Removal of Congo Red Dye using Activated Carbon Developed from Bio-waste

Madhu Agarwal[1*] and Karishma Maheshwari[1]

[1] Department of Chemical Engineering, Malviya National Institute of Technology Jaipur, Jaipur-302017, India,

Abstract**:** *In the present study, activated carbon developed from walnut shell (AWSC) was used as adsorbent to remove Congo Red dye (a carcinogenic dye) from water. Various parameters like contact time, pH, concentration, adsorbent dosage and temperature were observed for analyzing the dye removal efficiency of adsorbent. AWSC was characterized to study micro structure and morphology inculcating scanning electron microscope (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR). The percent removal obtained was more than 94% for initial dye concentration of 10 ppm at 2 h of contact time and adsorbent dosage of 0.2 g. Further, the Langmuir isotherm, Freundlich isotherm and Temkin isotherm were fitted into to the data. The Langmuir isotherm model fits best with high adsorptive capacity of 64 mg/g.*

Keywords: *Dyes; Congo Red; Adsorption; Kinetics; Isotherm*

1. Introduction

The dye effluent water, discharged in to aquatic systems, imposing risk due to the carcinogenic nature of dyes, causing inhibition of survival. An average of 70-150 L of water, 0.6 kg NaCl and 40 g of reactive dyes are required for dyeing of 1 kg of cotton. Greater than 80,000 metric tons of reactive dyes are produced and consumed every year. But more than 20% of dyes are released into water adding coloration and toxicity to the water [1]. Also, toxicity of dyes is a major issue for environmental conditions as dyes get remains in the environment for an extended time period due to high photo stability and thermal characteristics. Moreover,most of the dyes are not biodegradable due to which dyes remain unchanged after undergoing several water treatment processes like activated sludge process [2]. Hence, the complete removal of dyes is a challenging task.

Congo red dye is the sodium salt of benzidinediazo-bis-1-napthylamine-4-sulphonic acid. It is found to be highly resistant to biodegradation being strongly undesirable to environmental health. Adsorption is still considered to be e**ffective method for dye removal compared to several methods** inculcating chemical coagulation, advance chemical oxidation, adsorption, foam flotation, electrolysis, adsorption, etc. [3-6]. There are several studies carried out for dye removal utilizing low cost adsorbent made from agricultural wastes. Activated carbon prepared from coir pith was used by Namasivayam *et al*.[7] for removal of Congo red dye and found it to be good adsorbent with adsorptive capacity of 6.7 mg/g. Malik [8] studied adsorption of Acid yellow dye on activated carbon developed from saw dust and rice husk and reported 70% removal of dye at pH 2. Mall *et al*. [9] attempted the removal of Congo red dye using bagasse fly ash and activated carbon and found that bagasse fly ash can effectively used for dye removal provided initial dye concentration is low. The walnut mainly grown in Jammu & Kashmir, Himachal Pradesh, Uttar Pradesh and Arunachal Pradesh of India. Walnut shells the bio waste are discarded and burned resulting in waste of resources and air pollution.

Therefore, in this paper an attempt has been made to utilize the huge quantity of walnut shells for Congo red dye removal. Jiang *et al.[*10] has analyzed its utility and found that it has potential to get converted into activated carbon with good adsorptive capacity.

2. Materials And Methods

The walnut shells were obtained from local grocery shops in Jaipur (India). The Congo red dye (formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol) was purchased from sigma-Aldrich and the chemicals like HCl, NaOH where purchased from local market.

Walnut shells were washed with water and then dried, grinded and screened by 44 BIS sieve. The fraction obtained was kept in muffle furnace in air tight crucible at 400^{o}C for obtaining activated carbon. The characterizations of developed adsorbent were done through XRD, Fourier transform infrared spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM) with EDS etc. techniques. The Brunaurer-Emmet-Teller (BET) method was used to measure the surface area of adsorbent.

The batch adsorption studies were carried out in 100 ml conical flasks using 50 ml of dye solution of desired concentration and adding desired adsorbent dosage (0.05- 0.2 g). The parameters like pH and temperature were adjusted. The batch was kept for 2 h on the magnetic stirrer at 180 rpm. After that the dye solution was filtered using whatman filter paper. The dye concentration in filtrate after adsorption was measured using UV-visible spectrometer (Simadzu UV-1800). Further, per cent removal was calculated and adsorptive capacity was reported using equation 1 and 2.

$$\% \text{ Removal} = \frac{Co - Ce}{Co} * 100 \quad (1)$$

The amount of dye adsorbed at equilibrium condition was calculated as follows,

$$q_e = \frac{Co - Ce}{m} * v \quad (2)$$

The batch studies data were fitted to Langmuir, Freundlich, and Temkin isotherm models [11-12]. The linearized form of Langmuir, Freundlich, and Temkin isotherm models can be represented by Eq. 3-5 respectively.

