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RESEARCH ARTICLE

KINETICS OF ADSORPTION OF CONGO RED ONTO MULTI WALLED NANO CARBON

A.Rajappa[1], K.Ramesh[2], B.Amutha[3], V.Nandhakumar[4*] and Hema Ramesh[5]

[1,5]Department of chemistry, Sri Manakula Vinayagar Engineering College, Puducherry, India
[2]Department of chemistry, Arasu Engineering college, Kumbakonam, India
[3,4]*Department of chemistry, A.V.V.M Sri Pushpam college, Poondi, India
Corresponding Author: *vnchem13@gmail.com*

Abstract:

Adsorption of Congo Red dye (CR) onto Multi Walled Nano Carbon (MWNC) from aqueous solution was investigated under various experimental conditions. Batch mode experiments were conducted. Experimental data were fitted with linearised forms of Lagergren and Ho kinetic equations for pseudo first order and pseudo second order models respectively. Rate constants and theoretical adsorption capacities were calculated. The Sum of Error Squares Percentage (SSE %) for first order and second order kinetics were 4.78 & 6.81 respectively and hence it followed first order kinetics. Adsorption capacities MWNC were estimated from equilibrium studies for different initial concentrations of adsorbate which were found to be good.

Keywords: Adsorption; Multi Walled Nano Carbon; Congo Red; Adsorption Kinetics.

Introduction

Treatment of dye-manufacturing and textile industries wastewater is currently a major challenge for environmental managers. This is mainly due to the fact that coloured effluents are composed of non-biologically oxidizable component because of the molecular size and structure of the dye-stuff. Dyes are chemicals which on binding with a material, gives it colour. Coloured dye wastewater arises from the production of the dye and also as a consequence of its use in the textile and other industries (Allen and Koumanova, 2005). Congo red (sodium salt of benzidinediazobis-1- naphthylamine-4-sulfonic acid) is a benzidine-based azo dye and it was selected in this study as a model anionic dye, high solubility in aqueous solution and its persistence, once it is discharged into natural environment.

Congo red mainly occurs in the effluents discharged from textile, paper, printing, leather industries , etc. (Bhattacharrya and Sharma, 2004) during dyeing operation about 15% of its ends up in waster waters (Srivastava et al., 1988). It is investigated as a mutagen and reproductive effector. It is a skin, eye and gastrointestinal irritant. It may affect blood factors such as clotting and induce somnolence and respiratory problems (Alok et al., 2009).

Adsorption techniques for treatment of effluent have become increasingly popular due to their efficiency in the removal of pollutants which are too stable for biological methods. Adsorption is a physico-chemical process with great potential for effluent treatment, in that

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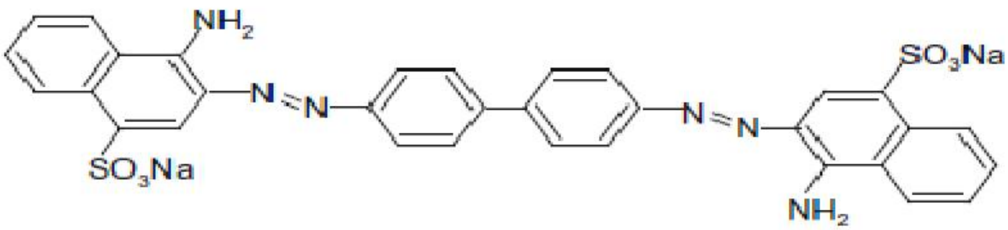
Figure.1 Structure of Congo Red:



CONGO RED

Nomenclature

q_e	–	Quantity adsorbed at equilibrium
q_t	–	Quantity adsorbed at equilibrium at specific time
k_1 and k_2	–	Rate constant for (I order & II order)
N	–	Number of data points
C_i	–	Initial concentration
C_e	–	Concentration of adsorbate in solution at equilibrium
Δq_e	–	Difference between $q_{e(cal)}$ and $q_{e(exp)}$
MWNC	_	Multi Walled Nano Carbon
$pH_{(ZPC)}$	_	pH of Zero Point Charge

effluents are rendered in a safe and reusable form (Gaikwad, R.W., Misal, 2010). The most widely used adsorbent in industrial concerns for effluent treatment is activated carbon. However, there are certain drawbacks associated with its use especially the expensive nature of high quality activated carbon. As such there has been increasing in research into cheaper and more readily available adsorbents (Ho and Chiang, 2001). Some biological adsorbents have been studied for the adsorption of dyes; these include amongst others; apple pomace and wheat straw, corncob and barley husk, maize cob, wood and rice husk. These adsorbents were found to be efficient in binding with basic dyes rather than acid dyes (Mumin et al., 2007). However some of these adsorbents do not have good adsorption capacities for the anionic dyes because most have hydrophobic or anionic surfaces. Hence, there is a need to search for more effective adsorbents (Sudipta et al., 2009).

