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RESEARCH ARTICLE

KINETICS OF ADSORPTION OF VINYL SULPHONE RED DYE FROM AQUEOUS SOLUTION ONTO COMMERCIAL ACTIVATED CARBON

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Abstract

The adsorption of Vinyl Sulphone Red dye onto commercial activated carbon from aqueous solution was investigated. Batch mode adsorption experiment was carried out. The influence of various parameters such as agitation time, concentration of the dye solution, and adsorption dose were studied. Experimental data were fitted to the pseudo first order, pseudo second order and intra particle diffusion models. Kinetic parameters were calculated and discussed in detail.

Key Words: Activated carbon, Kinetics, Intra particle diffusion, Vinyl Sulphone Red dye.

Introduction

Colour is the most obvious indicator of water pollution. Colour stuff discharged from these industries poses certain hazards and environmental problems in Coimbatore, Karur and Erode districts of Tamil Nadu, India. There are around 600 dyeing industries in and around Coimbatore and Tirupur cities, situated in the southern part of India and their number is constantly increasing. The effluent coming out from these dyeing industries contain many coloured compounds. They are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream affecting the aquatic ecosystem (Denold, 1984; Namasivayam et al., 1994; Tsai et al., 2001).

Many treatment methods have been used to remove dyes from waste water. These can be divided into physical, chemical, and biological methods (Hameed et al., 2005; Órfão et al., 2006; Malik, and Saha, 2003; Ciardelli et al., 2001). Among the various methods, adsorption is an effective separation process for a wide variety of applications (Feng-Chin Wu and Ru-Ling Tseng (2006; Malik et al., 2002; Arslanoglu et al., 2005; Senthilkumaar, et al., 2005; Akmil-Basar et al., 2005; Yamin Yasin et al., 2007). Activated carbon is the most widely used adsorbent for dye molecules due to its high porosity and good surface area for sorption of organic compounds (Silva et al., 2006). Vinyl sulphone dyes are vinyl sulphone based reactive dyes widely used for dyeing and printing of cellulose fibres for its very good fastness properties. Vinyl Sulphone Red dye is used as a model adsorbate for adsorption onto activated carbons.

The present study is carried out to evaluate the kinetics of adsorption of vinyl sulphone red dyes onto a commercial activated carbon adsorbent (CAC) form aqueous solution. In this paper, the applicability of kinetic models for the adsorption of Vinyl Sulphone Red dye onto activated carbon is reported in elaborately.

Materials and methods

Materials

All the chemicals used for this experiment are of analytical grade. Commercial Activated Carbon (CAC) used in this study is purchased from SD Fine chemicals, Mumbai and Vinyl Sulphone Red dye from Merck Company.

Preparation of Dye Solution

Vinyl Sulphone Red 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 1000 mg /L. The experimental solutions were prepared by proper dilution (Venkatraman et al., 2011; Arivoli et al., 2009).

Zero Point Charge

The pH at the potential of zero charge of the carbon (pH_{zpc}) was measured using the pH drift method (Jia and Thomas, 2002). The pH of the solution was adjusted by using 0.02 M sodium hydroxide or hydrochloric acid. 0.40 g/L mg of the activated carbon was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH used to determine the zero point charge of the activated carbon.

Dosage of adsorbent

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals.

Adsorption experiments

Adsorption of Vinyl Sulphone Red dye on CAC was carried by a batch method at 305K temperature. Predetermined dose of the adsorbent is mixed with 50 mL of dye solutions. pH of the solutions were brought to pH_{zpc} by adding required quantity of 0.02 N Hydrochloric acid. Sample solutions were withdrawn at predetermined time intervals after shaking in a rotary shaker at 150 rpm to determine the percentage removal of the dye from the solution. Concentrations of dye solutions were estimated by measuring absorbance at a wavelength of 500 nm with Systronics Double Beam UV-visible Spectrophotometer: 2202 (Akmil-Basar et al., 2005; Venkatraman et al., 2011; .Arivoli, et al., 2009).

Initial concentration of dye

Experiments were conducted with different initial concentrations of dyes ranging from 25 to 75 mg /L.

Contact time

The kinetic experiments were performed with the working pH 6.85 (pH_{ZPC} = 6.85) and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 minutes (Venkatraman et al., 2011; .Arivoli, et al., 2009).

