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Research Article

ISOTHERM STUDIES ONADSORPTION OF MALACHITE GREEN ON POWDERED ACTIVATED *EUPATORIUM ODORATUM* CARBON

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ABSTRACT
We studied the adsorption isotherm characteristics of aqueous Malachite Green dye solution – as model dye solution – by activated carbon prepared from the leaves of *Eupatorium Odoratum*plant. In the optimum pH range of 5 to 6, the adsorption reached equilibrium after 60 minutes. The effect of initial concentration and adsorbent dosage on the adsorption process were studied and reported. Experimental data were analysed by Freundlich, Langmuir and Temkin isotherms.

Keywords: Eupatorium Odoratum, effect of pH, C_i, adsorbent dosage, Adsorption isotherms.

1. INTRODUCTION
Dyes are compounds that can fix themselves onto the surface of various materials including fabrics. They have become one of the main sources of water pollution as a result of rapid development of textile industries. The release of colorant effluent into water bodies has been a major concern on the human health as well as marine lives[1,2].

There are various methods to remove dyes from industrial effluents which include chemical oxidation, froth floatation, coagulation, reverse osmosis, activated sludge, ozonation electro dialysis etc., The high cost and ineffectiveness to remove trace quantity of pollutants causes the conventional methods become unfavourable to be applied at a large scale[4].

Adsorption technique offer the best potential for overall treatment and it could be expected to be promising for a wide range of compounds[3]. It is a reliable alternative due to its simplicity and high efficiency as well as the availability of a wide range of adsorbents for e.g., activated carbon, clay, biomass, polymer, zeolite, nanomaterials etc. In particular, activated carbon offers an attractive option for the efficient removal of various pollutants from waters because of its high surface area and porous structure[11]. The most commonly used adsorbent is commercial coal based activated carbon. But it is limited to use because of its high price and high operation and regeneration cost. This leads to search the new, cheap and easily available and resource of carbon as a feedstock for activated carbon. Many cheap and easily available agricultural wastes and plant based materials have been used as precursors for the preparation of activated carbon to remove dyes and metals from waste waters[5,6].

In this study, the leaves of *Eupatorium Odoratum*, (common name: Christmas bush), which is abundant and cheap plant was used as precursor for the preparation of activated carbon. The plant belongs to Asteraceae family and it is a shrub plant and it grows mostly in every part of Tamilnadu, India.

2. EXPERIMENTAL
2.1. MATERIALS AND METHODS
2.1.1. Preparation of the activated carbon
The adsorption characteristics of the activated carbon depend on the method of activation; Chemical activation involves mixing precursor with dehydrating agents like H_2SO_4 and then activating at 400 - 900^0C. The chemical activation has various advantages including better porous structure, low temperatures and high yields[3].

For the present study, *Eupatorium odoratum* leaves were washed thoroughly bydouble distilled water to remove the dust and other impurities, dried in shade, then in hot air oven at 60^0C, made into fine powder and used as precursor. The activated carbon was prepared by chemical activation method using Conc. H_2SO_4. For this, the dried leaves were impregnated with conc. H_2SO_4 (1:1) for 24 hours, filtered, washed repeatedly with deionized water and then activated by heating at 500^0C for 5 hours. After activation, the carbon was sieved for uniform particle size and used as adsorbent.

2.1.2. Preparation of the dye solution
The dye used for the present study was Malachite Green hydrochloride. It was purchased from Ranbaxy, Mumbai and used as such. The stock solution was prepared by dissolving 1000 mg of dye in 1L of deionized water. Other concentrations (100 ppm to 200 ppm) were prepared from the stock solution by appropriate dilution with double distilled water. The pH of the solutions was adjusted to desired values with 0.1M HCl or 0.1M NaOH[6].

2.2. Batch adsorption studies
Adsorption experiments were done by adding a known amount (100 mg to 200 mg) of activated carbon to 50 mL of dye solution of known concentration (100 ppm to 200 ppm) in a glass stoppered flask. The suspension was shaken in an orbital shaker at 200 rpm speed. The effect of initial pH on dye adsorption was studied in the range 3.0 – 9.0. The studies were done for 60 minutes (time to reach equilibrium stage), the q_t was determined for every 10 minutes. For these experiments, the adsorbent dosage taken was140 mg and dye concentration was 120 ppm. The effects of initial concentrations of dye (100 ppm – 200 ppm) and adsorbent dosage (100mg – 200mg) on dye adsorption were studied at pH 6.0 and at room temperature. The dye concentration in supernatant solution was determined at characteristic wavelength of MG (λ_{max} = 617 nm) by double beam UV–visible spectrophotometer (Systronics, 2202). For adsorption isotherm studies, dye solutions of different concentrations (100 ppm to 200 ppm) were shaken with the known amount of adsorbent (0.14 g) at 303,313, 323 and 333K till the equilibrium was reached. Then the residual MG concentration was determined[8].

