



Research Article

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Thermodynamics and Instrumental Analysis of Congo Red Dye 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. The characteristics of CAC were determined by SEM, XRD and FTIR. Equilibrium studies were carried out by varying the parameters such as contact time, initial dye concentration, pH of the solution and temperature. The initial concentration studies were carried out by taking 100,150,200,250 mg/L of solutions and effect of temperature study was carried out at 303,313,323 and 333K. Thermodynamic parameters for such as H° , S° , and G° were determined using Van't Hoff plots. Analysis of these values inferred that the adsorption was endothermic, spontaneous, favorable. The FTIR and XRD studies confirmed that adsorption physisorption with partial chemisorption. The SEM image showed rough surface area with micropores and macropores. Adsorption capacity of the CAC for CR dye was good.

Keywords: Adsorption, Commercial Activated Carbon, Congo red, Thermodynamic parameters, SEM, XRD, FTIR Analysis.

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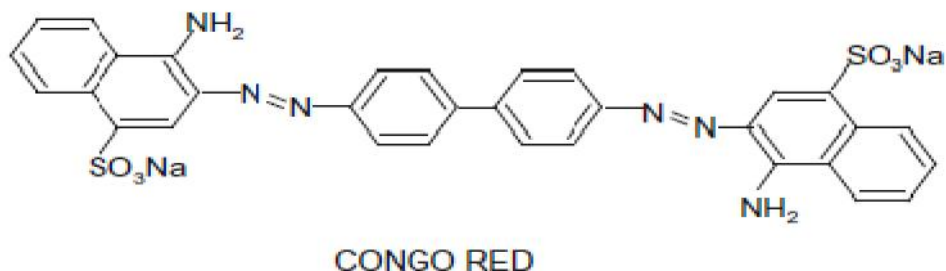
1. Introduction

The need to maintain a cleaner environment for the survival of both aquatic and terrestrial lives including human beings is very crucial and is a subject of increasing concern to the environmentalist. Pollution caused by agents such as heavy metals and dyes are amongst the list which rendered the environment unwholesome and posed serious health concern to the populace. Effluents from industries such as dyestuff, textiles, leather, paper, printing, plastic and food contains various dyestuffs [1]. Dye, a highly coloured and synthetic substance contain at least one

chromophores (colour bearing group) and auxochromes (colour helpers) which impart intense colours to them and are undesirable and disgusting in wastewater [2].

Water soluble dyes are characterized by their biodegradable ability and conventional treatment techniques such as flocculation, chemical oxidation, and membrane separation are not suitable. Nevertheless, adsorption has proven to be potentially powerful because of its imaginable opportunity to design the chemical composition of the adsorbent surface [3]. The process of adsorption has an advantage over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. The commercial activated (powdered or granular) is the most widely used adsorbents because it has excellent adsorption effectiveness for the organic compound. The 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. During dyeing operation about 15% of its ends up in waste waters [5].

Structure of Congo Red:



2. Materials and Methods

2.1 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 in Mumbai. The Congo red dye from merck Company. X-ray Diffraction studies of the commercial activated carbon were carried out using D8 Focus powder XRD, company Bruker, make Germany. The spectra were measured within the range of 400 – 4000 cm^{-1} in a FT- spectrometer, Make-Perkin Elmer, Model- Spectrem one, Version-5.0.1.

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 method⁶. 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 pH_{zpc} of commercial activated carbon was found to be 6.

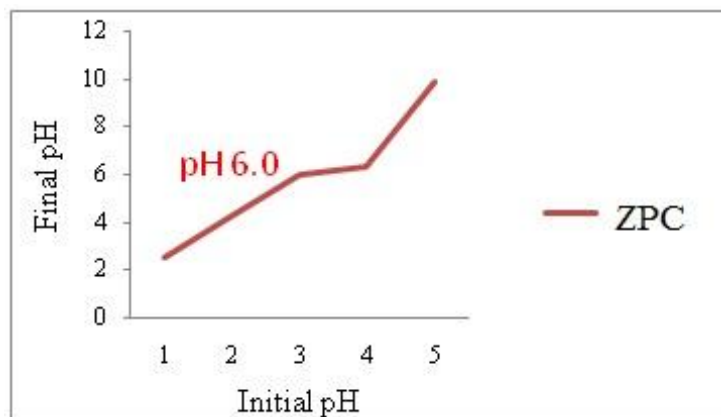


Figure 1

2.4 Equilibrium Studies using Batch Method:

15 mg of activated carbon was interacted with 50 ml of Congo Red (CR) dye 100 mg/L 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 mg/L) of the dye solution. The amount of adsorption at equilibrium, q_e (mg/g), was calculated 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 [7]. The percentage dye removal was calculated as:

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

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 the suspensions were brought to 6 by adding con 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 [8].