Results and Discussion

Determination of percentage of removal and quantity adsorbed

The percentage removal of the dye from the solution was calculated by the following mass balance relationships.

$$\% \text{ of Removal} = (C_i - C_t) \times V / C_i$$

$$q_e = (C_i - C_e)\times V/W$$

$$q_t = (C_i - C_t)\times V/W$$

Where, C_i , C_t and C_e are the liquid phase concentrations in mg/L of Vinyl Sulphone red dye at initial, at the time 't' and at equilibrium respectively. V is the volume of the dye solution in liter (L) and W is the mass of the adsorbent in gram (g) used (Venkatraman et al., 2011; .Arivoli, et al., 2009).

Effect of contact time and initial concentration on adsorption of Vinyl Sulphone red dye onto the adsorbent

The percentage of removal of Vinyl Sulphone red dye from aqueous solution with respect to different contact times and with different initial concentrations was shown in Figure 1.

The adsorption process is characterized by a rapid uptake of the adsorbate in the initial stages as shown by the curves. The adsorption rate however decreased marginally after the first ten minute and a nearer constant after 80 minutes. The percentage of removal increased with the increase in contact time. However, the percentage of removal of dye at equilibrium decreased with an increase of initial concentration of the Vinyl Sulphone red dye Figure 2. This is due to the decrease in the ratio between available adsorption sites and the concentration of solute in the solution (Abechi et al., 2011; Horsfall and Spiff, 2005; Garg et al., 2003). It is observed that the amount of solute adsorbed by the adsorbent, increased with the increase of initial concentrations of dye Figure 3. Similar trend has been reported in literature (Garg, et al., 2003; Selvi et al., 2001; Demirbas et al., 2004). Experimental values are shown in Table 1.

Kinetic models

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The following models were used to describe adsorption kinetics behaviour.

Pseudo first-order model

The adsorption kinetics can be described by a pseudo first order equation as suggested by Legergren. (Tsai et al., 2003; Demirbas et al., 2004).

$$\log (q_e - q_t) = \log q_e - k_1/2.303 \times t$$

k_1 and q_e were calculated using the slope and intercept of plots of log ($q_e - q_t$) versus t, shown in the Figure 4.

Kinetic parameters of first order equation is given in Table 2

Pseudo-second order kinetics

The adsorption kinetics can be described by a pseudo second order equation as suggested by Ho. (Tsai et al., 2003; Demirbas et al., 2004).

$$t/q_t = 1/k_2.q_e^2 + 1/q_e\, t$$

Pseudo second-order adsorption parameters $q_{e(cal)}$ and k_2 were determined by plotting t/q_t versus t, shown in the Figure 5. Kinetic parameter of second order equation is given in Table 2.

Intra particle diffusion

Weber–Morris equation is (Weber and Morris, 1963),

$$q_t = k_p t^{1/2} + C$$

Figure.1 Different contact times and with different initial concentrations

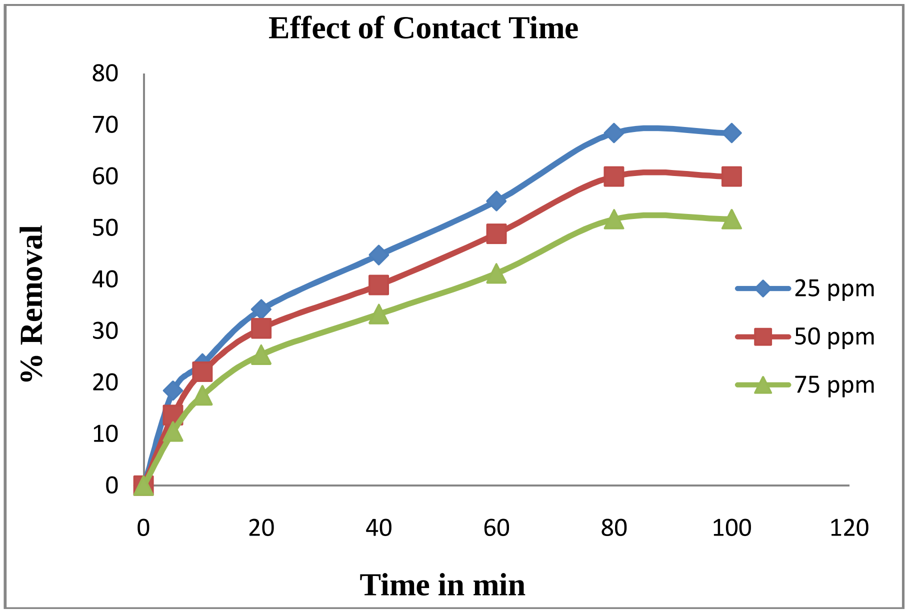

Figure.2 The percentage of removal of dye at equilibrium decreased with an increase of initial concentration of the Vinyl Sulphone red dye

