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Original Research Paper

Adsorption of Congo Red from Aqueous Solution by A Low-cost Novel Adsorbent Derived from the Inflorescence of Palmyra (*Borassus flabellifer* L.) Male Flowers

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ABSTRACT

Batch adsorption method was performed using a low cost acid activated novel adsorbent, inflorescence of palmyra male flowers carbon (IPMFC), for the removal of Congo red (CR) from aqueous solutions at 30±2°C. The effects of agitation time, adsorbent dose, initial dye concentration, pH and temperature were examined. The adsorption capacity was found to be 4.7037 mg/g of the adsorbent for the particle size of 0.15-0.25 mm. Acidic pH was favourable for the adsorption of Congo red. Equilibrium adsorption data were described by both Langmuir and Freundlich models, but Langmuir model was more fitted. Increase in temperature increased the percent removal of CR ions onto IPMFC and it was endothermic in nature.

INTRODUCTION

Industrialization is considered as sine qua non for economic development of a country. Though, development in science and technology have provided human kind with totally new ways of doing things and brought significant ease and comfort in our lives, our life supporting system, the environment is constantly subjected to degradation. The textile industry plays an important role in the economy of many countries like India, but at the same time, the huge quantity of the wastewater released from it is the major source of water pollution since it contains dye residues and a variety of other chemicals. Over 7×10^5 tonnes and more than 1,00,000 different types of dyes are being produced annually across the world (Clark & Anlinker 1980) of which two-third production is used by textile industries. It is estimated that 10-15% of the dyes used is inevitably lost in the effluent (Zollinger 1987, Khraisheh et al. 2003). The presence of even very low concentration of dyes (less than 1 ppm for some dyes) makes water highly coloured and aesthetically undesirable (Nigam et al. 2000). Coloured wastewater containing even 1% of dye is unsuitable for human use. Discharge of such coloured wastewater into waterbodies without proper treatment causes irreparable damage to the surrounding ecosystems. The colour interferes with light penetration and reduces aquatic photosynthetic activities. Several commonly used dyes or their metabolites have toxic effects as carcinogenic, mutagenic, genotoxic and teratogenic on aquatic biota and humans (Culp et al. 1999). Therefore, the coloured wastewater should be decolourised before its release into the pristine water bodies.

Currently, the most widely used efficient method for removing dyes from aqueous solutions is adsorption with activated carbons, based on non-renewable and relatively expensive starting materials such as coal and wood. However, high cost and lack of suitable technology to manufacture good quality activated carbon in developing countries (Amin 2008) has prompted many workers for searching or in the production of activated carbons from solid wastes of industry and agriculture. The advantage of using agricultural by-products and plant biomass is that these raw materials are renewable, inexpensive, and readily and abundantly available. India produces over 400 million tonnes of agricultural wastes annually (Raghuvansi et al. 2004). The exploitation and utilization of these materials must bring obvious economic and social benefit to mankind. This is one of the eco-friendly solutions by transforming negative value wastes to valuable chemicals. Numerous agricultural by-products and residues have been investigated to remove dyes from aqueous solutions. Some of them are cotton waste, rice husk, park, saw dust, palm-fruit bunch, jack fruit peel, sugar industry mud, wood, orange peel, sugarcane dust, peat, jambonut and cassava peel (Ho et al. 2005, Hameed, et al. 2007, Kumar 1991). Identifying new economical, highly effective and easily available adsorbents are still needed.

In the present study, acid activated inflorescence of palmyra male flowers carbon was used as a novel adsorbent. A survey of literature revealed that no work has been done on utilization of this material to prepare carbon as adsorbent. Palmyra is a unisexual and perennial tree, native of Africa. It is the official tree of Tamil Nadu. It belongs to Arecaceae family. It has been estimated that there are 8.6 crores of these trees existing in India which grow in dry areas. It is enduring, versatile, and highly renewable one that people have known and utilized for thousands of years (Kumar et al. 2003). There are innumerable commercial applications of this tree. The male flowers are produced in big clusters of long, white string like inflorescence. The mature inflorescence is black in colour and discarded as waste. Conversion of this material into a valuable chemical will benefit the rural poor, in general, and the farmers in particular. This would also help to protect this important natural species from extinction.

