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APPLICATION OF BIO-WASTE MATERIAL FOR PREPARATION OF ACTIVATED CARBON FOR REMOVAL OF DYE FROM AQUEOUS SOLUTIONS

Y.C. Sharma[1] and Uma[2]

Abstract: *Textile industries have an important role in the society and they consume large amount of dyes. In addition to textile, other industries consuming dyes are pulp and paper, paint, cosmetics, and food. Discharge of untreated effluents of these industries to water sources results in water pollution at large scale. Control of water pollution by conventional technology requires high capital investments and thus, there is an urgent need for waste water treatment technology at low cost with high efficiency. The usual treatment technologies such as precipitation coagulation, flocculation, and adsorption are available but adsorption is an efficient method for water treatment due to its simplicity and low cost maintenance. Present work has been devoted to prepare a low cost adsorbent and its subsequent application for the removal of a basic dye, malachite green (MG) from aqueous solutions. The aim of this work is to investigate adsorption characteristics of coconut coir activated carbon (CCAC) for the removal of malachite green (MG). The effect of contact time, adsorbent dosage and temperature on the removal of MG were investigated. The results reflected that the increase in the adsorbent dosage from 3g/l to 7g/l significantly increased the adsorption from 92.91 to 98.38 % of malachite green. The removal of MG was fast, and it acquired equilibrium in 40 min. The Langmuir and Freundlich adsorption models were used for mathematical description of the adsorption equilibrium and it was found that experimental data fitted very well to both Langmuir and Freundlich models. The maximum adsorption capacity of CCAC for malachite green is 27.44 mg/g at 303 K.*

Keywords: *format; conference; headings; details.*

INTRODUCTION

Industries like, textile, pulp and paper, leather, and paint manufacture produce large amount of coloured effluents. The colours are generally non-biodegradable and pose serious environmental problems(Banat et al., 1996; Ciardelli et al., 2000; Namasivayam, et al.,1996). There are many treatment technologies like precipitation, coagulation, flocculation and adsorption which are are used for the treatment of coloured effluents (Sivaraj et al., 2001; Özacar,2005; Ho and

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Mckay,2001). Among all these treatment technologies adsorption has been found to be an adequate method for the removal of dyes from coloured aqueous solutions(Özacar and engil, 2005; Namasivayam and engil,2005).
Activated carbon has been promising adsorbent for treatment of wastewaters and coloured effluents but its high cost limits its large scale application in developing countries like India. To reduce the cost of treatment, a number of non conventional materials viz. orange peel, coir pith, banana pith, sawdust, maize cob, rice husk , and bagasse pith (Namasivayam et al., 2001; Namasivayam and Kadirvelu, 1994; Namasivayam and Kanchana, 1992;McKay et al., 1996) have been used for removal of colour from industrial effluents.
Present work addresses the preparation of activated carbon from coconut coir, a biowaste material. The coconut coir activated carbon (CCAC) has been prepared under optimized conditions and subsequently used for the removal of MG, a cationic dye from aqueous solutions. Effect of important parameters namely contact time and initial concentration, adsorbent dose and effect of temperature on the removal has been studied. Kinetic studies and equilibrium modeling have also been carried out.

ADSORBATE

The stock solution of MG was prepared by dissolving its accurately weighed amount (1 g/l) in distilled water (100 mL) and subsequently diluted to required concentrations. The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42,000, chemical formula = $C_{52}H_{54}N_4O_{12}$, MW = 927.00, λ_{max} = 618 nm was supplied by Merck.

Adsorbent

Preparation of activated carbon

The coconut coir used in the present investigations was procured from durga mandir, Varanasi. It was chopped into small pieces, washed and dried in hot air oven at 110 ^oC. Afterwards, carbonization of the washed and dried material was carried out at 700 ^oC for 1 h in an indigenous experimental set up. A constant nitrogen (99.99%) flow of 150 ml/min was maintained throughout the process of carbonization. Primary carbon was obtained on carbonization which was then activated at 700 ^oC for 2 h under optimized conditions. The activated carbon was then cooled to room temperature in inert atmosphere of nitrogen and washed with hot deionized water and 0.5 N hydrochloric acid until pH of the sample reached 7.0. The carbon was then dried in hot air oven at 110^{0}C, ground and sieved to obtained desired particle size(150 µm) and stored in desiccators for further use.

