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Kinetics of Adsorption of Congo Red Dye onto Commercial Activated Carbon from Aqueous Solution

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Abstract

Adsorption of Congo Red dye (CR) onto Commercial Activated Carbon (CAC) from aqueous solution was investigated under various experimental conditions. Batchmode experiments were conducted. The pH_{zpc} *of CAC was 6. Hence all experiments were carried out at solution pH 6. 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 3.57 & 7.05 respectively and hence this adsorption followed first order kinetics. Adsorption capacities of CAC estimated from equilibrium studies for different initial concentrations of adsorbate were found to be good.*

***Keywords**: Activated Carbon; Adsorption; Adsorption kinetics; Commercial Congo red; pHzpc.*

1. INTRODUCTION

Colour is considered as the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries such as paper, rubber, leather, cosmetics, textile, pharmaceuticals, plastics and food industries (Siew-Teng *et al*. 2010). More than 100,000 dyes are commercially available and world widely more than $7x10^5$ tones/year of these dyes are produced in the world for the textile industry alone (Ricardo *et al*. 2008). When these colored effluents enter rivers or any surface water system, they upset biological activity. Ground water systems are also affected by these pollutants because of leaching from the soil. In addition, many dyes are difficult to degrade due to their complex aromatic structure and they tend to persist in the environment and creating serious water quality and public health problems such as allergic dermatitis, skin irritation, cancer and mutation (Alau *et al*. 2010) and tetragonic effects on aquatic organisms and human beings (Gongo *et al*. 2007). Hence, the removal of dyes from wastewater is essential to prevent continuous environmental pollution.

Therefore many methods such as activated carbon sorption, chemical coagulation, ion exchange, electrolysis and biological treatments have been developed for removing dye pollutions from wastewater before being discharged into the environment (Gupta *et al*. 2004). There are two basic processes to activate carbon materials are physical and chemical properties. 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

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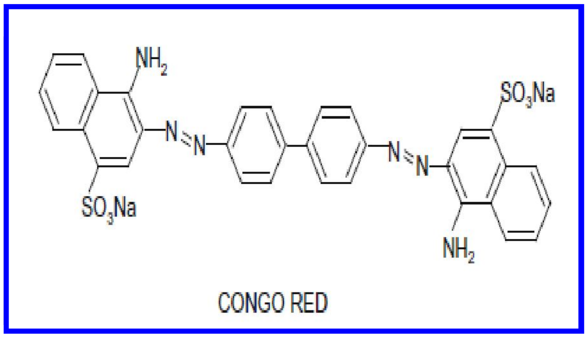
a need to search for more effective adsorbents (Sudipta *et al.* 2009; Karthikeyan *et al.* 2012) Congo red (sodium salt of benzidinediazobis-1- naphthylamine-4-sulfonic acid) is a benzidine-based azo dye and it was selected in this study as a model anionic dye because of its complex chemical structure, high solubility in aqueous solution and its persistence, once it is discharged into natural environment. Congo red mainly occurs in the effulents discharged from textile, paper, printing and leather industries (Srivastava *et al.* 1988). About15% of dyes end up in waster waters during dyeing operation (Tahir *et al.* 2009).

Structure of Congo Red:



2. MATERIALS & MATHODS

2. 1. Materials

All the chemicals used for these experiments are of analytical grade. Commercial Activated Carbon (CAC) used in this study is purchased from SD fine chemicals in Mumbai. The Congo Red (CR) dye was from Merck Company.

2.2 Preparation of Dye Solution

Congo red 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.

2.3 Determination of Zero Point charge

The pH at the potential of zero charge of the carbon (pH$_{zpc}$) was measured using the pH drift method (Jia *et al.* 2002). The pH of the solution was adjusted by using 0.01 M sodium hydroxide (or) hydrochloric acid. 50 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. The pHzpc of commercial activated carbon was found to be 6.

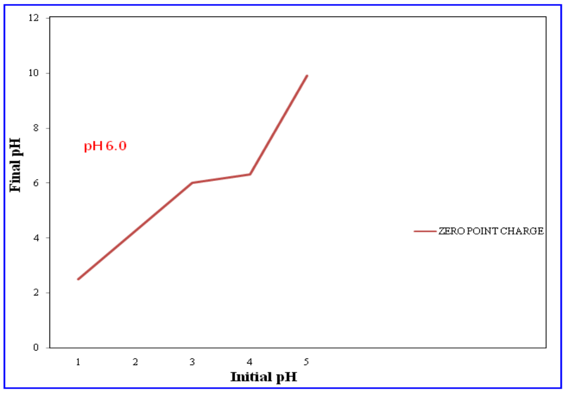


Fig. 1: Effect of pH$_{zpc}$

2.4 Equilibrium Studies using Batch Method

15 mg of activated carbon was interacted with 50 cm^3 of Congo Red (CR) dye 100 mgL^{-1}solution at 303K and at the solution pH of 6. The mixtures were agitated on Mechanical shaker (180 rpm) continuously for 60 minutes. It was then centrifuged. The concentrations of dye solutions were determined by their absorbance of the wave length 510 nm using Systronics Double Beam UV-visible Spectrophotometer: 2202. This process was repeated for different initial concentrations (100, 150, 200 and 250 mgL^{-1}) of the dye solution.