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (3)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (4)$$

K_f $(mg^{1-1/n} L^{\frac{1}{n}}/g)$ is the capacity of the adsorbent and n is the intensity of adsorption constant for Freundlich. The kinetics of the dye adsorption by developed adsorbent was analyzed by monitoring the extent of adsorption as a function of time. These data were then analyzed for pseudo first order [13] pseudo second order [14] using Eq. 6 and 7 respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (7)$$

3. Results And Discussions

3.1. Surface morphology of synthesized adsorbent

The surface morphology of adsorbent shown in fig. 1 was found to exhibit a heterogeneous porous surface having average pore diameter of 0.9435 µm. The Energy dispersive analysis shows that synthesized AC have C, O, Ca, K, and Mg elements.

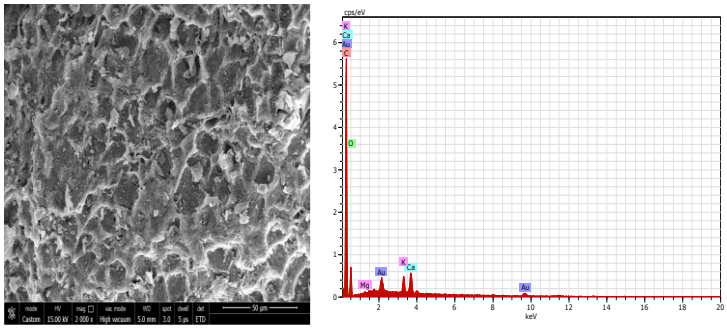

Fig. 1 SEM with EDS structure morphology

The Fourier transform infrared spectroscopy of walnut shell activated carbon before and after dye adsorption has been shown in fig-2. The bands of 3500 in FTIR correspond to stretching vibrations of O-H typically ranging from alcohol, amide, amine and carboxylic groups were observed. Also, the stretching vibrations was observed at 1700 cm^{-1} and 1200 cm^{-1} clearly indicating carboxylic groups and C-O stretch bands respectively as shown in figure 2. The shrinking of peak around 3419 cm^{-1} in AC after adsorption, and generation of new peak at 3000 cm^{-1} indication dye adsorption.

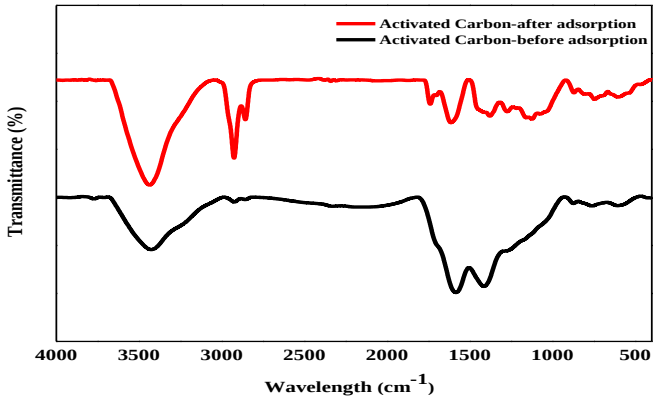

Fig. 2 FTIR spectrum of AC before (a) and after (b) adsorption.

The XRD of walnut shell and AC were analyzed. The presence of Cabon was noted with the help of jcpds card. The AC having high C peaks were noticed, as shown in fig. 3.

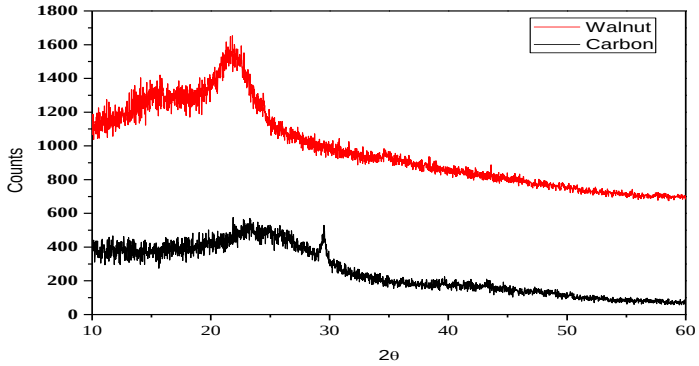

Fig. 3 XRD characterization of walnut shell and activated walnut shell carbon

3.2. Effect of operating parameters on dye removal

Effect of contact time on dye removal

The effect of contact time was noted by performing batch experiments at the initial dye concentration of 10 mg/L at room temperature and dosage being 0.2 g in each batch. As can be seen from fig.4 that there is gradual increase in the removal percentage with increase in contact time from 15 min. to 120 min., but no appreciable increase has been observed between 120 min. to 360 min. This may be due to the fact that active sites present in the adsorbent got saturated and there were less sites left vacant for further adsorption to take place.