Physicochemical analysis of the adsorbent

The surface area of the adsorbent was determined by Nitrogen adsorption isotherm method using a Micromeritics ASAP 2020 surface area analyzer by Brunauer Emmett Teller (BET) method (Barret et al.,1951) and Pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method. Mercury porositometer was used to determine porosity of the adsorbent. X-ray diffraction of the adsorbent was obtained using a Scifert and Co. Model ID- 3000, Germany. Infrared spectra of the adsorbent were recorded using an infrared spectrometer (Simadzu/8400S), in the range from 4000 to 200 cm^{-1}. Physical characteristics of coconut coir activated carbon have been given in table 1.

METHODS

In the present investigations, the batch mode experiments were carried out to measure the progress of adsorption. It was carried out by shaking 0.25 g of the coconut coir activated carbon with 50 ml aqueous solution of malachite green of different concentrations (60, 80 and 100 mg l^{-1}) at different temperatures (303, 313,323 K) and different pHs (4.0, 6.0, and 8.0) in 100 ml reagent bottles shaking at a constant speed of 150 rpm in a thermostat water bath. The pH of dye solution was adjusted by adding HCl or NaOH.

Table 1. Physical characteristics of coconut coir activated carbon

BET surface area (m^2/g)	205.27
Total pore volume, V_p (cm^3/g)	0.025
Mean pore diameter, D (Å)	41.24
pH_{zpc}	5.10
Density(g/cm^3)	2.23
Porosity	0.71

The progress of adsorption was noted at different time intervals till the attainment of equilibrium. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by high-speed centrifugation at 10,000 rpm and the supernatant liquid was analyzed by a UV-visible spectrophotometer (Spectronic 20, Bausch and Lomb, USA) at 618 nm.
The percentage removal of malachite green and uptake at equilibrium on solid phase, q_e (mg/g), was calculated using the following relationship:

$$\text{Percentage dye removal} = 100(C_o - C_e) / C_o \quad (1)$$

Amount of adsorbed dye molecules per g of solid,

$$q_e = (C_o - C_e)V/ w \quad (2)$$

where, C_o(mg/l) is the initial concentration of malachite green, C_e(mg/l) is the equilibrium concentration of dye in the soluion, V is the volume of solution (l) and w(g) is the mass of the rice husk activated carbon . In order to find out rate of the process of removal of MG by adsorption on CCAC, the data obtained were fitted to pseudo first order kinetic equation.

RESULTS AND DISCUSSION

Effect of contact time and initial concentration

A series of experiments was performed at different initial dye concentrations, viz., 60, 80 and 100 mg l^{-1} and time intervals and at a temperature of 303 K. The percentage removal of malachite green was found to be 96.60, 95.75, and 94.70% at the above initial concentrations of the dye, respectively. The extent of adsorption increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium. Equilibrium time for the adsorption of malachite green on CCAC at various initial concentrations malachite green was found to be 40 min, which showed that equilibrium time was independent of initial dye concentration (MacKay and Ho, 1999).

