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RESEARCH ARTICLE

EQUILIBRIUM AND ISOTHERM STUDIES OF CONGO RED ADSORPTION ONTO COMMERCIAL ACTIVATED CARBON

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Abstract

Adsorption of Congo Red (CR) from aqueous solution onto Commercial Activated Carbon (CAC) was investigated under various experimental conditions. Batch mode experiments were conducted. Equilibrium studies were carried out by varying the parameters such as effect of contact time, initial concentration and temperature. The initial concentration studies were carried out by taking 100,150,200 and 250 mg/L of solutions and effect of temperature studies were carried out at 303,313,323 and 333K. The equilibrium adsorption data were analyzed with four isotherm models. Best fitting isotherm models were in the following order, Langmuir > Freundlich > Tempkin > Dubinin Raduskevich. Isotherm parameter values indicated that the adsorption was physical nature.

Keywords: Adsorption, Commercial Activated Carbon, Congo Red, isotherms.

Introduction

Textile dye produces huge amount of polluted effluents that are normally discharged to surface water bodies and ground water aquifers. These wastewater causes damages to the ecological system of the receiving surface water capacity and certain a lot of disturbance to the ground water resources. Most of the dyes are used in the textiles industries are stable to light and are not biodegradable. In order to reduce the risk of environmental pollution from such waste, it is necessary to treat them to before discharging it receiving in the environment (Arami et al., 2005). Today more than 10,000 dyes have been incorporated in colour index (Jalajaa et al., 2009). In order to remove hazardous materials like dyes, adsorption is a method which has gain considerable attention in the recent few years adsorption is such a useful and simple technique (Kanan et al., 2001).

Congo red (sodium salt of benzidinediazobis-1-naphthylamine-4-sulfonic acid) is a benzidine-based azo dye highly soluble in water solution and it was selected in this study as a model anionic dye. Congo red mainly occurs in the effulents discharged from textile, paper, printing, leather industries , etc. (Bhattacharrya et al., 2004) during dyeing operation about 15% of it 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 clotting and induce somnolence and respiratory problems (Alok et al., 2009).

The purpose of the work was to study the removal of Congo Red (CR) by using Commercial Activated Carbon (CAC) to degrade the dye.

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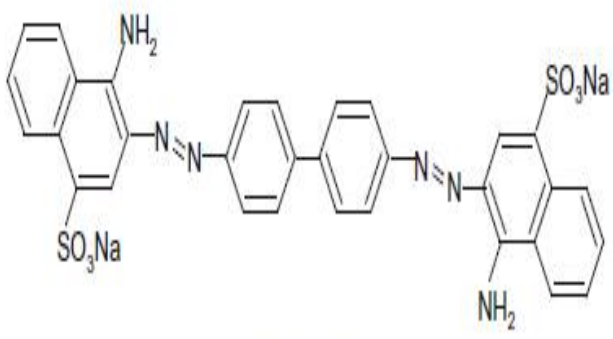
Structure of Congo Red



CONGO RED

Materials and methods

Commercial Activated Carbon

All the chemicals used for this experiment are of analytical grade. Commercial Activated Carbon (CAC) was purchased from SD Fine chemicals, Mumbai.

Preparation of Stock Solution

Congo Red dye was used without further purification. The dye stock solution was prepared by dissolving appropriate amount of accurately weighed dye in distilled water to a concentration of 1000 mg/l. The experimental solutions were prepared by proper dilution.

Adsorption Experiment

15 mg of activated carbon was interacted with 50 mL of Congo Red dye known concentration solution in a iodine flask at. The mixtures were agitated on Mechanical shaker at (180 rpm) continuously for predetermined time intervals. The process was carried out for different concentration of the dye solution (100,150,200 and 250 (mg/L^{-1}). Each dye sloution was separated through centrifuged. The absorbance of the solution standard series and each filtrate after interction was taken using Systronics Double Beam UV-visible Spectrophotometer:2202 at maximum wave length of 510 nm.

The amount of adsorption at equilibrium,q_e(mg/g), was calcualated as follows:

$$qe = \frac{(C_o - C_e)\,V}{W}$$

Where, C_o and C_e (mg/L) are the liquid-phase concentrations of CR dye at initial and equilibrium respectively. V(L) volume of the congo red dye solution and W(g) is the weight of the adsorbent used The percentage dye removal was calculated as:

$$\%\,\text{Congo red dye removal} = \frac{(C_o - C_e)}{C_o} x100$$

Results and discussion

Effect of Time, Initial concentration and Temperature

The effect of time on percentage removal of CR dye from aqueous solution with respect to different contact times and with different initial concentrations were shown in Figure 1. The adsorption of dye from the solution increases with the time and finally attained equilibrium in 80,120, at140 and 180 mins for 100,150,200 and 250 mg/L^{-1} respectively (table 1). when the concentration of dye is increased 100 to 250 mg/L^{-1} The percentage of removal increased with the increase in contact time.