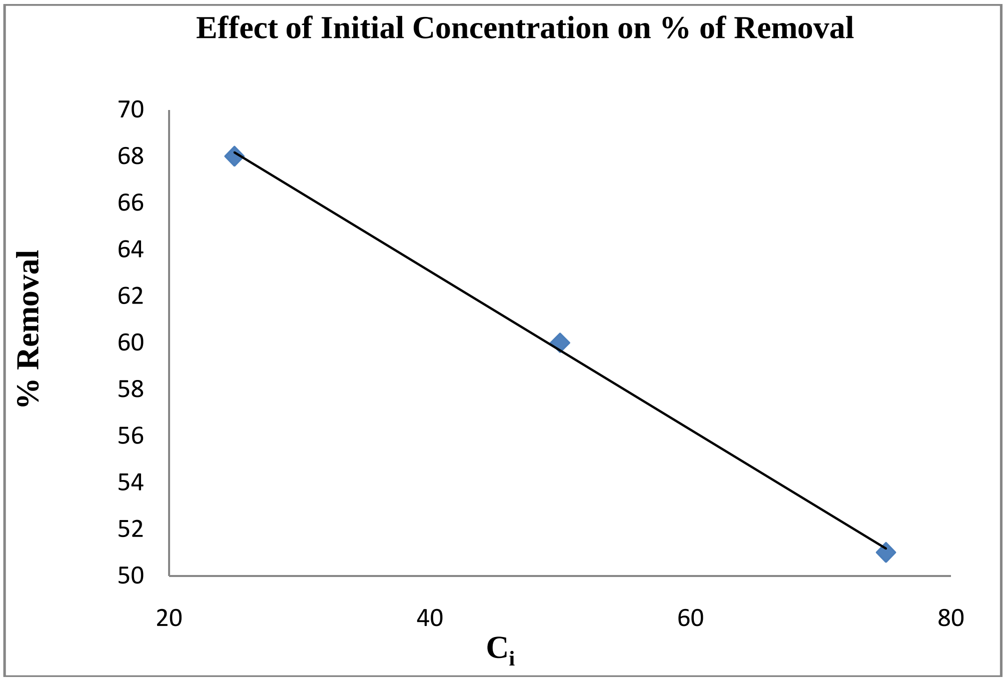

Figure.3 Amount of solute adsorbed by the adsorbent, increased with the increase of initial concentrations of dye

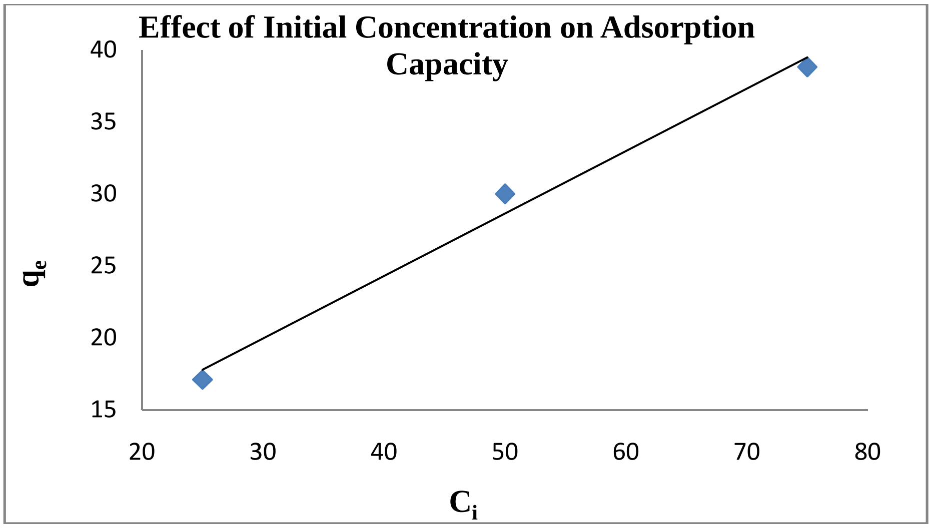

Table.1 Percentage of removal of dye and amount of dye adsorbed

Initial Concentration (mg/L)	Percentage of removal of dye at equilibrium	Amount of dye adsorbed at equilibrium
25	68	17.11
50	60	30.00
75	51	38.82

Figure 4. k_1 and q_e were calculated using the slope and intercept of plots of log $(q_e - q_t)$ versus t,