3. Result and 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 Figure 2. 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 mg/L 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.

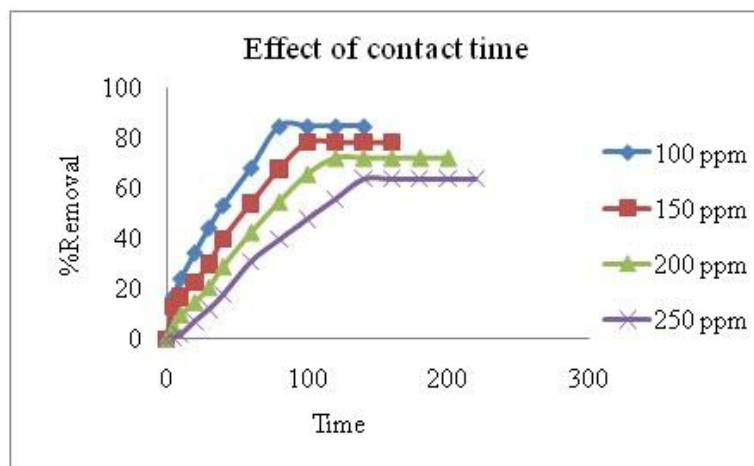


Figure 2

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 mg/L. The initial pH 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 1 and depicted in Figure 3. 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.

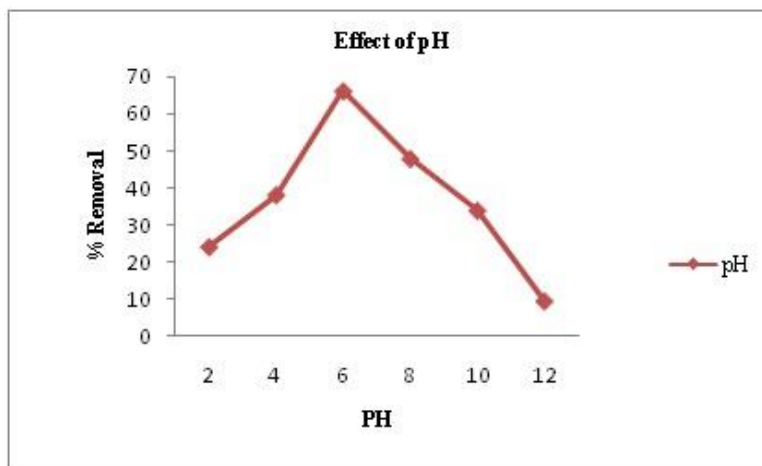


Figure 3

Table 1: Effect 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

3.3. Effect of temperature: To observe the effect of temperature on the adsorption capacity, experiments are carried out at three different temperature (30,40,50 and 60°C) using using 15 mg of CAC per 50 ml of the solution. The experiment was carried out in a constant temperature water bath. First the optimum conditions were found out. Then, at these conditions the effects of temperature was studied. It was seen that as the temperature was increased, the dye removal was increased [9].

4. Thermodynamics studies

The thermodynamics of the adsorption process were studied at four different temperatures in a thermostated water bath. The adsorption capacity increased between 303,313,323 and 333K (figure. 4). Thermodynamic parameters like H° , S° and G° were measured based on van't Hoff plot.

$$G = -RT \ln K_L \quad (\text{Gibbs Equation})$$

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (\text{Van't Hoff Equation})$$

Where, k_L is the equilibrium constant, H° and S° are the standard enthalpy and entropy changes of adsorption respectively and The values of H° and S° are calculated from the slopes and intercepts of the linear plot of $\ln k_L$ vs $1/T$. The free energy of specific adsorption G° (kJ/mol) is calculated from the following expression

$$G^\circ = H^\circ - T S^\circ$$

The thermodynamical parameters calculated from Eyring's plot are given in table 5. Negative standard free energy of adsorption indicates that the adsorption process is favourable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive H° value. The bonding between CR and CAC surface is very weak,

since H° values are found to be in between 37.93 to 47.14 kJ mol^{-1} . Positive values of S° suggested good affinity of the dye towards the adsorbent and the adsorption is spontaneous in nature [10].