Figure 1.Effect of contact time

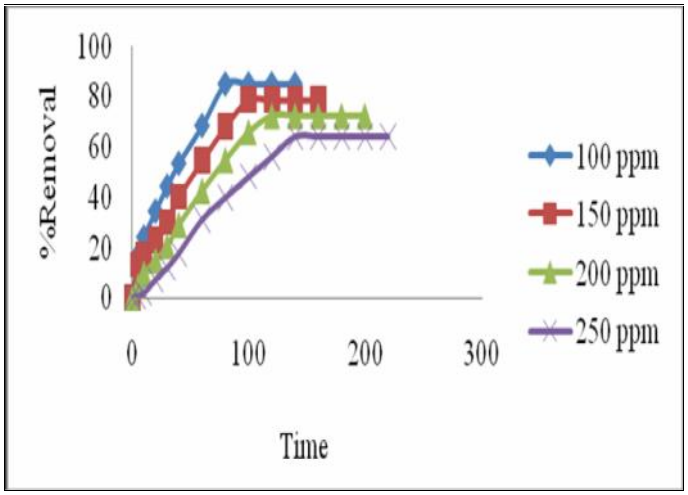


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Table 1. Percentage of removal of dye and amount of dye adsorbed

Ci (mg/L)	% of removal of dye At equilibrium	Adsorption capacity at equilibrium (mg/g)
100	84.86	282.86
150	78.66	393.33
200	72.16	481.06
250	64.00	533.33

Isotherm studies

For solid–liquid adsorption system, adsorption isotherm is important model in the adsorption behaviour. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid and liquid phase (Chen et al., 2011). It is significant for understanding the adsorption behaviour to identify the most appropriate adsorption isotherm model. In this paper, Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models were employed to investigate the adsorption behaviour. Adsorption isotherm was studied at four different temperatures viz 303,313,323and 333K.

Langmuir isotherm

The langmuir isotherm is rested on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place. Thus, an equilibrium value can be reached and the saturated monolayer curve be express in the equation below which has been successful for the monolayer adsorption. Linear form of the rearranged Langmuir model is

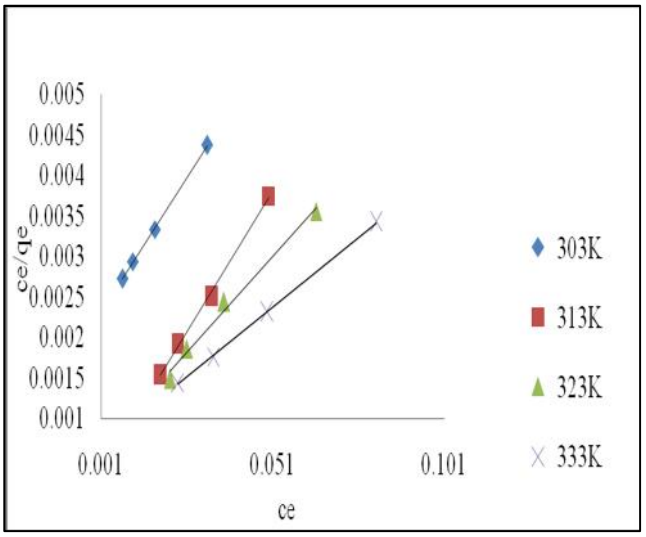
$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), and q_0 and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively (Ramuthai, S., Nandhakumar,V., et al, 2009).The constants q_0 and b can be calculated from the slope and intercept of the plot of C_e/q_e vs C_e are listed in Table 2. The essential characteristics of Langmuir isotherm can be expressed by dimensionless separation factor, R_L (Satish Manocha et al., 2002).

$$R_L = \frac{1}{(1+b.C_e)}$$

The value of separation factor R_L indicates the nature of the adsorption process as given below $R_L > 1$ Unfavourable, $R_L = 1$ Linear, $0 < R_L < 1$ Favourable, $R_L = 0$ Irreversible.