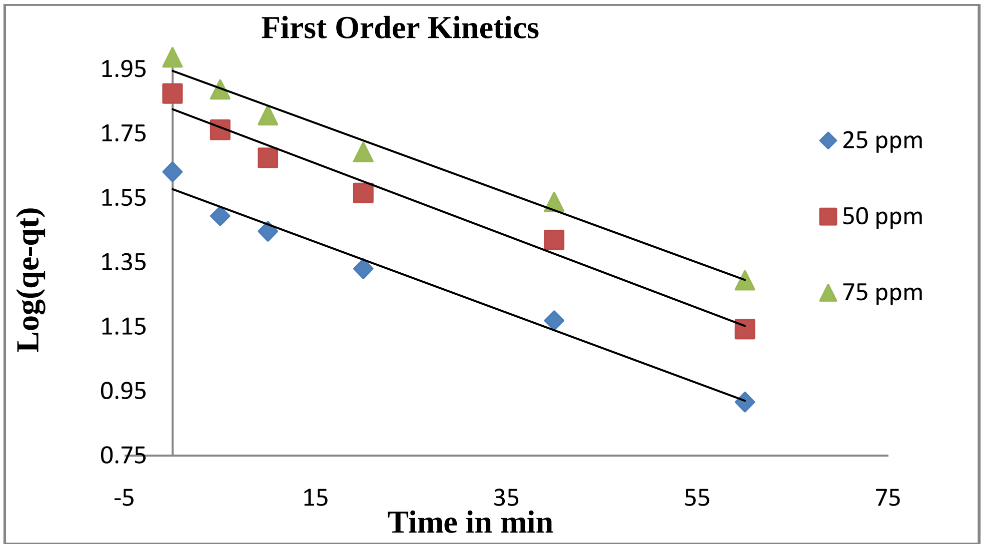

Figure 5. Pseudo second-order adsorption parameters $q_{e(cal)}$ and k_2 were determined by plotting t/q_t versus t