Now days there are numerous low cost, commercially available adsorbents for the dye removal. However, the adsorption efficiencies of these adsorbents are not very high, this lead to the need of further research on the use of adsorbents with very high efficiencies. In recent years MWNC can play vital role as adsorbent. Hence it was chosen for the present study.

Materials and methods

All the chemicals used for this experiment are of analytical grade. The Multi Walled Nano Carbon (MWNC) purchased from Applied Science Innovations Private Ltd., Pune. Congo Red dye from Merck company.

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Preparation of Dye Solution

Congo 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 500 mg/L. The experimental solutions were prepared by proper dilution.

Adsorption Experiments

$pH_{(ZPC)}$ of MWNC was determined (Venkatraman et al., 2011). The $pH_{(ZPC)}$ of MWNC was 6.65. Adsorption of Congo red dye (CR) on MWNC was carried by a batch method at 303K temperature and at $pH_{(ZPC)}$. The effect of contact time and initial concentration of CR dye were investigated. The adsorption process was carried out with three different initial concentrations at 100, 150 and 200 mg/L of CR dye. 10 mg of adsorbent was taken in 100 mL iodine flask. 50 mL of CR dye solution was added to the flask. pH of the solutions were brought to 6.65 by adding 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 510 nm with Systronics Double Beam UV- visible Spectrophotometer: 2202. All experiments were conducted in duplicate and the controls (with no adsorbent) were simultaneously carried out to ensure that adsorption was by adsorbent and not by the container (Akmil-Basar et al., 2005).

Results and discussion

Effect of contact time and initial concentration on adsorption of CR onto MWNC

The percentage of removal of CR 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 minutes. The percentage of removal and the amount of dye adsorbed increased with the increase of contact time. However the percentage of removal of dye decreased with an increase of initial concentrations of the CR dye (Table 1).This is due to the decrease in the ratio between the available adsorption sites and the solute in the solution (Abechi et al., 2011).Similar trend has been reported in literature (Demirbas et al., 2004).

Kinetic models

The kinetics adsorption data were processed to understand the dynamics of adsorption process in terms of the rate constant and order. Thus the kinetics of CRdye adsorption onto MWNC was analysed using pseudo-first-order and pseudo-second-order kinetics models.

Pseudo first-order model

The adsorption kinetics can be described by a pseudo first order equation as suggested by Legergren (Hameed et al., 2006).

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (1)$$

k_1 and q_e were calculated using the slope and intercept of plots of log $(q_e - q_t)$ versus t (Figure 2 for MWNC).
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 (Hameed et al., 2006).

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

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Figure.1 Effect of contact time

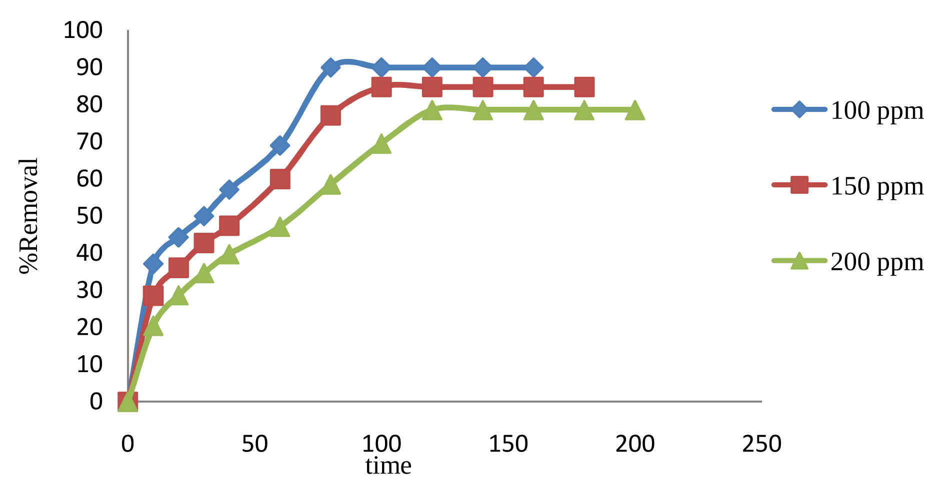
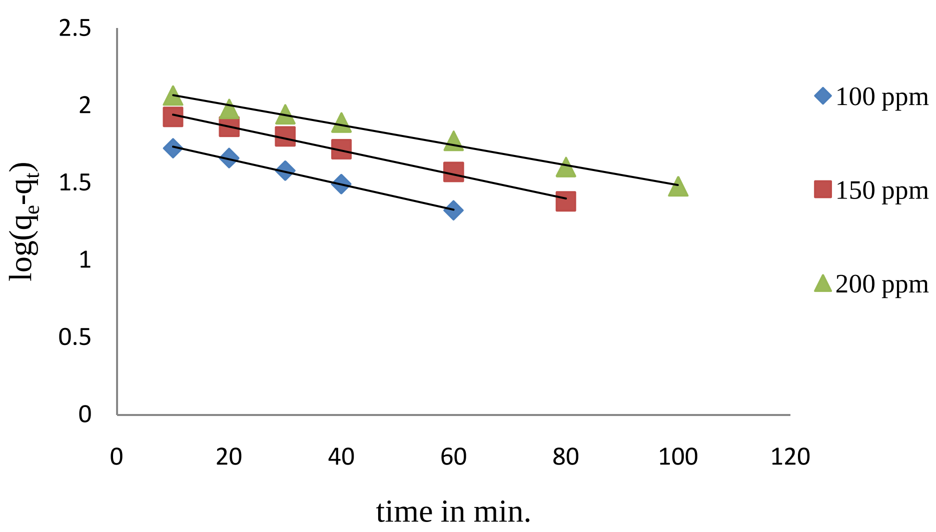