Figure 2 Langmuir Isotherm



Freundlich isotherm

Freundlich isotherm model is used to describe hetergeneous adsorption process i.e adsorption which takes place on a heterogeneous surface through a multilayer adsorption mechanism. (Freundlich, et al.,1906). Linear form of Freundlich equation is

$$\text{Log qe} = \text{Log } K_F + \frac{1}{n}\text{Log } C_e$$

where q_e is the amount of CR dye adsorbed (mg/ g), *Ce* is the equilibrium concentration of CR dye in solution(mg/l), K_f and *n* are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. A plot of log q_e v_s log C_e gives a linear with a slope of 1/n and intercept of log k_f and the results are given in Table 2

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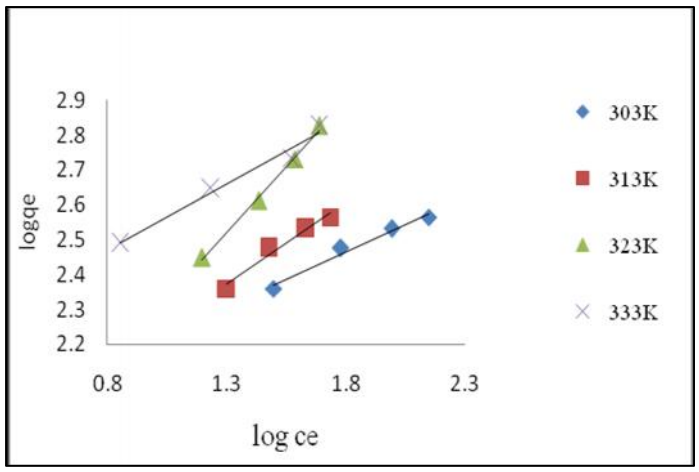
Figure 3. Freundlich isotherm



Tempkin isotherm

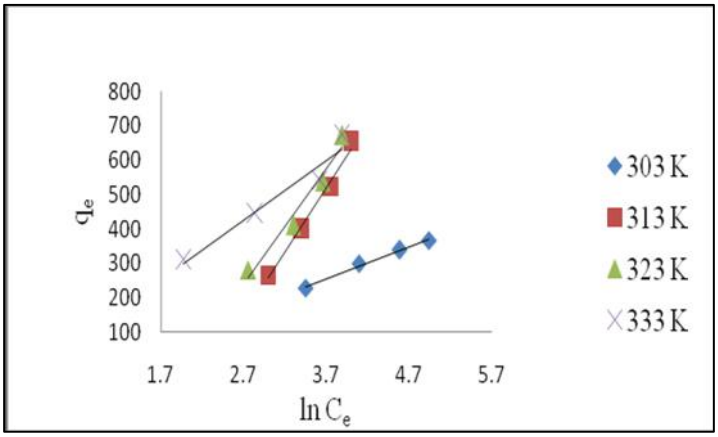
Temkin isotherm model considers the effect of indirect adsobent – adsorbate interactions on adsorption, and suggests that the heat of adsoption of all the layer would decrease linearly with coverage due to these interactions .

Tempkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic as stated in Freundlich expression (Teles de Vasconcelos, L.A.,et al., 1993). The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The linear form of Tempkin equation is (Tempkin, M.J., et al.1940).

$$Qe = B_1 \ln K_T + B_1 \ln C_e$$

The K_T equilibrium binding constant (Lmg^{-1}), B1 Tempkin constant related to the heat of adsorption Tempkin constants K_T and B_1 are calculated from the slopes and intercepts of q_e vs ln C_e are given in Table 2

Figure 4. Temkin Isotherm



Dubinin – Raduskevich Isotherm

The Linear form of Dubinin-Radushkevich isotherm (Vikal Guptha, et al.,2007) is

$$\ln q_e = \ln q_D - B\varepsilon^2$$

Where, q_D is the theoretical saturation capacity (mg/g) B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and ε is polany potential which is related to the equilibrium as follows;

$$\varepsilon = RT \ln(1+1/C_e)$$

A plot of ln q_e vs ε^2 gives a linear trace and the constants q_D and B calculated from the slope and intercept respectively. The mean free energy of adsorption E calculated from B using the following equation

$$E = 1/ (2B)^{½}$$

Based on this energy of activation we can predict whether an adsorption is physisorption or chemisorption. If the energy of activation is <8 kJ/mol, the adsorption is physisorption and if the energy of activation is 8–16 kJ/mol, the adsorption is chemisorption in nature (Vikrant Sarin et al., 2006) Based on the mean free energy calculated from the constant B (table 2), we can predict that the adsorption of CR dye onto CAC is physisorption dominating chemisorption in nature.

