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Fast Removal of Malachite Green by Adsorption on Rice Husk Activated Carbon

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Abstract: Application of activated carbon developed from rice husk, an agricultural waste product has been investigated for the removal of malachite green from aqueous solutions and wastewaters. Batch adsorption experiments were carried out for the removal of malachite green from aqueous solutions onto rice husk activated carbon. Effect of important parameters namely initial concentration of dye and contact time, and temperature was studied on removal of the dye. The removal increased from 93.75 to 94.91% by decreasing the initial concentration from 100 to 60 mg/l. Equilibrium data were fitted to Freundlich and Langmuir isotherm equations and the isotherm constants were determined. The monolayer adsorption capacity of rice husk activated carbon for adsorption of the dye was found to be 63.85 mg/g at room temperature.

Keywords: Activated carbon, adsorption, aqueous solution, malachite green.

1. INTRODUCTION

Dyes and colours are frequently usd in industries and textile and pulp and paper industries are reported to utilize large quantities of a number of dyes. According to an estimate more than 1,00,000 commercially available dyes with over $7X10^5$ tonnes of dyestuff are produced and used annually. The discharge of effluents from these applications is one of the potential sources of their contamination and pollution [1-3]. These industrial discharges are highly colored with high Biochemical Oxygen Demand(BOD) as well as Chemical Oxygen Demand(COD) [4]. Malachite green(MG) is a popular dye and is used extensively. It also finds applications in medical sciences. MG is highly toxic to flora and fauna. It induces risk of cancer, acts as a liver tumor-enhancing agent and many other diseases. The dyes check the biological activity in aquatic lives. They also poses in human. It has mutagenic and carcinogenic characteristics [5,6]. It can cause severe effects on nervous system, reproductive system, liver, brain and kidney. Precipitation, coagulation, flocculation, ion exchange, biosorption, and adsorption are the conventional methods used for removal of dyes. Activated carbons are widely used as industrial adsorbents for separation, purification of solid and liquid phase, and as recovery processes due to their texture being highly porous and they have large capacity to adsorb pollutants but their large scale application is cost intensive [7,8]. The use of activated carbon for removal of malachite green has also been reported [9]. Commercial activated carbons are expensive and therefore, there is a need to search for effective adsorbents for economical wastewater treatment. Utilizing wastes and bio-wastes of environment as adsorbents for the removal of dyes from wastewater is of interest. Number of materials such as coconut coir, bagasse pith, rice husk, neem tree leaves, and orange peel have been used to prepare carbon from agricultural wastes as low-cost adsorbent materials for the removal of dyes from wastewater [10-14].

In the present studies, rice husk, a non conventional agricultural-waste material, has been indirectly used to prepare activated carbon for the removal of MG from its aqueous solutions.

2. MATERIALS AND METHODS

2.1. Adsorbent

The rice husk used in the present investigation was procured locally. It was washed and dried in hot air oven at 110^oC. Carbonization was carried out in a quartz tube reactor placed in a tubular muffle furnace at 450^oC for 1 hr in an indigenous experimental set up. A constant nitrogen (99.99%) flow of 150ml/min was maintained throughout the process. Activation of primary carbon was carried out at 650 ^oC for 2 hrs under conditions. The carbon was then cooled in inert atmosphere in the presence of nitrogen at room temperature and washed with hot deionized water and 0.5N hydrochloric acid until the pH of sample reached 7.0.The carbon was then again dried in hot air oven at 110 °C, ground and sieved to obtained desired particle size(150 μm) and stored in desiccators for further use.

2.1.1. Adsorbate

All reagents used in the experiments were analytical grade chemicals and were obtained from Merck, Mumbai, India. Stock solutions of the test reagents were made by dissolving the dye in distilled water. 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 (measured value) was supplied by Merck. The chemical structure of malachite green oxalate is shown in Fig. (**1**).

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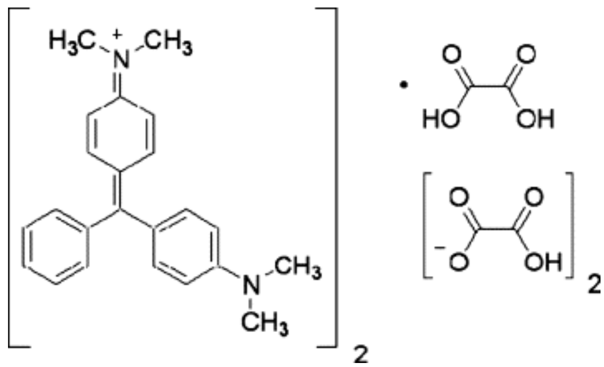

Fig. (1). Chemical structure of malachite green.