Table.1 Percentage of removal of dye and amount of dye adsorbed

Ci (mg/L)	% of removal of dye At equilibrium	Adsorption capacity at equilibrium (mg/g)
100	90	450
150	84.76	635
200	78.57	785

Figure.2 Pseudo first order kinetics



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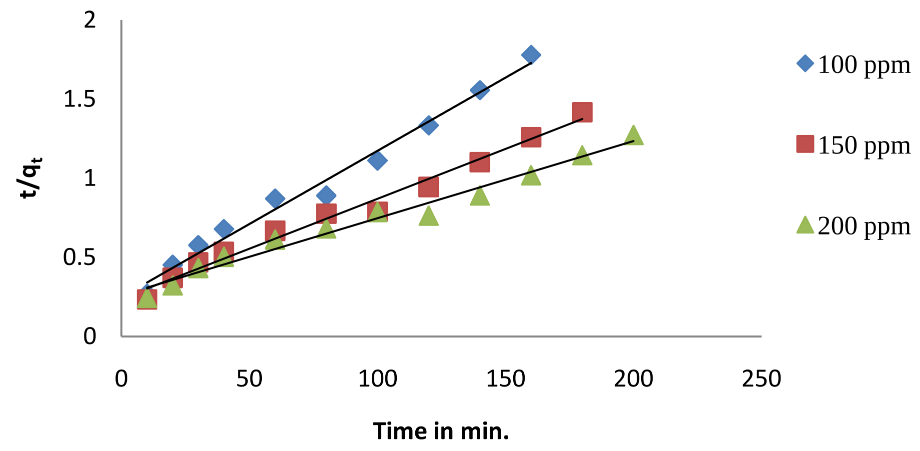

Figure.3 Pseudo second order kinetics

Table. 2 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}) (mg g^{-1} min^{-1})	First order	Second order	First order	Second order	First order	Second order	First order	Second order	First order	Second Order
100	1.84	3.28	90.00	90.00	65.31	111.00	24.69	21.00	0.997	0.984		
150	1.61	1.52	127.14	127.14	104.71	166.00	22.43	38.86	0.994	0.983	4.78	6.81
200	1.38	6.17	157.14	157.14	135.51	250.00	21.63	92.86	0.993	0.977		

Pseudo second-order adsorption parameters $q_{e(cal)}$ and k_2 in Eq. (2) were determined by plotting t/q_t versus t (figure 3 for MWNC).

Test on kinetics models:

The sum of error squares percentage (SSE, %) (Hameed et al., 2006) 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;

$$SSE\ (\%) = \sqrt{\frac{\sum[(q_e)_{exp}-(q_e)_{cal}]^2}{N}} \longrightarrow (3)$$

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.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 second order model ranged between 0.977 and 0.984 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 followed pseudo first order kinetics.

Conclusion

The adsorption of Congo Red dye onto Multi Walled Nano Carbon (MWNC) was studied. Adsorption experiments were carried out as a function of contact time, initial concentration in a batch mode process. Experimental data indicated that MWNC adsorbent was effective in removing CR dye from aqueous solution. The percentage of removal increased with an increase in contact time and achieved equilibrium around 80,100 and 120 minutes for 100,150 and 200 mg/L when 10 mg MWNC was used as adsorbents for 50 mL solution. Adsorption capacity of MWNC was found to be higher at higher initial concentrations. In the kinetics studies, R^2 value and SSE(%) revealed that the process of adsorption followed pseudo first order kinetics.

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