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RESEARCH ARTICLE

KINETICS OF ADSORPTION OF METHYLENE BLUE ONTO ACTIVATED CARBON PREPARED FROM *ADINA CARDIFOLIA* HOOK

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Abstract

Adsorption Methylene Blue dye from aqueous solution by *Adina cardifolia* Hook was experimented under batch mode. The influence of initial concentrations of dye solution and contact time on the removal process were investigated. An adsorbent dosage of 0.040 g/L showed maximum dye uptake capacity (q_e) of 41.60 mg/g for an initial dye concentration of 100 ppm. Sorption equilibrium time was observed in 80 min. The kinetics of adsorption was analyzed with pseudo first order, pseudo second order and intra particle diffusion models. It was found that the pseudo second order kinetic model followed with intra particle diffusion as the rate determining step.

Keywords: Adsorption; Kinetics; Methylene Blue dye; Pseudo first order, Pseudo second order.

Introduction

Synthetic dyes are used extensively by dye industries, paper industries, textile dyers, colour photography and as additives in petroleum products. The effluents thus generated by these industries are highly coloured and disposal of wastes into the environment are extremely harmful. In the past a number of conventional biological treatment processes have been used which were not effective, some of which include coagulation and chemical oxidation, membrane separation process, electrochemical, reverse osmosis and aerobic and anaerobic microbial degradation but all these methods suffer from one or more limitations and none of them were successful for the complete removal of dye (Ramuthai et al., 2009). Among the various methods, adsorption is an effective separation process for a wide variety of applications. 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 (Ramesh et al., 2014).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. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust, buffing dust of leather industry, coir pith, crude oil, residue tropical grass, olive stone and almond shells, pine wood, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater (Arivoli, 2007; Venkatraman et al., 2011). The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated *Adina cardifolia* Hook for the removal of Methylene Blue (MB) dye in aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, the applicability of kinetic and mass-transfer models for the adsorption of MB dye onto acid activated carbon is reported.

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Nomenclature			
C_i , C_t and C_e	Initial Concentration, at the time 't' and at equilibrium respectively	k_1	First order rate constant
q_e and q_t	Quantity adsorbed at the time 't' and at equilibrium respectively	k_2	Second-order rate constant
V	Volume of the dye solution in liter (L)	t	Time in minutes
W	Mass of the adsorbent in gram (g)	k_p	Intra-particle diffusion rate constant
R	Gas Constant	C	Thickness of the boundary film
T	Temperature (K)	N	Number of data points

Materials and Methods

Preparation of adsorbent

The activated carbon was prepared from the wood of *Adina cardifolia* Hook. The wood were cut into smaller pieces and soaked in concentrated H_2SO_4 at 1:1 ratio (weight of raw material/volume of acid) for 24 h and activated at 160°C for 5 h. The activated carbon was repeatedly washed with distilled water until the pH of the wash water became the pH of the distilled water (nearly 7). The carbon obtained was dried at 110 ± 1°C for nearly 2 h to remove the moisture. The above prepared carbon was named ACHC.

Preparation of stock Solution

Analar grade Methylene Blue 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 from the stock solution by proper dilution (Venkatraman,2011; Arivoli et al., 2009).

Adsorption experiments

Adsorption of Methylene Blue dye on ACHC was carried by a batch method at 305K temperature. 40 mg of the adsorbent is mixed with 50 mL of dye solution of known concentration and the mixture was agitated in a mechanical shaker. 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 680 nm with Systronics Double Beam UV-visible Spectrophotometer: 2202 (Ramesh et al., 2014; Arivoli, 2007; Venkatraman, et al., 2011; . Arivoli et al., 2009; Akmil-Basar et al., 2005). The adsorption capacities for different initial concentrations were determined at definite time intervals.

Initial concentration of dye

Experiments were conducted with different initial concentrations of dyes ranging from 50 to 150 mg /L.

Contact time

The kinetic experiments were performed with the working pH 7.0 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 minutes (Ramesh et al., 2014).

Result and Discussion

Effect of contact time and initial concentration on adsorption of methylene blue dye onto the adsorbent

The percentage of removal of MB dye from aqueous solution with respect to different contact times and with different initial concentrations was shown in Figure 2.

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

Table 2 Data Processing Tools

S. No.	Parameters		Formulae
1.	**Mass balance relationships**	% of Removal	$(C_i - C_t)\times V/C_i$
		Quantity adsorbed at equilibrium, q_e	$(C_i - C_e) \times V/W$
		Quantity adsorbed at the time t, q_t	$(C_i - C_t) \times V/ W$
2.	**Kinetic Models & SSE %**	Pseudo First order kinetics (Legergren equation)	$\log (q_e-q_t)=\log q_e - k_1 /2.303 \times t$
		Intra particle diffusion (Weber–Morris equation)	$q_t = k_p t^{1/2} + C$
		Sum of error squares	$SSE (\%) = \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2/ N}$

minute and become constant around 80 to 120 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 MB dye (Figure 3). 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 4). 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 2.