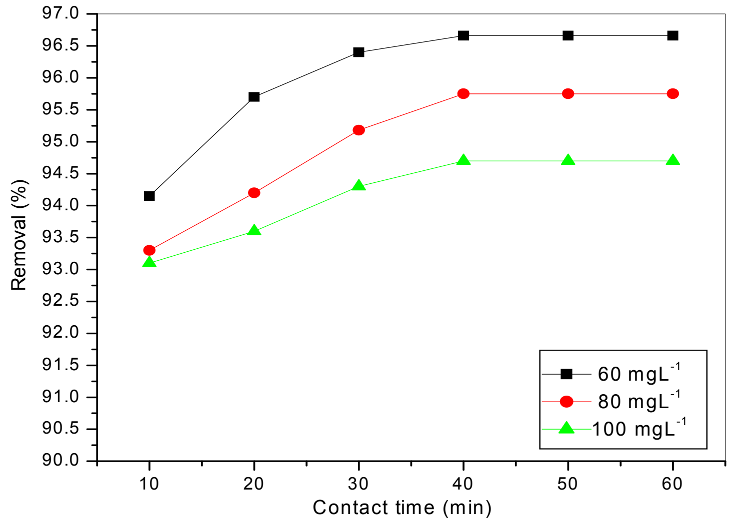

Figure 1. Effect of initial concentration on removal of malachite green by CCAC

Effect of adsorbent dose

The effect of different doses of CCAC on the removal of MG was also carried out. The amount of adsorbent dose was varied from 3.0-7.0 g/L in 50 ml dye solution while all the variables such as pH, rpm, contact time, and temperature were kept constant. The removal increased from 86.75 to 99.83 % by increasing adsorbent dose. As expected, higher removal of dye was obtained at increased adsorbent dose (Figure 2). The higher removal at increased dose may be attributed to larger availability of active sites (Kumar et al., 2005).

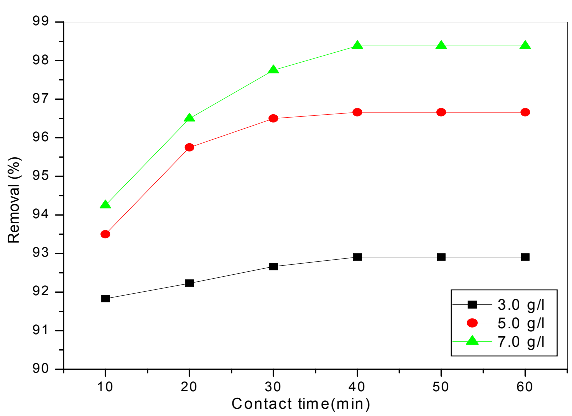

Figure 2. Effect of adsorbent dose on percent removal of malachite green on CCAC

Effect of temperature

Temperature is an important parameter for adsorption processes. It showed significant influence on the adsorption of malachite green on CCAC also. The effect of temperature was investigated in the temperature range 303 to 323 K. The experimental results show that the removal of MG increased from 94.92 to 96.50 % by increasing the temperature from 303 to 323 K (Figure 3).

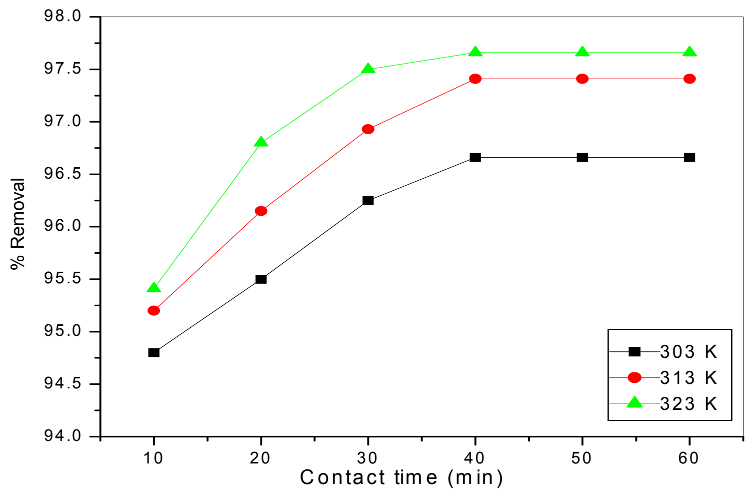

Figure 3. Effect of temperature on percent removal of malachite green on CCAC

Most of the adsorption processes are governed by exothermic processes, but the present system lies in few examples of endothermic adsorption (Malik, 2003).

KINETIC STUDIES

The kinetics of the adsorption of MG on CCAC was studied with respect to different initial concentrations. For evaluating the adsorption kinetics of MG, the pseudo-first-order kinetic model, popularly known as Lagergren's model has been used for the present system and was found suitable the experimental data:

$$\log (q_e - q) = \log q_e - (K_{ad}/2.303)t \qquad (3)$$

where q_e and q (both in mg/g) are the amounts of malachite green adsorbed at equilibrium and at any time respectively, and K_{ad} (min^{-1}) is the rate constant of adsorption.

