated using the following equation:

$$\text{Removal (\%)} = (C_i - C_e)/C_i \times 100$$

RESULT AND DISCUSSION

Effect of Contact time and initial concentration

The effect of contact time on percentage removal of BV14 dye for different initial concentration have been shown in figure 1. Adsorption of dye from the solution increases with the time and finally attains equilibrium at 60,80 and 100 minutes for the initial concentrations 100,150 and 200 mg/L respectively. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the dye. However the amount of dye adsorbed on the adsorbent increased with the increase of initial concentration of the dye solution (Gupta,V.K. et al., 2004). Which is depicted in figure 2 and given in table 2.

Effect of pH

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of BV14 dye on different adsorbents. This is partly due to the fact that hydrogen ions themselves are a strong competing sorbate and partly to the fact that the solution pH influences the chemical speciation of adsorbate. The effect of pH on adsorption of BV14 onto DRZAC is shown in Figure 3. As shown in this figure, at low pH values, the adsorption percentage is low due to the increase in positive charge density(protons) on the surface sites, resulting in electrostatic repulsion between the BV14 dye and positive charge on the surface. Electrostatic repulsion decreases with increasing pH because of the reduction of positive charge density on the sorption edges. In an alkaline medium, percentage of removal was not good. This may be due to the role of inter ionic attraction between the OH^- ion and the adsorbate. According to Figure 3, the maximum adsorption of BV14 dye were found at pH 8.0. which is the pHzpc of the carbon where the surface of the adsorbent is neutral. Therefore, an optimum pH 8.0 was selected for further experiments (Torab-Mostaedi, M. et al., 2010).

Adsorption kinetics

Experimental datas were fitted into two kinetics models such as pseudo-first-order and pseudo-second-order kinetics models to examine the adsorption kinetics.

Pseudo-First-Order Model

The adsorption kinetics can be described by a pseudo first order equation as suggested by Legergren (Demirbas, E. et al.,2004).

$$\text{Log}\,(q_e - q_t) = \text{Log}\,q_e - K_1 / 2.303 \times t$$

Where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t (min) respectively and k_1 is the rate constant of adsorption (l/min). The values of k_1 and theoretical q_e for different initial concentrations calculated from the slope and intercepts of these curves respectively were presented in Table 3.

Pseudo-Second-Order Model

The adsorption kinetics can be described by a pseudo second order equation as suggested by Ho (Demirbas,E. et al., 2004).

$$t/q_t = 1/ K_2 q_e^2 + 1/q_e \times t$$

Theoretical equilibrium adsorption capacity (q_e), and the second-order rate constant k_2 (g/(mg min) can be determined experimentally from the slope and intercept of plot of t/q_t versus t(Figure 5). The k_2 (g/(mg min) and correlation coefficients values calculated were listed in Table 3.