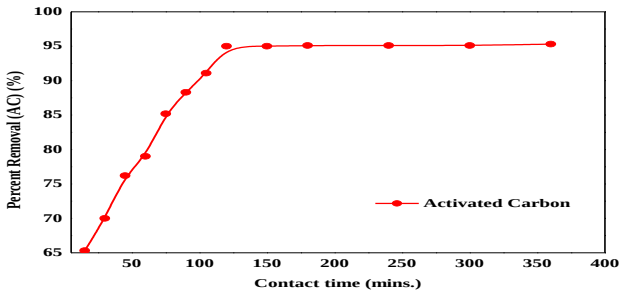

Fig. 4 Effect of contact time with regards to CR dye adsorption for AC

Effect of adsorbent dose on dye removal

The quantity of adsorbent plays important role in dye removal. Thus the experiments were carried out to optimize adsorbent dose by varying the adsorbent dosage from 0.05 g to 0.25 g. The results obtained were shown in fig.5. Increase in dye adsorption with increase in adsorbent dose was observed upto 0.2 g of adsorbent dose. Further increase in adsorbent dose did not improve dye removal. This may be due to the fact that maximum ads sorption has been achieved with respect to initial dye concentration.

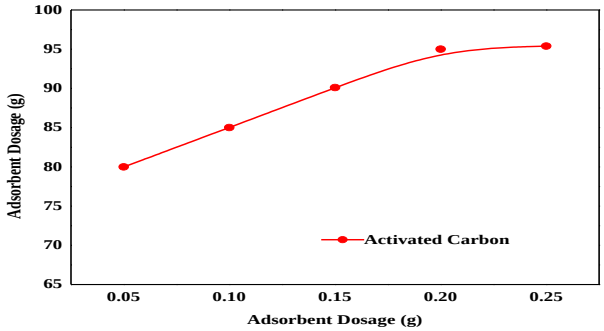

Fig. 4 Effect of adsorbent dosage with regards to CR dye adsorption for AC

Effect of Initial dye concentration on dye removal

The figure 5 shows the behavior of initial dye concentration to the percentage of dye removal. It leads to the outcome that as initial dye concentration increases removal percentage decreases. At 0.2 g of adsorbent dose optimum dye removal of 95% was noted. The adsorption sites on adsorbent was limiting factor for percent removal [15]. Hence, there was decrement in the percent removal for increase in the concentration of CR-dye.

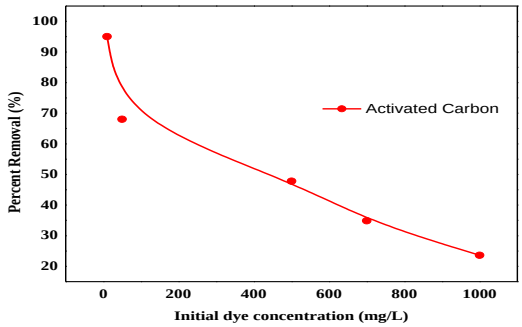

Fig. 5 Effect of initial concentration with regards to CR dye adsorption for AC

Effect of solution pH on dye removal

Adsorption process is greatly influenced by changing the pH of solution. The effect of pH on percent removal of CR dye is shown in fig 6. Increasing the pH from 5 to 7 there was increment in the removal percentage, on further increasing the pH decrement in the percentage removal was observed. The CR-dye being anionic in

nature has better removal capacity around the 7 pH as observed. At pH above 7 the surface of adsorbent became surrounded by OH ions causing repulsive effect on anionic dye adsorption.

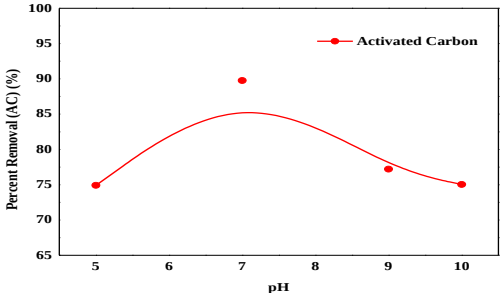

Fig. 6 Effect of pH with regards to CR dye adsorption for AC

3.3. Kinetics of adsorption

The criticality of adsorption was investigated by adsorption kinetics, which is major factor for process characteristics and efficiency of the adsorption mechanism. The two Kinetic models were fitted with experimental values i.e. the pseudo first order and second order kinetics study [16]. The pseudo first order was found to be better fitted in the analysis as shown in fig.8. The Adsorption parameters were recorded and shown in table 1. The best fitted R^2 was 0.9817 for first order kinetics applied for adsorbent-AC.