The straight line plots of 'log (q_e- q) vs t'(Figure not given) confirm that the process of removal is governed by first-order kinetics. The values of rate constant of adsorption were determined by slopes of the above figure and the value of K_{ad} at 3303 K were found to be 3.88 x10^{-2}. The pseudo-first-order shows straight lines for most initial concentrations indicating suitability of this model.

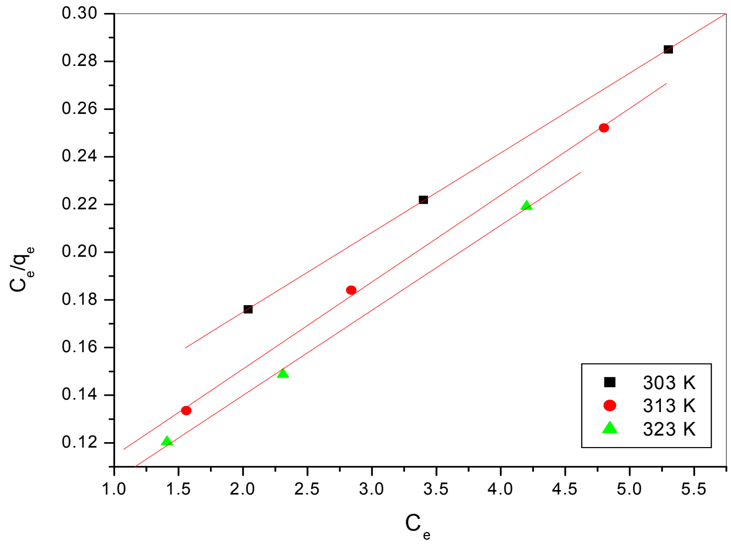

Figure 4. Langmuir plot for the removal of malachite green by adsorption on CCAC

EQUILIBRIUM MODELING

Equilibrium modeling of the removal of MG by adsorption on CCAC was carried out by Langmuir and Frendulich isotherm equations. These provide basic requirements for the design of adsorption systems. Selection of an isotherm equation depends on the nature and type of the system. The adsorption capacity of activated carbon prepared from coconut coir was determined by fitting the experimental data in the proposed equations.

Langmuir isotherm

The Langmuir model assumes that uptake of malachite green occurs on a homogeneous surface by monolayer adsorption. The Langmuir equation is expressed by the following expression (Weber and Chakkravorti,1974) :

$$C_e/q_e = 1/Q^o b + C_e/Q^o \quad (4)$$

where C_e (mg/l) is the equilibrium concentration of the solute (mg/l), q_e is amount adsorbed at equilibrium (mg/g), and Q^o (mg/g) and b (l/mg) are constants related to the adsorption capacity and energy of adsorption, respectively.

A plot of C_e/q_e versus C_e (Figure 4) gives a straight line. The values of Q^0 and b were determined by the slopes and intercepts of Figure 4 and are given in table 2.

Freundlich isotherm

Adsorption data for the dye on activated carbon of coconut coir was fitted to the linear form of Freundlich isotherm equation(Freundlich, 1885):