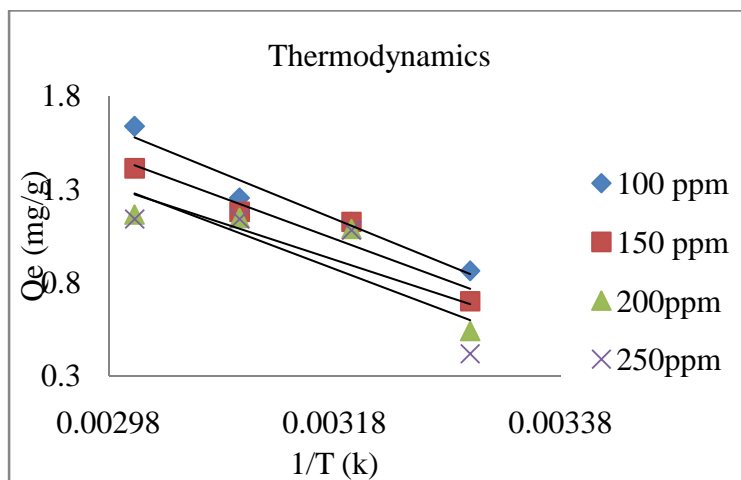


Figure 4: Thermodynamics

Table 2: Thermodynamics parameters for the adsorption of CR onto CAC

Ci Mg/L ⁻¹	- G kJ/mol				H kJ/mol	S kJ/mol
	303K	313K	323K	333K		
100	- 3.14	-4.80	-6.46	-8.12	47.14	0.1660
150	-2.70	-4.19	-5.68	-7.18	45.52	0.1493
200	-3.97	-5.35	-6.74	-8.12	43.82	0.1383
250	-3.47	-5.03	-6.59	-8.15	37.93	0.1561

5. Instrumental Analysis

5.1 XRD Study:

It is noticed there is a change in the XRD pattern of before and after adsorption new five peak are formed found after adsorption 2- θ value between 15 to 30. Which may be due to formation of new chemical bonds. The results leads to concluded that partial chemisorption also took place.

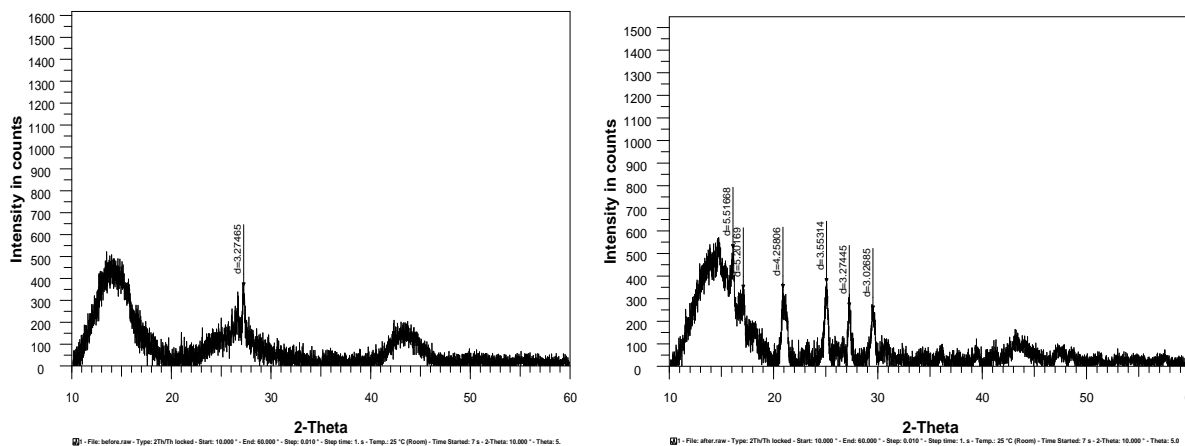


Figure 5: XRD Pattern of CAC Before and after adsorption of CR dye

5.2 FTIR Study:

Fourier transform infrared spectroscopy (FTIR) was used to determine the function group on the Commercial Activated Carbon surface. it is noticed there is a change in the FTIR pattern of before and after adsorption ten new peaks were formed found after adsorption between the range 400-4000 cm^{-1} Which may be due to formation new chemical bonds. This results leads to concluded that partial chemisorption also took place.