TABLE I. Adsorption Kinetics

Pseudo First Order		
K_F=0.051	**q_e= 1.22**	**R^2= 0.9817**
Pseudo Second Order		
q_e=558.6	**K_2= 0.0000051**	**R^2= 0.9799**

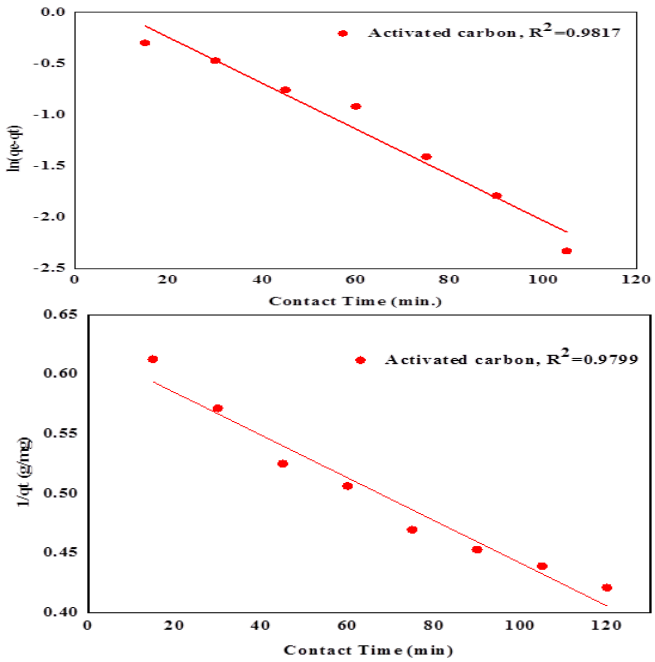

Fig. 8 Kinetic Adsorption study (a) pseudo first order kinetics, and (b) pseudo second order kinetics.

3.4. Adsorption Isotherm models

An adsorption isotherm provides the state of equilibrium in between synthesized adsorbent and adsorbate, which is the correlation of amount of dye adsorbed and the capacity of adsorbent to absorb the dye. The

adsorption isotherm model, Langmuir, Freundlich, and Temkin were tried to fit with experimental results as shown in fig. 9. The Langmuir Isotherm model was found to be best fitted with R^2 = 0.9852 with the best adsorptive capacity of 64.14 mg/g for the synthesized activated carbon noted in the table 2.

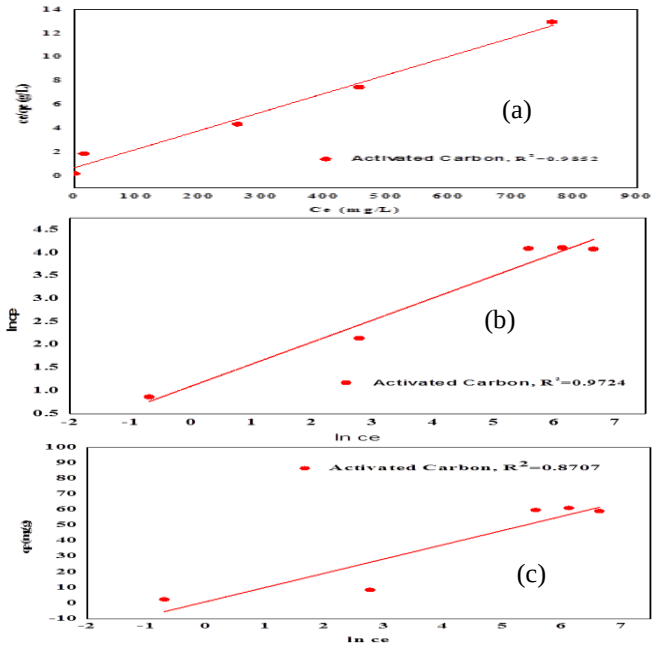

Fig. 9 Adsorption Isotherm Models (a) Langmuir Isotherm, (b) Freundlich Isotherm, and (c) Temkin Isotherm

TABLE II. Isotherm Model

	Langmuir Isotherm Model	**Freundlich Isotherm Model**	**Temkin Isotherm Model**
Muffle Furnace	K_L=0.022 , q_m=64.14 mg/g R^2= 0.9852	K_f=2.99, n=2.08 R^2= 0.9724	a= 0.8611, b=9.133 R^2=0.9331

Conclusion

Activated carbon (AC) was successfully synthesized from carbonization of walnut shell and it exhibited highly effective adsorbent for Congo red dye adsorption, which is mainly attributed to its high surface area of 256.66 m^2/g and confirming the presence of the abundant hydroxyl and carboxyl groups. Equilibrium data fitted well with Langmuir isotherm (maximum monolayer adsorption capability of 64.14 mg/g). The utilization of walnut shell as a precursor of AC not only lowers the cost of AC, but also offers a cost effective and environmental friendly way of recycling waste, reducing the environmental problems related to its disposal.

4. Acknowledgements

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