2.2. METHODS

2.2.1. Adsorption Studies

Adsorption experiments were carried out by agitating 0.25 g of rice husk activated carbon(RHAC) to 50 ml of dye solution of the desired dye concentrations in 250 ml stoppard conical flasks, at 150 rpm, 30°C in a thermo stated water bath shaker to reach equilibrium. The dye solution was separated from the adsorbent by centrifugation at 10,000 rpm for 10 min. Residual concentration of dye in supernatant was estimated spectrophotometrically by monitoring the absorbance at 618 nm λ_{max} using a UV–vis spectrophotometer (Spectronic 20, Bausch & Lomb, USA). Amount of adsorbed dye molecules per g of solid was determined as follows:

$$q_e = (C_o - C_e)V/ w \qquad (1)$$

where, C_o is the initial concentration of malachite green (mg/l), C_e is the equilibrium concentration of dye (mg/l), V is the volume of the solution (l) and w is the mass of the rice husk activated carbon (g). The kinetic data were fitted to pseudo first order reaction for the removal of malachite green onto rice husk activated carbon.

3. RESULTS AND DISCUSSION

3.1. Effect of Contact Time and Initial Concentration

Effect of contact time and initial concentration for removal of malachite green from aqueous solutions is quite important. The adsorption data for 'uptake of dye vs. contact time at different concentrations' are presented in Fig. (**2**). The removal increased from 93.75 to 94.91 % by decreasing the initial concentration of MG from 100 to 60 mg/l (Fig. **2**).

It is clear from Fig. (**2**) that the graphs are single and smooth, indicating monolayer coverage of the surface adsorbent by MG. Further, the removal is rapid in initial stages, decreases slowly, and acquired a maxima at 40 min., and maximum removal was found to be 94.91% at 60 mg/l malachite green concentration. The removal increased from 93.75 to 94.91% by decreasing the initial concentration from 100 to 60 mg/l at 30°C, 150 rpm, and 150 µm adsorbent particle size.

3.1.1. Kinetic Studies

The kinetic modeling of the removal of dye malachite green by rice husk activated carbon was carried out and data were treated with pseudo first order kinetic model [15].

$$\log (q_e - q) = \log q_e - (K_{ad}/2.303).t \qquad (2)$$

where q and q_e (both in mg/g) are amounts of dye adsorbed at any time and at equilibrium respectively, and K_{ad} (min^{-1}) is the rate constant of adsorption. The straight line plots of 'log (q_e - q) vs t' (Fig. **3**) confirm that the process of removal is governed by first-order kinetics. The linear plots also demonstrate the applicability of pseudo first order nature of the process of removal. The values of K_{ad} were determined by the slopes of the graphs of Fig. (**3**) and the value of K_{ad} was found to be 2.38×10^{-2} min^{-1} at 60 mg/l concentration of malachite green and 30°C.The values of K_{ad} show that rice husk activated carbon is a good adsorbent for removal of MG from aqueous solutions.

3.1.2. Equilibrium Modeling

Equilibrium modeling shows how does the adsorption the process acquire equilibrium state. The Langmuir model assumes that uptake of MG molecules occurs on a homogeneous surface by monolayer adsorption. Selection of an isotherm equation depends on the nature and type of the system. Linear form of langmuir equation is as under [16,17]:

$$(C_e/q_e)=1/Q^o b+C_e/Q^o \qquad (3)$$

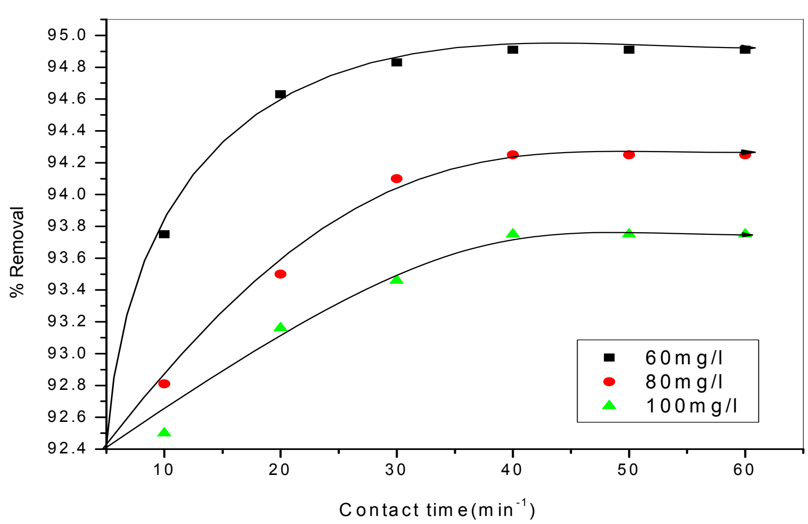

Fig. (2). Effect of initial concentration on percent removal of malachite green on RHAC.

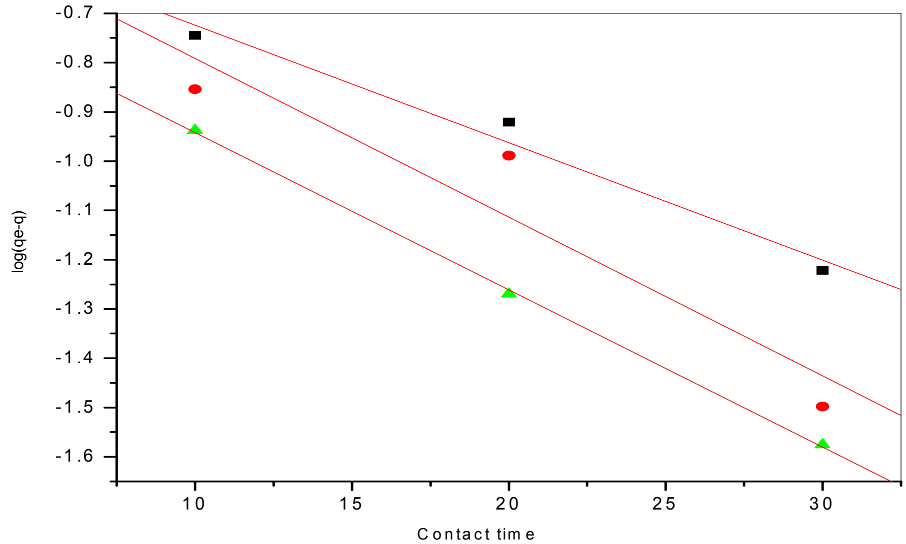

Fig. (3). Lagergren's plot for kinetic modeling of the adsorption process of malachite green on RHAC.

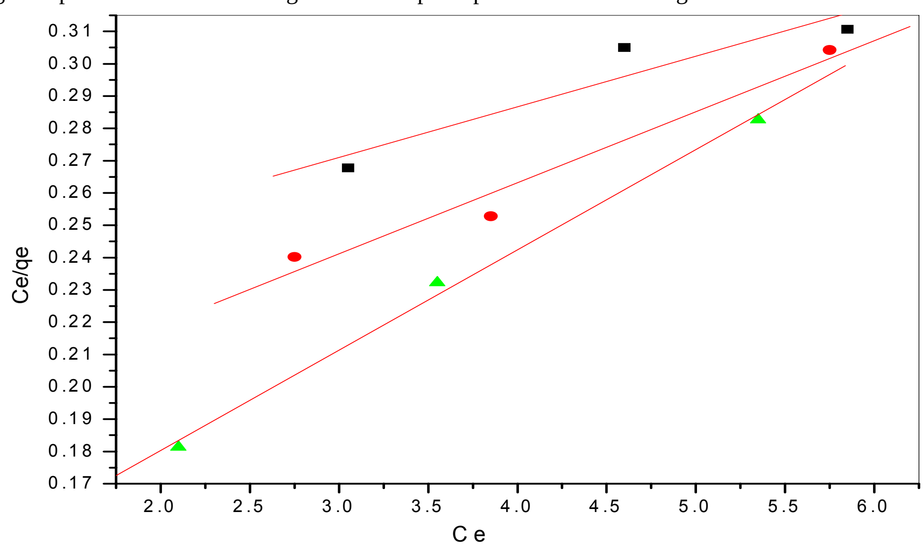

Fig. (4). Langmuir's isotherm plot for the adsorption of malachite green on RHAC.