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

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

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 (Hameed, *et al.* 2006). The percentage dye removal was calculated as:

$$\%\ \text{Congo red dye removal} = \frac{(C_o - C_e)\text{x}100}{C_o}$$

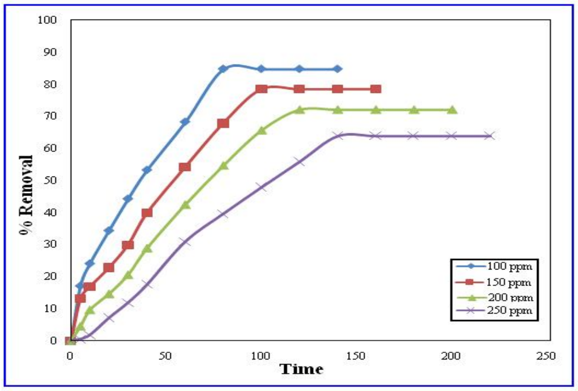


Fig. 2: Effect of contact time

2.5 Adsorption Kinetics Experiments

The kinetics experiments were performed using a procedure similar to the equilibrium studies. Accurately 15 mg of the adsorbent was thoroughly mixed with 50 mL of CR dye solution of predetermined concentrations and the pH of suspensions were brought to 6 by adding conc. HCl acid and shaken at 303 K temperature. Then the mixtures were taken from shaker at appropriate time intervals (5, 10, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 and 240) and the concentrations of the left out solutions were estimated as explained before. In order to determine the best kinetic model which describes the adsorption, experimental data were fitted into Pseudo first order and pseudo second orders kinetic models (Venkatraman *et al*. 2009).

3. RESULT & DISCUSSION

3.1 Effect of time and initial concentration

The effect of time on percentage removal of CR dye from aqueous solution with respect to different initial concentrations was shown in Fig 1. The adsorption of dye from the solution increased with the time and finally attained equilibrium in 80,100, 120 and 150 minutes for the dye solutions of initial concentrations 100, 150, 200 and 250 mgL^{-1} respectively. Percentage of removal of dyes decreased with the increase of initial concentrations of dyes from 100 to 250 mg/L because, the ratio of the amount of dye adsorbed to the initial concentration of the dye decreased with the increase of initial concentrations of the dye solutions. However the amount of dye adsorbed on to the adsorbent found to increase with the increase of initial concentrations because, the ratio of the amount of dye present in the solution to available adsorbent site increased with the increase of initial concentrations of the dye solutions and hence large fraction of dyes were driven to adsorbent phase.

3.2 Effect of pH

To study the effect of pH on CR adsorption, 15 mg of CAC was added to dye solutions of concentration dye 100 mgL^{-1}. The initial pHs of the solutions were adjusted from 2 – 10 using HCl and NaOH. These suspensions were shaken for 60 minutes (equilibrium time) at temperature 303K. They were centrifuged. Then the percentage removal of the dyes from solutions was determined which were given in Table 1and depicted in Fig. 3.

Table 1. Eeffect of pH

pH Solutions	% Removal
2.0	23.94
4.0	38.02
6.0	66.20
8.0	47.82
10.0	33.8
12.0	9.23