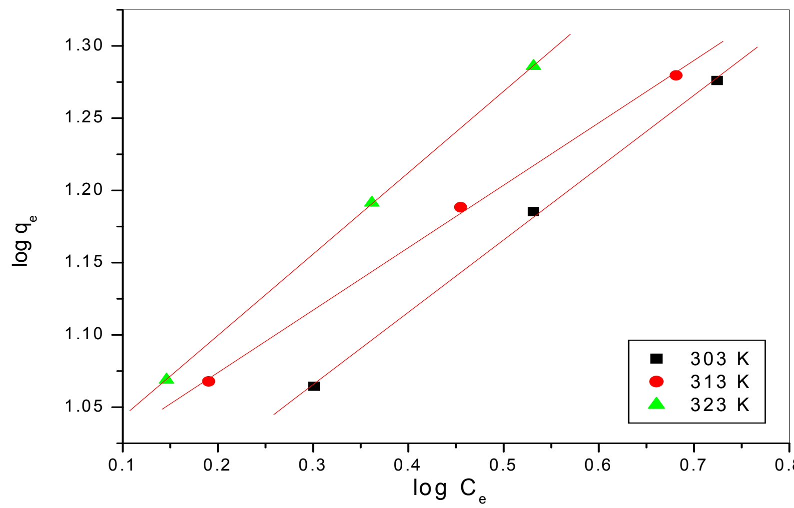

Figure 5.Freundlich adsorption isotherm for the removal of malachite green on CCAC

$$\log x/m = \log K_f + 1/n \log C_s \quad (5)$$

where x/m is the amount adsorbed per unit mass of the adsorbate, C_s the equilibrium concentration, and 1/n and K_f are Frendulich constants. The constant K_f is related to the degree of adsorption, 'n' provides the tentative estimation of the intensity of the adsorption.

The values of these parameters were determined from the straight line plots of 'log x/m vs C_s'(Figure 5). K_f and n, were calculated from the slopes and intercepts of the straight line plots and are given in Table 2. It may be noted that the value of K_f and n increase with an increase in temperature for all the dyes on activated carbon indicating that adsorption is favourable at higher temperature.

THERMODYNAMIC STUDY

Experiments were conducted at three different temperatures 303, 313 and 323 K. The thermodynamic parameters namely, change in standard enthalpy (ΔH^o), standard entropy (ΔS^o), and standard free energy (ΔG^o), for the present process were determined(Sharma et al.,2009).

$$K_c = C_{ae} / C_e \quad (6)$$

$$\Delta G^o = - RT \ln K \quad (7)$$

$$\Delta H^o = R (T_2T_1/T_2\text{-}T_1). \ln(K_2/K_1) \quad (8)$$

$$\Delta S^o = (\Delta H^o\text{-} \Delta G^o)/T \quad (9)$$

where R (1.987Kcal/mol) is the universal gas constant, and T (K) is the absolute temperature. C_e is the equilibrium concentration of malachite green in the solution (mg/l) and C_{ae}(mg/l) is the amount adsorbed on adsorbent at equilibrium. The values of K_c increased by increasing the temperature, which indicates the endothermic nature of the process of removal. K, K_1 and K_2 are equilibrium constants at temperatures T, T_1 and T_2 respectively.

Table 2. Values of Langmuir and Freundlich isotherms parameters for the adsorption of malachite green on CCAC

Isotherms	Temperature(K)	Parameters		
Langmuir		Q^o (mg/g)	b(l/mg)	R^2
	303	27.44	0.30	0.9928
	313	28.01	0.46	0.9918
	323	29.92	0.52	0.9420
Freundlich		K_f(l/g)	1/n (l/g)	
	303	0.915	0.432	0.9945
	313	0.986	0.500	0.9937
	323	0.987	0.563	0.9934

Table 3. Thermodynamic parameters for removal of malachite green on CCAC

Temperature (K)	ΔG^o (kcal mol^{-1})	ΔH^o (kcal mol^{-1})	ΔS^o (kcal$mol^{-1}K^1$)
303	-1.05	4.94	19.76
313	-1.25	1.9	10.06
323	-1.36		

CONCLUSION

On the basis of above observations the following can be concluded:
CCAC has been found to be a very effective adsorbent for the removal of malachite green from its aqueous solutions. Removal of MG was dependent on the physicochemical characteristics of the adsorbent. Kinetic and isotherms studies were carried out. The maximum removal of MG was found to be 96.60 %, at initial concentration of 60 mg l^{-1}, and 303 K. The best correlation coefficients were obtained using the pseudo-first-order kinetic model, indicating that the malachite green removal process followed the pseudo-first-order rate expression. Removal of malachite green was found to be higher in low concentration ranges, and this finding has an industrial applications.

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