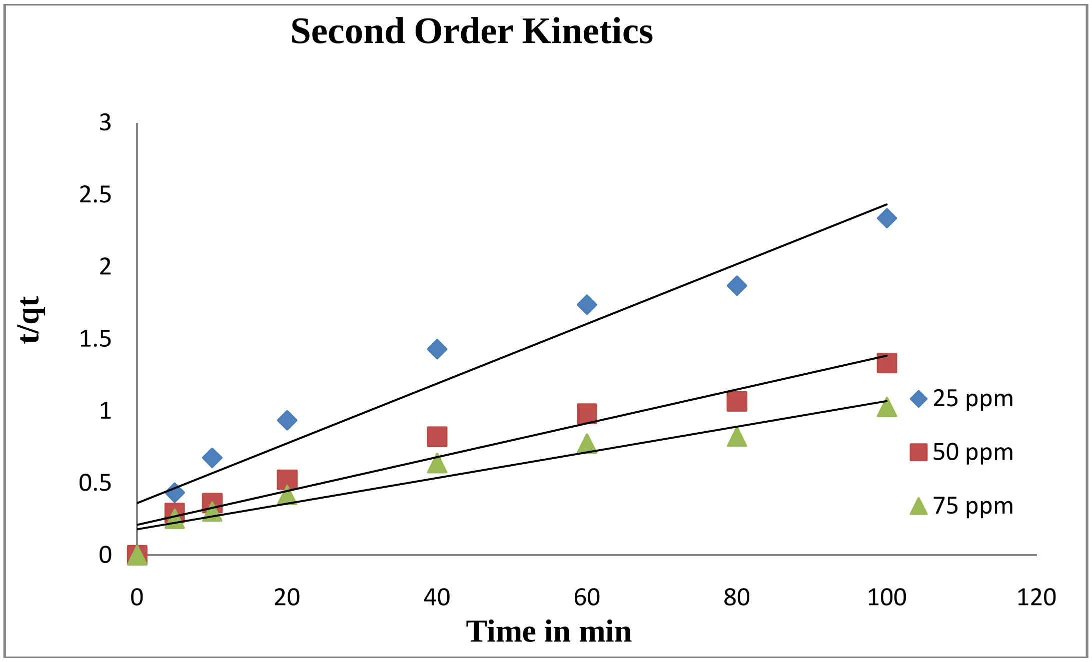

Figure.6 Intra particle diffusion

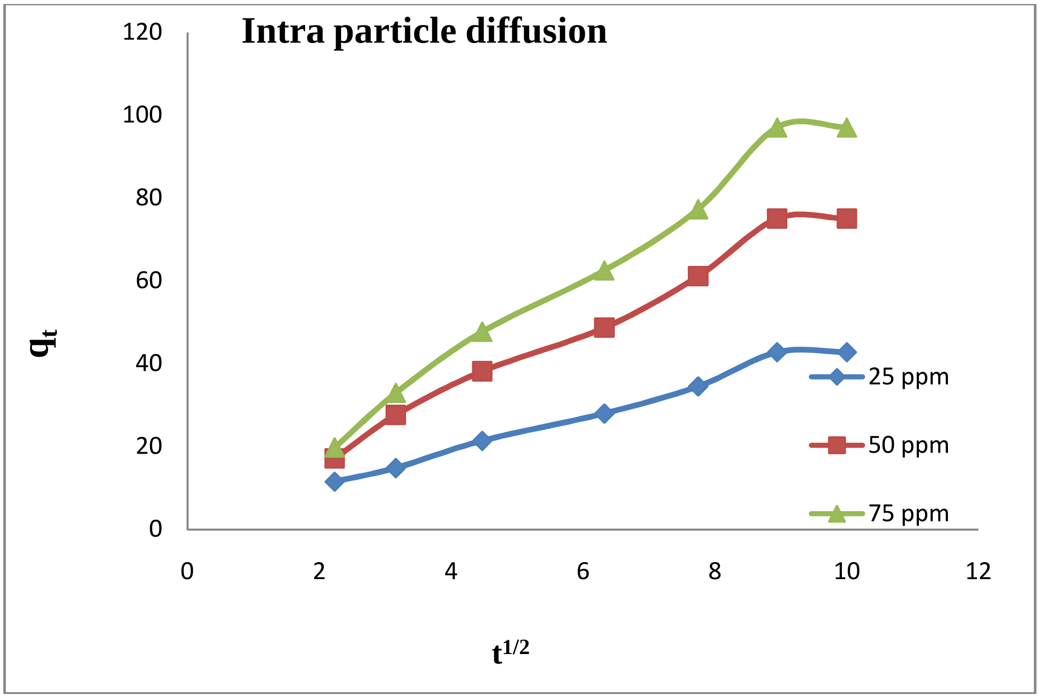

Table. 2 kinetics parameters for CAC

Concentration (ppm)	**First Order Kinetics**					**Second Order Kinetics**				
	$k_1 \times 10^{-2}$ (min^{-1})	$q_{e(cal)}$	$q_{e(exp)}$	R^2	SSE %	$k_2 \times 10^{-3}$ (g/mg.min)	$q_{e(cal)}$	$q_{e(exp)}$	R^2	SSE %
25	2.303	37.84	42.77	0.982	2.36	1.108	50.00	42.77	0.938	5.66
50	2.533	66.99	75.00	0.979		57.63	90.90	75.00	0.939	
75	2.303	88.10	97.05	0.985		35.55	125.0	97.05	0.928	

Where k_p is the intra-particle diffusion rate constant, a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_p which is the rate constant for intra particle diffusion and intercept C is the thickness of the boundary film (Kannan, and Sundaram, 2001).

Test on kinetics models

The sum of error squares (SSE, %) (Tsai, et al., 2001) is one method which has been used in literature to test the validity of models used. The sum of error squares is given as follows;

$$SSE\ (\%) = \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2 / N}$$

Where N is the number of data points.

Experimental q_e, calculated q_e and SSE for the pseudo first order and pseudo second order kinetics were given in Table 2. It shows that qe $_{(exp)}$ is close to $q_{e\ (cal)}$ for first order kinetics for CAC. It can be seen that SSE (%) value is lower for the first order kinetic model than that of pseudo second order kinetic model. This confirms the applicability of the pseudo first order kinetic model.

The determination coefficient (R^2) for pseudo first order model ranged between 0.979 and 0.985 whereas these values for the first order model were close to 1. It indicates that the experimental data best fitted into pseudo first order. The Δq_e values and SSE values suggest that the process of adsorption follows pseudo first order kinetics.

Conclusions

The adsorption of Vinyl Sulphone Red dye onto Commercial Activated Carbon (CAC) was studied. Adsorption experiments were carried out as a function of contact time, initial concentration in a batch mode process. Experimental data indicated that chosen adsorbent CAC was effective in removing Vinyl Sulphone red dye from aqueous solution. The percentage of removal increased with an increase in contact time and achieved equilibrium around 80 minutes. In kinetics studies, R^2 value and SSE revealed that the process of adsorption follows pseudo first order kinetics.

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