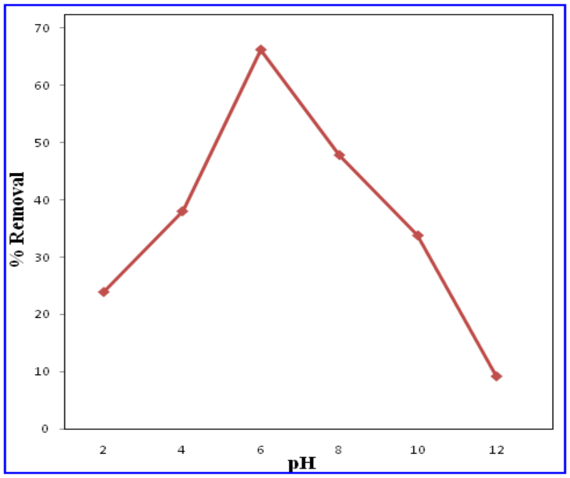


Fig. 3: Effect of pH

As the pH increased, the percentage removal of the dye increased and found to be high (more than 60%) at pH 6, after that the percentage of removal decreased with the increase of pH beyond 6. pH_{zpc} of the carbon is 6 .So at pH 6, surface of the carbon was neutral that is neither positively charged nor negatively charged and hence the percentage of removal of the dye was maximum. Below this pH, the approach of dye anion towards the surface of the carbon may be prevented by inter ionic attraction of the accumulated hydrogen ions present in the solution. Therefore the percentage of removal of dye might be decreased with the decrease of pH. Above the pH 6, the surface of the carbon possessed negative charge which might repel the approach of the dye anion.

4. KINETIC MODELS

For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer several kinetics models were used to test the experimental data. For this present study, two kinetics models were applied to understand the mechanism of adsorption of the dye onto the adsorbent.

4.1 Pseudo First order kinetics

The pseudo – first order kinetic model can be represented by Lagergren rate equation: (Mansour *et al.* 2011).

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

Where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min) respectively and k_1 is the rate constant of adsorption (l/min) show in fig. 4a. The values of k_1 and theoretical q_e for different initial concentrations were calculated from the slope and intercepts f of these curves respectively were presented in Table 2.

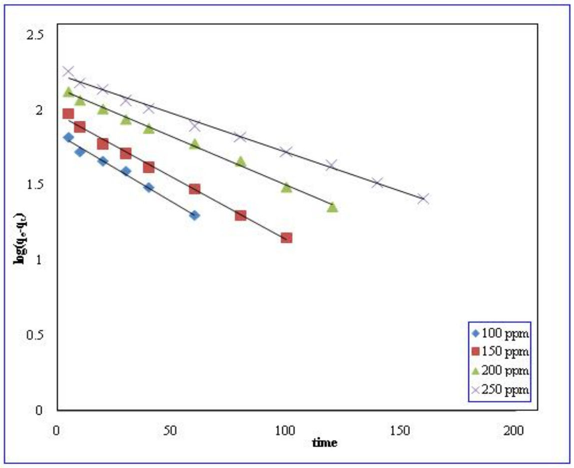


Fig. 4a: Pseudo first order kinetics

Table 2.Pseudo First order kinetic parameters

Ci	$K_1 x10^{-2}$ (min^{-1})	R^2
100	0.0184	0.938
150	0.0161	0.978
200	0.0299	0.939
250	0.0115	0.968

4.1.1 Pseudo Second order kinetics

The pseudo second order kinetic model can be represented with the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Theoretical equilibrium adsorption capacity (q_e) and the second-order constant k_2 (g/(mg min))can be determined experimentally from the slope and intercept of plot of t/q_t versus t (Fig. 4b). The k_2 (g/ (mg min)) and correlation coefficients values calculated from were listed in Table 3.

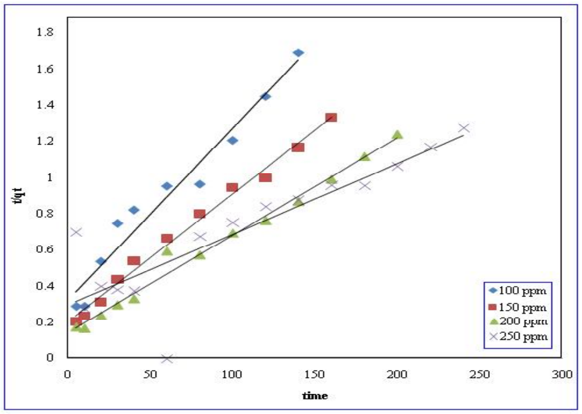


Fig. 4b: Pseudo second orderkinetics

Table 3. Pseudo Second order kinetic parameters

Ci	$K_2 x10^{-3}$ ($gmg^{-1}min^{-1}$)	R^2
100	2.60	0.957
150	1.00	0.990
200	5.35	0.984
250	2.65	0.747

4.1.1.1Test for kinetics models

The sum of error squares (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;

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

Where, N is the number of data points.

Experimental $q_{e(exp)}$, calculated $q_{e(cal)}$ and SSE for the pseudo first order and pseudo second order kinetics were given in Table 4. It shows that $q_{e(exp)}$ 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.