In our laboratory a series of studies are being conducted to evaluate the possibility of using low-cost materials for pollution control. The focus of this research is to evaluate the adsorption potential of inflorescence of palmyra male flowers carbon for Congo red dye as a model dye. Congo red was the first synthetic dye used in textile industry to give wool, cotton and silk red colour with yellow florescence. The dye is known to metabolize to benzidine, a known human carcinogen (Indra Deo Hall et al. 2005). Its molecular formula and molecular weight are $C_{32}H_{22}N_6Na_2O_6S_2$ and 696.7 g/mol respectively. It has maximum absorbance at 500nm wavelength.

MATERIALS AND METHODS

Adsorbent: Mature inflorescences were collected from local area. They were cut into small pieces, washed well with freshwater and distilled water, sun-dried for seven days and then dried in hot air over at 110°C for 6 hrs. The dried material was then mixed well with concentration sulphuric acid and kept overnight. The acid activated carbon was washed with deionised water, soaked with 1% $NaHCO_3$ for 12 hours and then washed with deionised water till the pH reaches 6.9. Finally, it was taken in an iron vessel and heated in muffle furnace. The temperature was raised gradually up to 550°C and kept for half an hour. The carbonized material was ground well and sieved to different particle size. It was labelled as IPMFC, and stored in a plastic container for further studies. In this study particle size of 0.15-0.25 nm was used.

Adsorbate: A stock solution containing Congo red (1000 mg/L) was prepared by dissolving required amount of dye in deionised water, which was later suitably diluted to solutions of four different concentrations (10, 20, 30 and 40mg/L). Solution pH was adjusted by adding either 0.1N HCl or 0.1N NaOH as required. The chemicals used were of AR grade.

Adsorption studies: Batch method was followed by agitating 50 mL of four different dye solutions

(10, 20, 30 and 40 mg/L) at their natural pH 6.9 with 100 mg of IPMFC in 150 mL stoppered conical flasks at room temperature (30±2°C) in a temperature controlled water bath shaker at 140 rpm. The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifuging at 10,000 rpm for 10 min. The absorbance of supernatant solution was measured using UV-VIS spectrophotometer (Cyber Lab, 100) at wave length 500 nm. The amount of CR adsorbed was calculated from the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad ...(1)$$

Where, q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g); C_o the initial concentration of CR (mg/L); C_e the concentration of CR in solution at equilibrium time (mg/L); V the volume of working solution (L); W is the adsorbent dosage (g). Blanks, with only the adsorbate in 50 mL of distilled water were conducted simultaneously at similar conditions to account for adsorption by glass containers. It was found that no adsorption of CR by container walls occurred. The experimental parameters studied were adsorbent dosage, contact time, initial dye concentration, pH and temperature. Langmuir and Freundlich isotherms were employed to study the adsorption capacity of the adsorbent.

RESULTS AND DISCUSSION

Effects of agitation time and concentration of dye on adsorption: Effects of agitation time and dye concentration (10, 20, 30, 40 mg/L) on removal of CR by IPMFC are presented in Fig. 1. The percent removal of Congo red increased with increase in agitation time and reached equilibrium at 150 min. The percent dye removal at equilibrium decreased from 69.7 to 49.9 as the dye concentration was increased from 10 to 40 mg/L. It is clear that the removal of dyes depends on the concentration of the dye. The removal curves are single, smooth and continuous leading to saturation.

Effect of adsorbent dose: The removal of Congo red by IPMFC at different adsorbent doses (100mg to 600mg/50mL) for the dye concentrations 10, 20, 30 and 40 mg/L is given in Fig. 2. Increase in adsorbent dose increased the percent removal of dye, which is due to the increase in adsorbent surface area of the adsorbent.