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. Plots of different kinetic models applied were given in the Figure 5 and the kinetic parameters calculated were given in the Table 3.
Between the first order and second order kinetic models, second order kinetic model seems to best describe the above adsorption system as it has R^2 values were very close to unity. Moreover, difference between q_e (cal) and q_e (exp) values of second order kinetic model is small when compared to first order kinetic model. Statistically it is tested with the tool called 'Sum of error squares' (SSE %)[16]. The Δq_e and SSE % values were given in the Table 3, from which it was concluded that second order kinetic model was more appropriate rather than first order kinetic model. In Figure 6, plot of mass of dye adsorbed per unit mass of adsorbent (q_t) versus $t^{1/2}$ is presented. The linear plots are attributed to the macro pore diffusion which is the accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The values of k_p obtained from the slopes of straight lines are listed in Table 3.

Test on kinetics models

Experimental q_e, calculated q_e and SSE for the pseudo first order and pseudo second order kinetics were given in Table 3. It shows that $qe_{(exp)}$ is close to $q_{e\ (cal)}$ for second order kinetics for ACHC. It can be seen that SSE (%) value is lower for the second order kinetic model than that of pseudo first order kinetic model. This confirms the applicability of the pseudo second order kinetic model.

The determination coefficient (R^2) for pseudo first order model ranged between 0.879 and 0.96 where as these values for the second order model were close to 1. It indicates that the experimental data best fitted into pseudo second order. The Δq_e values and SSE values suggest that the process of adsorption follows pseudo second order kinetics.

Conclusions

The adsorption of MB dye onto wood of *Adina cardifolia* Hook (ACHC) 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 ACHC was effective in removing MB dye from aqueous solution. The percentage of removal increased with an increase in contact time and achieved equilibrium around 80 to 120 minutes. In the kinetics studies, R^2 value and SSE revealed that the process of adsorption follows pseudo second order kinetics.