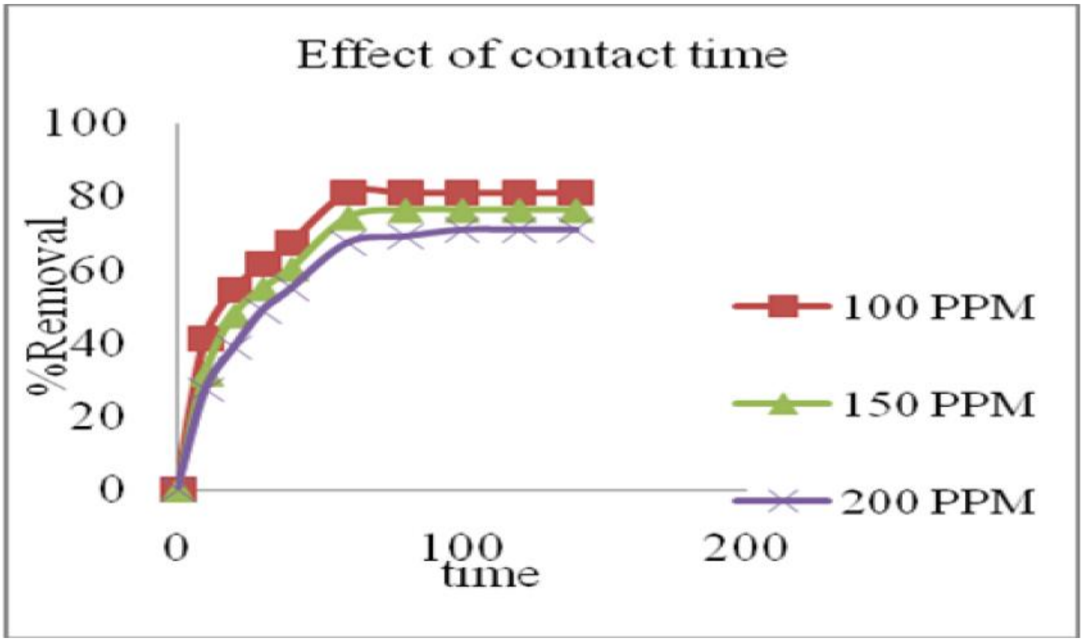

Figure: 1 Effect of contact time

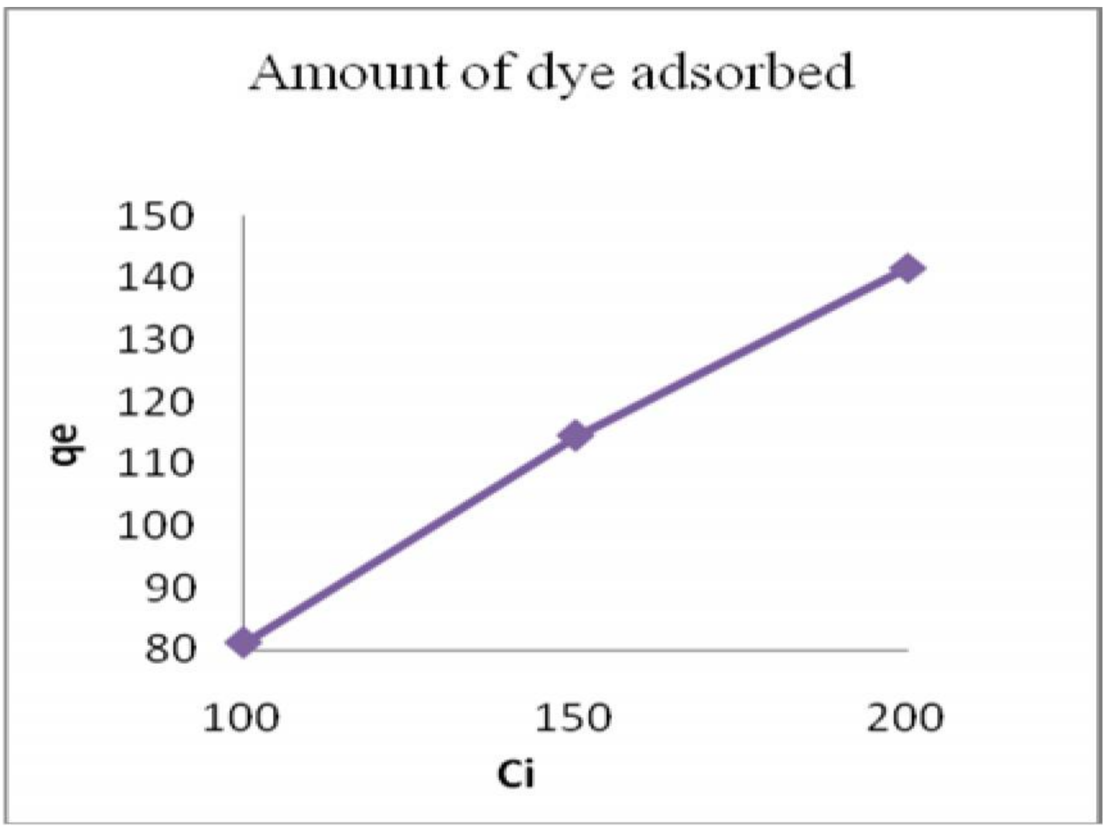

Figure: 2 Amount of dye adsorbed

Table: 2 Percentage of removal of dye and amount of dye adsorbed

C_i (mg/L)	% of Removal of Dye at equilibrium	Adsorbed amount of Dye at equilibrium (mg/g)
100	81.14	81.14
150	76.36	114.55
200	69.01	141.68