Table 1. Values of Isotherm Constants at Different Temperature

Isotherms	**Temperature(K)**	**Parameters**	
Langmuir		**Q^o(mg/g)**	**b(l/mg)**
	303 313 323	63.85 45.49 32.21	285.05 259.62 272.43
Freundlich		K_f(L/g)	1/n
	303 313 323	0.76 0.67 0.52	0.68 0.77 0.89

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 vs C_e' (Fig. **4**) gives a straight line. The values of Q^0 and b were determined by the slopes and intercepts of Fig. (**4**) and are given in Table **1**.

For Langmuir isotherm the essential characteristics can be expressed in terms of a dimensionless equilibrium parameter (R_L) [18]:

$$R_L = 1/1+KC_o \tag{4}$$

where K is the Langmuir constant (l/g) and C_o is the initial dye concentration (mg/l).The value of R_L indicates the type

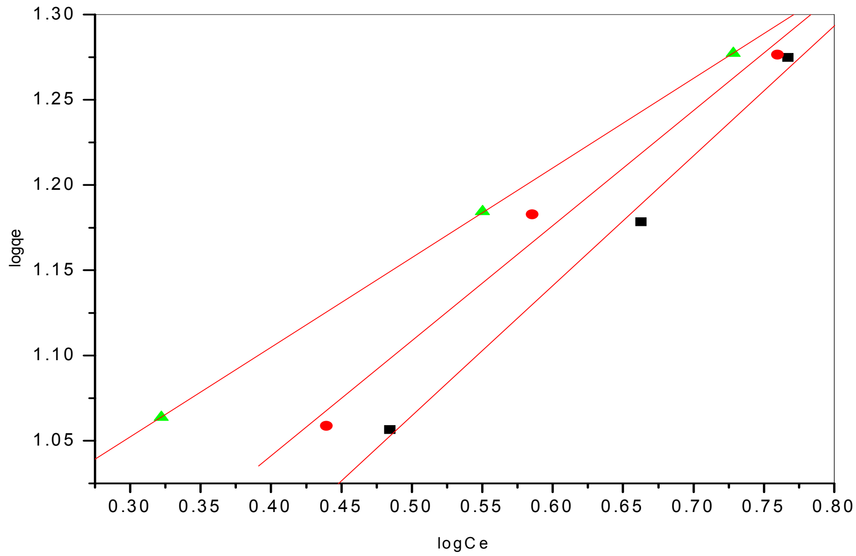

Fig. (5). Plot of freundlich adsorption isotherms of malachite green on RHAC.

Table 2. Comparison of Adsorption Capacities of Different Adsorbents for Dye Removal

Adsorbent	(q_m in mg g^{-1})	Reference
Coconut husk	99.00	[20]
Banana peel	21.0	[21]
Date pits	17.3	[22]
Rice husk	19.83	[23]
Wood sawdust	05.99	[24]
Orange peel	14.30	[21]
Sugarcane dust	04.88	[25]
Activated carbon	40.06	[26]
Rice husk	63.85	This work

of the isotherm to be either unfavourable, linear or favorable. If $R_L > 1$, it follows an unfavorable adsorption, a value 1.0 of R_L indicates a linear, R_L lesser than 1.0 a favourable and a value of R_L equal to zero suggests an irreversible adsorption.

Values of R_L at different temperature show favourable nature of adsorption for malachite green on rice husk activated carbon.

Freundlich isotherm data for the dyes on activated carbon of rice husk was fitted to the linear form of Freundlich isotherm [19]:

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

where x/m is the amount adsorbed per unit mass of the dye species, C_s the equilibrium concentration, and 1/n and K_f are constants. The values of these constants were determined from the straight line plots of 'log x/m vs C_s'(Fig. **5**). K_f and n, were calculated from the slopes and intercepts of the graphs and their values are given in Table **1**.

Table **2** gives a comparative account of the adsorption capacities of various adsorbents. It is clear from the table that adsorption capacity of RHAC used in the present studies is significant viz. 63.85 mgg^{-1}. Except that from the active carbon prepared from coconut husk, the adsorption capacity displayed by activated carbon prepared and used in present studies displays higher capacity of adsorption for MG.

4. CONCLUSION

Removal of MG by RHAC increased from 93.75 to 94.91% by decreasing the initial concentration dye from 100 to 60 mg/l. Time of equilibrium was found to be 40 min. The process of removal follows first order kinetics. Equilibrium studies were performed and the data fitted well in Langmuir and Freundlich adsorption isotherm equations. It can be concluded that the agro-waste rice husk which is available in plenty in India and other countries can be successfully used as an adsorbent also.

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