Effect of pH: Effect of pH on the removal of Congo red is shown in Fig. 3. For 40 mg/L dye concentration the percent removal decreased from 86.50 to 55.65 when the pH was increased from 2 to 9 and the percent removal remained almost the same up to pH 12. At pH 2.0 a significantly high electrostatic attraction exists between the positively changed surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively changed sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of Congo red anions due to the electrostatic repulsion. Also, lower adsorption of Congo red at alkaline pH is due to the presence of excess OH^- ions competing with the dye aninos for the adsorption sites.

Effect of temperature: The effect of temperature of adsorption of Congo red (Fig. 4) for concentration 40 mg/L adsorbent was carried out at 35, 40, 50 and 60°C. The percent removal of dye was from 27.8 to 61.9 at equilibrium time. This indicates that increase in adsorption with increase in temperature may be due to increase in the mobility of the large dye ions. Moreover, increasing temperature may produce a swelling effect within the internal structure of the adsorbent, penetrating the large dye molecule further.

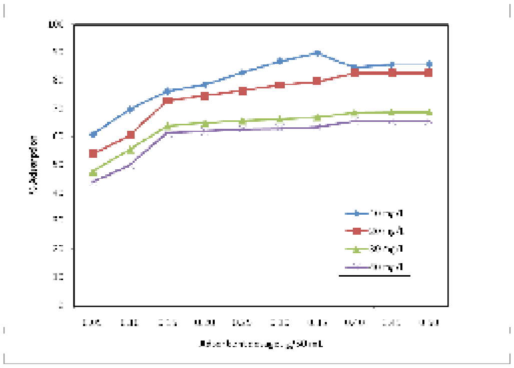

Fig. 1: Effect of agitation time and concentration of Congo red on removal.

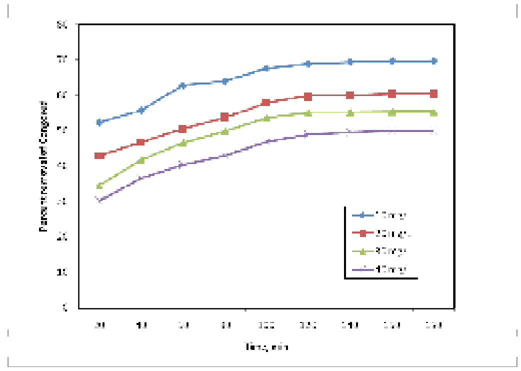

Fig 2: Effect of adsorbent dosage on removal of Congo red by IPMFC.

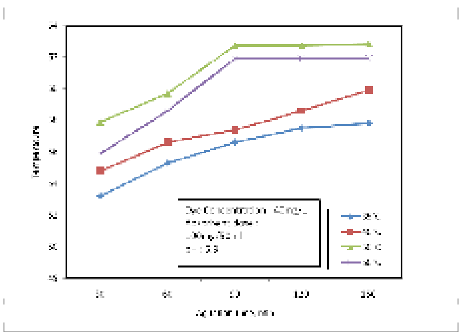

Fig. 3: Effect of pH on removal of Congo red by IPMFC.

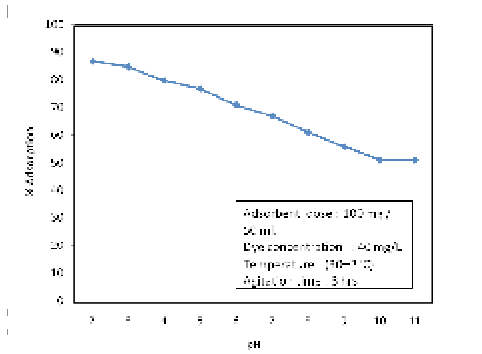

Fig. 4: Effect of temperature on removal of Congo red by IPMFC.