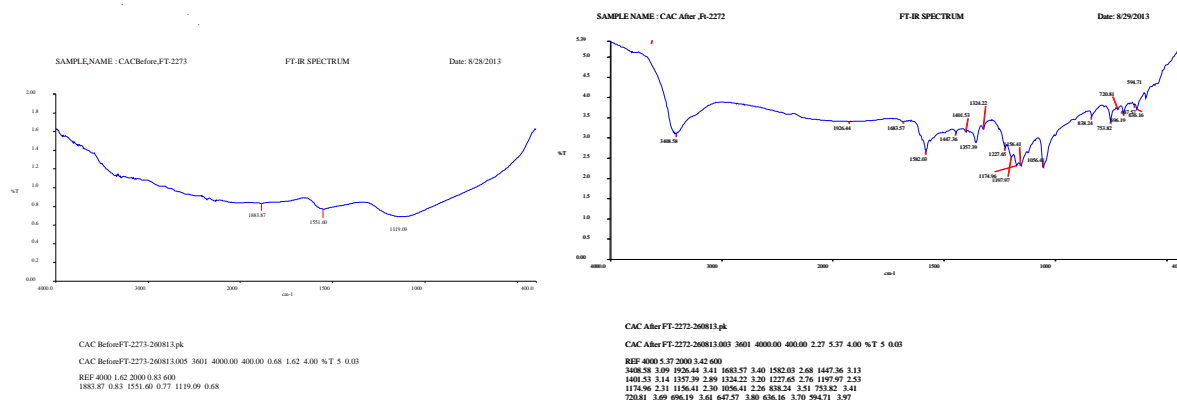


Figure 6: FTIR Spectrum onto CAC Before and After adsorption of CR dye.

5.3 SEM Analysis:

The surface morphology of the commercial activated carbon was examined using scanning electron microscopy (SEM), before and after adsorption at an accelerating voltage of 15kv at 1000 x magnification 3kv at 1500x (figure 7). At such magnification, the activated carbon particle showed rough areas of surface on which micro pores were clearly identifiable.

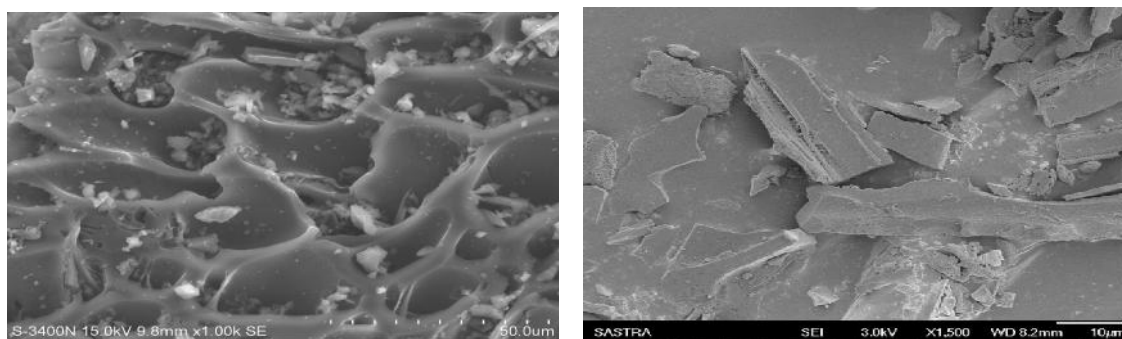


Figure 7: SEM micrograph of CAC before and after adsorption of CR dye

6. Conclusion

The equilibrium and thermodynamics for the uptake of Congo Red dye by Commercial Activated Carbon from aqueous solution were studied. The negative values of G° and positive values of H° and S° indicated adsorption process as spontaneous, endothermic and favorable. The FTIR and XRD studies confirmed that adsorption physisorption with partial chemisorption. The SEM image showed rough surface area with micropores and macropores. Besides, the results indicated that the Commercial Activated Carbon adsorbent is capable for the removal of Congo Red dye with high affinity and capacity indicating its potential use as a low cost adsorbent in near future.

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