Figure 5. Dubinin Raduskevich

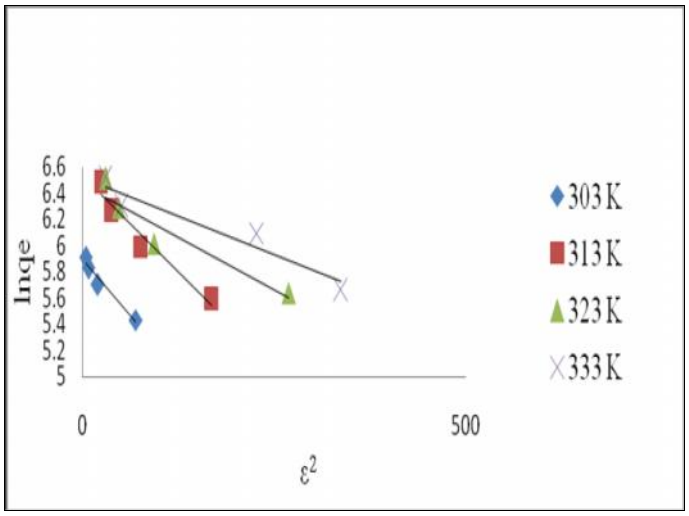


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Table 2. Isotherm parameters for removal of Congo red onto CAC

Isotherm Models	Temp (K)	Parameters and their results			
		Q_0 (mg/g^{-1})	b(L/mg^{-1})	R_L	R^2
Langmuir	303	15.15	33.00	0.00041	0.999
	313	18.19	28.00	0.00050	0.997
	323	21.28	22.00	0.00064	0.991
	333	66.67	15.00	0.00115	0.990
Freundlich		1/n	k_f (mg/g^{-1})		R^2
	303	3.16	78.70		0.975
	313	2.14	57.94		0.966
	323	1.31	50.07		0.995
	333	2.65	22.13		0.978
Tempkin		B1 (J/mol)	K_T (L/g)		R^2
	303	6.90	0.0996		0.991
	313	8.01	0.0985		0.988
	323	15.98	0.1379		0.965
	333	27.26	0.2813		0.949
Dubinin Raduskevich		q_D (mg/g)	E	B × 10^{-4} (mol^2/J^2)	R^2
	303	359.10	0.006	7.9	0.963
	313	677.64	0.005	6.6	0.953
	323	641.21	0.003	5.4	0.894
	333	579.30	0.002	5.2	0.845

Analysis of Isotherm

Langmuir isotherm

In the present study Q_0 value ranges from 15.15 to 66.67, as the temperature increases the monolayer adsorption capacity also found to increase. the kind of results were obtained in various similar studies (Ramuthai et al., 2009) . The separation factor R_L values in between 0 to 1 indicates the favourable adsorption. R^2 values of isotherm plots revealed that Langmuir isotherm well describes in the present system, that was the existence of identical adsorption site.

Frendlich isotherm

The values of 1/n were between 1 and 10 which indicates cooperative adsorption (Fytianos et al., 2000)**.** The R^2 value was low when compared to langmuir isotherm.

Temkin Isotherm

B1-Temkin constant is related to the heat of adsorption. This B1 value increased from 6.90 to 27.26 as the temperatrue of adsorption increased. The temkin parameter K_T value give on idea about nature of adsorption, if K_T value is in between from 0 to 8 the physical nature. Otherwise its chemical nature (Tempkin et al., 1940). In our present study the K_T values ranged from 0.0996 to 0.2813 which indicate the adsorption is physical nature. The R^2 value was low compared to langmuir and frendlich isotherm.

Dubinin-Raduskevich

The activation energy E value ranges from 0.002 to 0.006 and B value from 7.9 to 5.2 indicates the physisorption (Vikrant Sarin et al., 2006). The R^2 value was very low when compared to other three isotherms.

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Conclusions

The equilibrium data of present investigation model with Langmuir, Freundlich,Tempkin and Dubinin Raduskevich isotherms. Its found that the adsorption data was well fitted to the Langmuir isotherm adsorption model. The fitness of Langmuir's model indicated the formation of monolayer coverage of the sorbate on the identical statistics surface of the adsorbent. The separation factor R_L value, activation energy E values and Temkin parameters B1, K_T values which indicated at adsorption is more favourable physisorption.

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