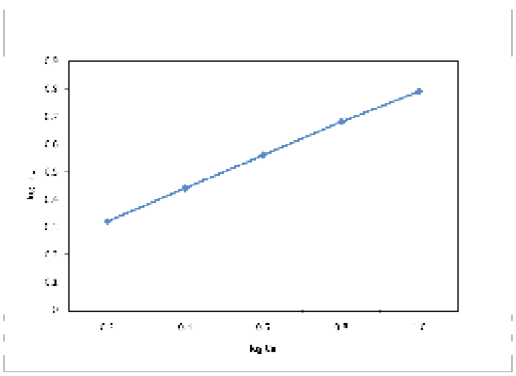

Fig. 5: Langmuir adsorption isotherm.

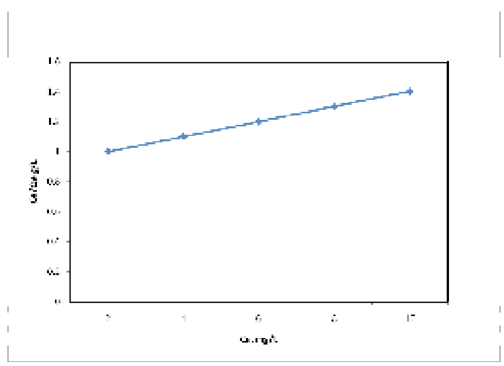

Fig. 6: Freundlich adsorption isotherm.

Adsorption isotherms: Langmuir isotherm is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{Qob} + \frac{C_e}{Q_o} \qquad ...(2)$$

Where, C_e is the concentration of dye solution (mg/L) at equilibrium. The constant Q_0 signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The linear plot of C_e/q_e vs C_e shows that adsorption follows a Langmuir isotherm (Fig. 5). Values of Q_0 and b were calculated from the slope and intercept of the linear plots are presented in Table 1. From the correlation coefficient it is obvious that Langmuir isotherm describes the adsorption of CR on IPMFC very well. This means there is monolayer coverage of the dye on the surface of IPMFC.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L defined by:

$$R_L = \frac{1}{1 + b\,C_0} \qquad ...(3)$$

Where, b is the Langmuir constant and C_0 is the initial dye concentration (mg/L). R_L value between 0 and 1 indicates favourable adsorption. The R_L values were found to be 0 and 1 for dye concentrations of 10, 20, 30 and 40 mg/L (Table 1).

The Freundlich isotherm was also applied for the adsorption of the dye.

$$\mathrm{Log}_{10}(q_e) = \left(\frac{1}{n}\right)\mathrm{Log}_{10} C_e + \log_{10} k_f \qquad ...(4)$$

Where, q_e is the amount of dye adsorbed (mg) at equilibrium, C_e is the equilibrium dye concentration in solution (mg/L) and k_f and n are constants incorporating all factors affecting the adsorption process, adsorption capacity and intensity of adsorption. Linear plot of $\log_{10}q_e$ vs $\log_{10}C_e$ shows that the adsorption also follows Freundlich isotherm (Fig. 6). In general, higher the k_f value, greater will be the adsorption capacity. Values of k_f and n were calculated from the intercept and slope of the plots and are presented in Table 1. The correlation co-efficients show that surface heterogeneity of IPMFC exists and it is due to presence of widely different sized pores in the adsorbent used.

CONCLUSION

The present study shows that carbon from inflorescence of palmyra male flowers is an effective adsorbent for the removal of Congo red from aqueous solution. Adsorption followed both the Langmuir and Freundlich isotherms. The adsorption capacity was found to be 4.7037 mg/g.

Table 1: Langmuir and Freundlich constants for adsorption of CR onto IPMFC.

Initial dye concentration mg/L	Langmuir				Freundlich		
	Q_0(mg/g)	b(L/g)	R^2	R_L	K_f (mg/g/(L/g))	1/n	R^2
10	4.7037	0.2501	0.9888	0.28.56	1.5136	0.6249	0.9878
20				0.1666			
30				0.1176			
40				0.0909			

Complete removal of the dye can be achieved using an appropriate dosage of the adsorbent and pH for wastewaters. The results would be useful for the fabrication and designing of wastewater treatment plants for removal of the dye. Since the raw material is freely available in large quantities the treatment method seems to be economical.

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