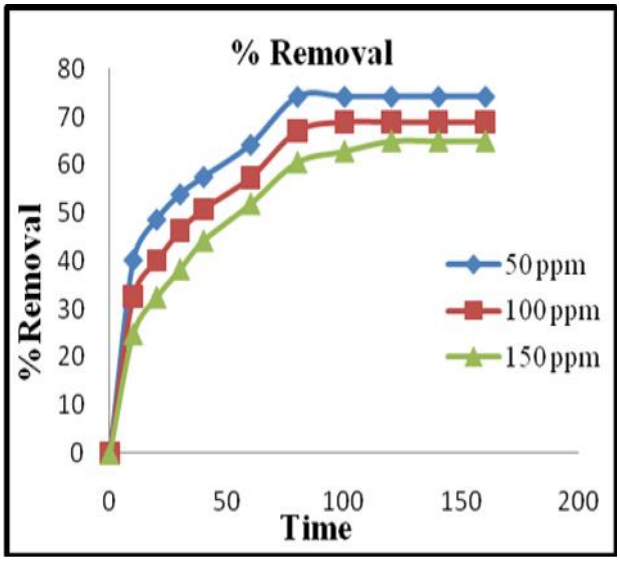


Figure 2

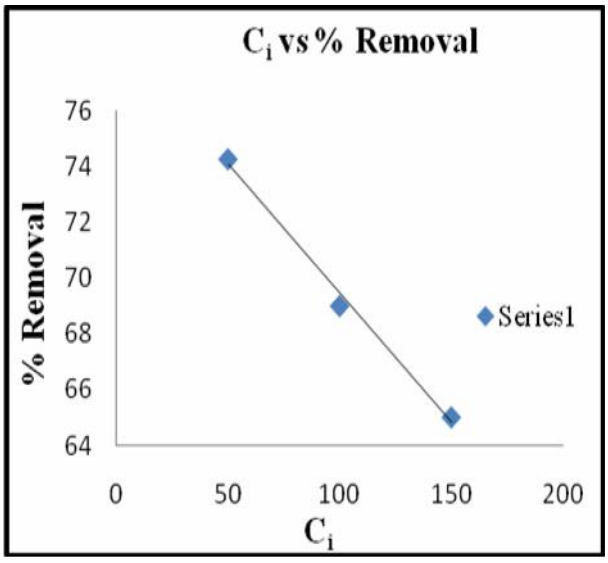


Figure 3

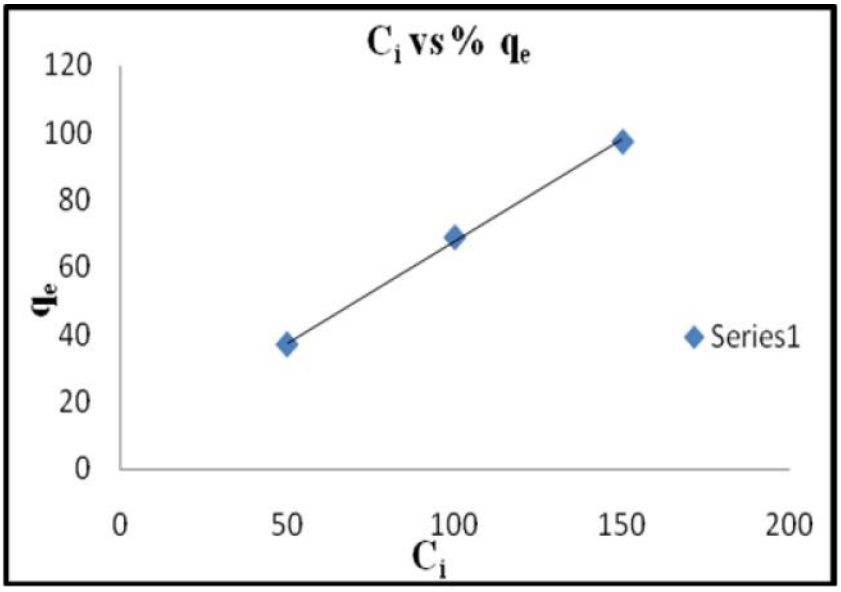
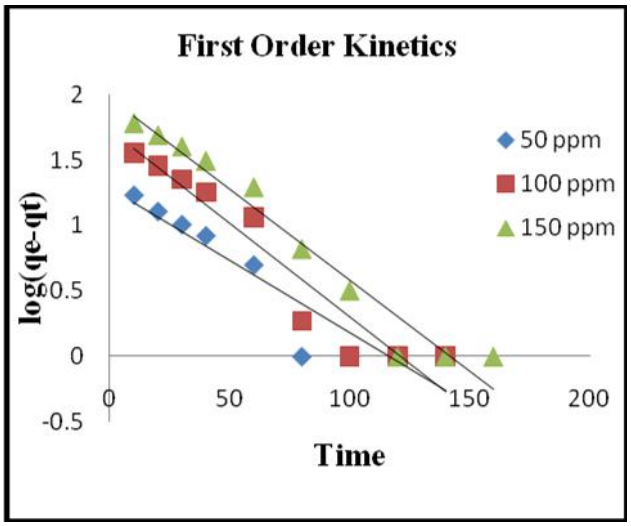


Figure 4

Table 2: 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
50	74.28	37.14
100	69.02	69.02
150	65.03	97.55



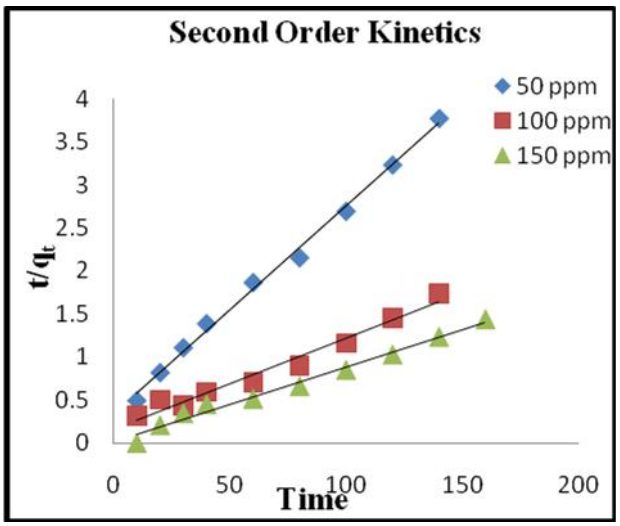


Figure 5

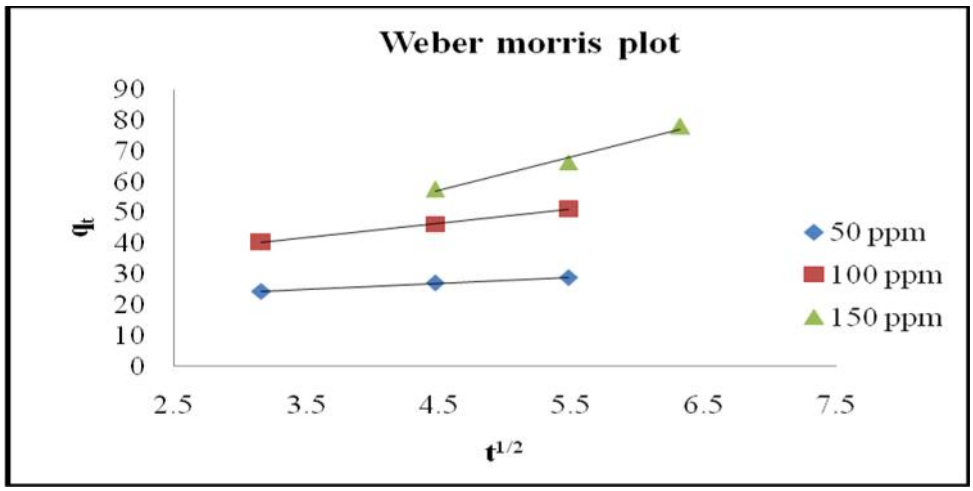


Figure 6

Table 3: kinetics parameters for ACHC

C_i (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	2.53	37.14	19.36	0.879	8.22	1.7	37.14	41.6	0.995	5.14
50	3.22	69.02	100	0.917		6.17	69.02	30.98	0.971	
75	2.99	97.55	125	0.96		5.33	97.55	27.45	0.984	

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