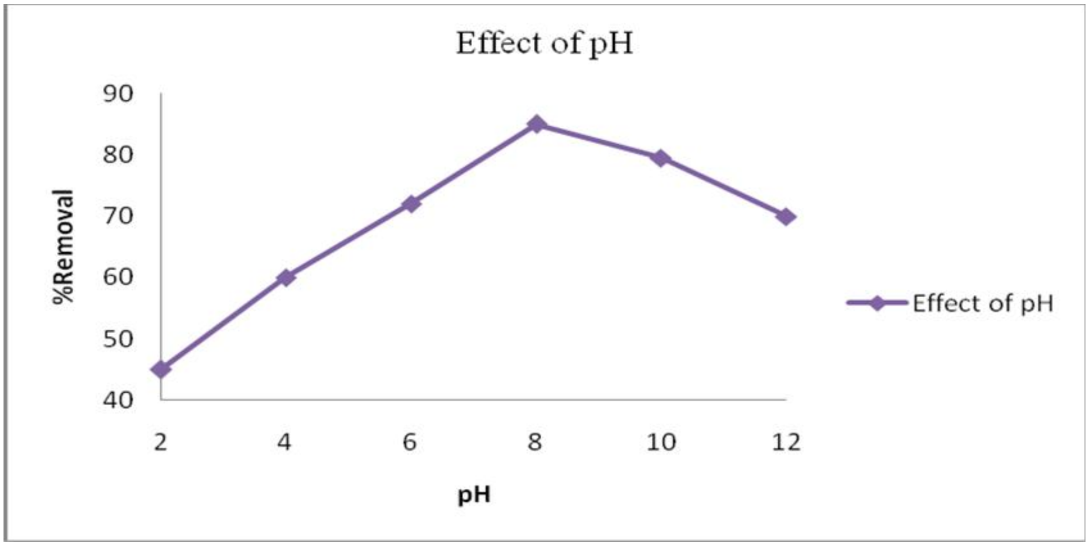

Figure : 3 Effect of pH

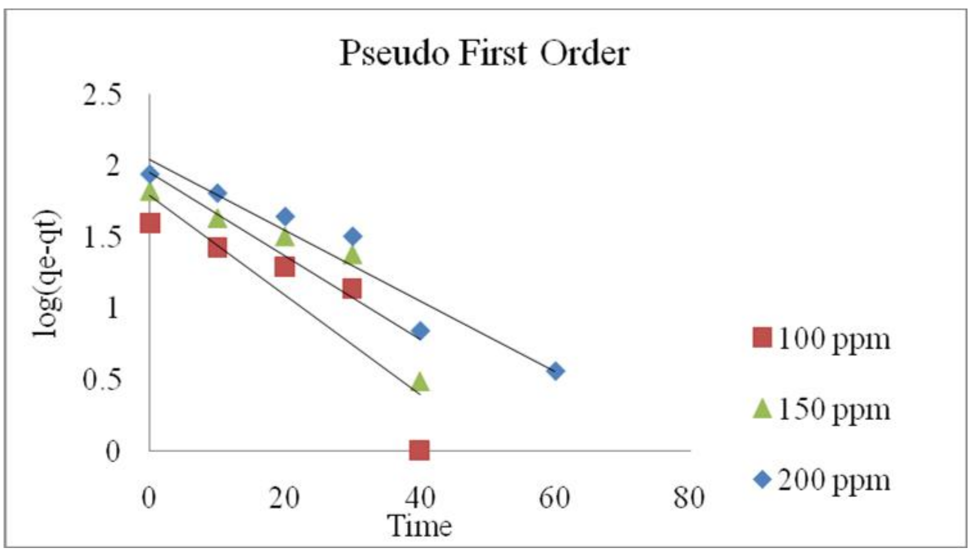

Figure: 4 Peseudo First Order

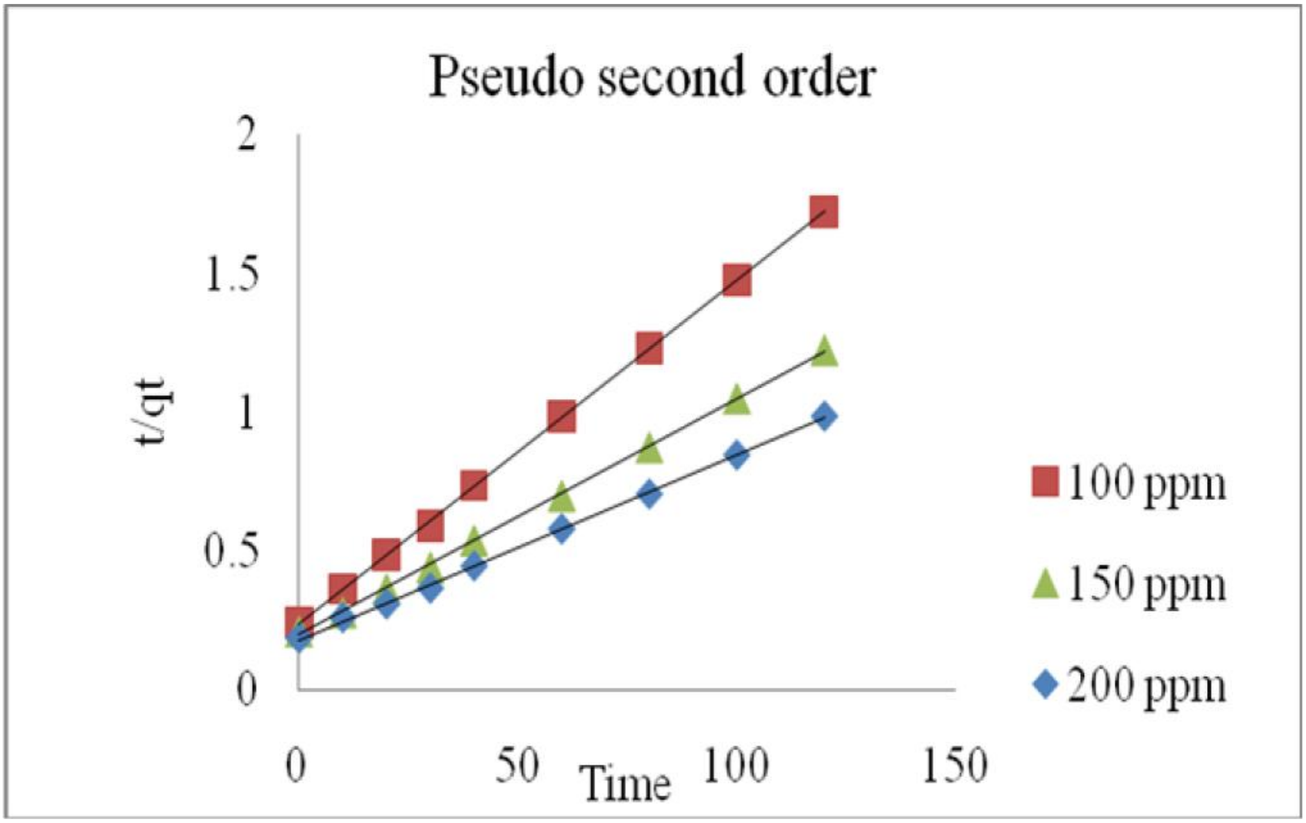

Figure: 5 Pseudo Second Order

Table:3 Kinetic parameters

Ci mg/L	Rate constants		$q_{e(cal)}$ mg/g		$q_{e(exp)}$ mg/g		Δq_e		R^2		(SSE %)	
	k_1 (10^{-2}) (min^{-1})	k_2 (10^{-3}) ($gmg^{-1} min^{-1}$)	First Order	Second order	First order	Second Order	First order	Second Order	First order	Second Order	First order	Second Order
100	7.8	6.05	81.14	81.14	61.38	83.33	19.76	2.19	0.759	0.999	4.98	3.23
150	6.6	3.25	114.55	114.55	89.74	125	24.81	10.45	0.799	0.999		
200	5.5	2.03	141.68	141.68	110.92	166.67	30.72	24.99	0.931	0.999		

Conclusion

The present investigation shows that DRZAC is an effective adsorbent for the removal of BV14 dye from aqueous solutions. From the kinetic studies, it is observed that adsorption of dye is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial concentration. The percentage removal of dye increases with the increase in adsorbent dosage and decreases with increase in initial concentration. Adsorption of BV14 dye obeys pseudo-second order equation with good correlation.

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