Table 4. Calculated SSE % of the adsorption of CR dye onto CAC

Ci	$q_{e\,(cal)}$	$q_{e\,(exp)}$	Δq_e	R^2	SSE (%)
	First Order				
100	82.86	74.30	8.56	0.938	3.57
150	120	112.20	7.80	0.978	
200	161.43	141.57	19.86	0.935	
250	188.57	171.40	17.17	0.968	
Second Order					
100	82.86	111	28.14	0.957	7.05
150	120	142	22	0.990	
200	161.43	200	38.57	0.987	
250	188.57	333	144.43	0.747	

This confirms the applicability of the pseudo first order kinetic model. The determination coefficient (R^2) for pseudo Second order model ranged between 0.747 and 0.990 whereas these values for the First order model were ranged between 0.938 and 0.978. It indicates that the experimental data best fitted into pseudo First order. Similar phenomena have been observed in the adsorption of CR on CAC (Namasivayam *et al.* 2002, 2003).

5. CONCLUSION

The adsorption of Congo 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 CAC 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, 140 minutes for 100, 150, 200, 250 mg/L when 15 mg CAC was used as adsorbent for 50 mL solution. Adsorption capacity of CAC 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.

REFERENCES

Alau, K. K., Gimba, C. E. and Kagbu, J. A., Removal of dyes from aqueous solution using neem (AzadirachtaIndica) husk as activated carbon, *Archives of Appl. Sci. Res*., 2(5), 456 - 461(2010).

Gongo, R., Jin,Y., Chen, J., Hu, Y. and Sun, J., Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw, *Dyes Pigments*., 73, 332-337(2007). doi:10.1016/j.dyepig.2006.01.037

Gupta, V. K., Mittal, A., Krishnan, L. and Gajbe,V., Adsorption kinetics and column operations for the removal and recovery of malachite green from waste water using bottom ash, *Sep. Purif. Technol.*, 40(1), 1179-1184(2004). doi:10.1016/j.seppur.2004.01.008

Gupta, V. K., Suhas, A. I., Saini, V. K., Removal of rhodamineB, fast green and methylene blue from wastewater using red mud, an aluminum industry waste, *Ind. Eng. Chem. Res.*, 43, 1740-1747(2004) doi:10.1021/ie034218g

Hameed, B. H., Din, A. T. M., Ahmad, A. L., Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies, *J. Hazard Mater*., 141(3), 819-825(2006).

Jia, Y. F. and Thomas, K. K., Adsorption of metal ion on nitrogen surface functional groups in activated carbon, *Langmuir.*,18(2), 470(2002). doi:10.1021/la011161z

Mansour, M. S., Ossman, M. E. and Farag, H. A., Removal of Cd (II) ion from waste water by adsorption onto polyaniline coated on saw dust, *Desalination*., 272(1-3), 301-305(2011). doi:10.1016/j.desal.2011.01.037

Namasivayam, C., Kavitha, D., Adsorptive removal of 2-chlorophenol by low-cost coir pith carbon, *J. Hazard. Mater., 98(1-3), 257-274*(2003). doi:10.1016/S0304-3894(03)00006-2

Namasivayam, C., Kavitha, D., Removal of congo red from water by adsorption onto activated carbon prepared from coir pith and agricultural solid waste, *Dyes Pigments*., 54, 47-58(2002). doi:10.1016/S0143-7208(02)00025-6

Ricarto, A., Carletto, F., Bosco and Ferrero, F., Adsorption of congo red dye on Hazelnut shells and degradation with Phanerochattechrysosprium, *Bio Resour.*, 3 (4), 1146-1155(2008).

Siew-Teng, O., Lee,W., Keng, P., Hung, Y. and Ha, S., Equilibriun studies and kinetics mechanism for the removal of basic and reactive dyes in both single and binary systems using EDTA modified rice husk, *Intl. J. Physical sci*., 5(5), 582 - 595(2010).

Srivastava, K., Balasubramanian, N. and Ramakrishna, T. V., Studies on chromium removal by rice husk carbon, *Indian J. Environ. Health*., 30(4), 376 - 387(1988).

Sudipta, C., Lee, D. S., Lee, M. W. and Woo, S. H., Enhanced adsorption of congo red from aqueous solution by chitosan hydrogel beads impregnated with cetyltrimethyl ammonium bromide, *Bioresour. Technol.*, 100, 2803-2809(2009). doi:10.1016/j.biortech.2008.12.035

Tahir, H., Sultan, M. and Jahanzeb, Q., Remediation of azo dyes by using household used black tea as an absorbent, *Afr. J. Biotechnol.*, 8(15), 3584-3589(2009).

Venkatraman, B. R., Hema, K., Nandhakumar, V. and Arivoli, S., Adsorption thermodynamics of malachite green dye onto acid activated low cost carbon, *J. Chem. Pharm. Res.*, 3(2), 637-649(2009).