3. RESULTS AND DISCUSSION
3.1. Effect of pH
The pH of a solution is a key factor in the adsorption process because it influences functional groups on the adsorbent surface and also determines the solubility of dyes in the aqueous medium[5,7]. The effect of solution pH on the adsorptive removal of MG by EOC is shown in Fig.1. Since the pH of the solution affects the stability of the structure of MG, its colour intensity changes with pH. The effect of pH on the efficiency of decolorization malachite green by activated carbon was carried out at out at different pH ranging between 3 to 9.The amount of MG dye adsorbed increases with increasing pH from 3 – 5, the maximum absorption was noted at pH 5 with 90 % removal of MG dye. The percentage of removal decreases with increasing pH after that.

At lower pH, the amount of adsorbed MG decreased because of the electrostatic repulsion between positively charged dye ions. It may also due to the competition between excess H^+ ions and dye cations for adsorption sites. At higher pH values, the surface of the adsorbent become negatively charged, enhances the affinity for positively charged dye ions. Further increase of pH leads to deprotonation of MG. It also leads to aggregation of MG molecules, unable to enter the porous structures of adsorbent[13].

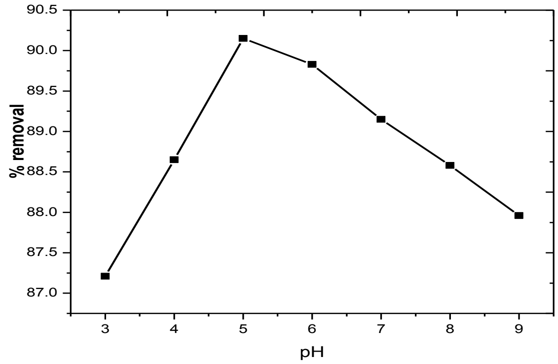

Fig. 1: Effect of pH on adsorption of MG dye

3.2. Effect of initial concentration of dye

The effect of initial concentration on the adsorption of MG dye by EOC was studied and the result is shown in the Fig.2.The study was carried out with the fixed adsorbent dose of 140mg and at pH 5.The initial concentrations were varied from 100 ppm to 200 ppm. It can be observed from the figure that percentage adsorption decreases with increase in initial MG concentration.

The percentage removal of dye is highly dependent on the initial dye concentration due to the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface[4,12]. Generally the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. At low concentrations, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will decrease[12].

In this case, the percentage removal of dye was found to be 95.00, 93.90, 88.45, 83.30, 80.68 and 76.88 with 100, 120, 140, 160, 180 and 200 ppm initial concentrations of dye, respectively.

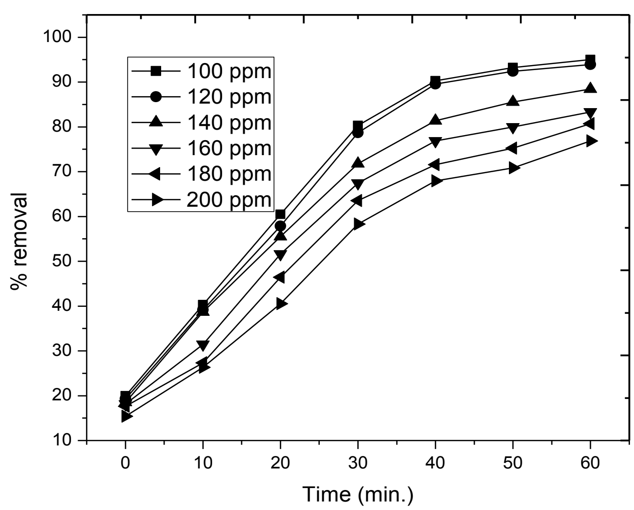

Fig. 2: Effect of initial concentration of dyeon activated carbon (adsorbent dosage: 140 mg)

3.3. Effect of adsorbent dosage

Adsorbent dosage is an important parameter influencing the adsorption process since it determines the adsorption capacity of an adsorbent for a given concentration of the adsorbate at the operating conditions. The effect of EOC dosage on the removal of MG dye was studied in range 100 mg to 200 mg. Fig. 3 show the effect of EOC dosage on adsorption. The percentage removal of dye was 74.07, 79.28, 83.48, 87.12, 92.59, and 96.29 for the adsorbent dosage of 100, 120, 140, 160, 180, and 200 mg respectively. This trend is attributed to an increase in the adsorptive surface area and the availability of more binding sites[7, 13].

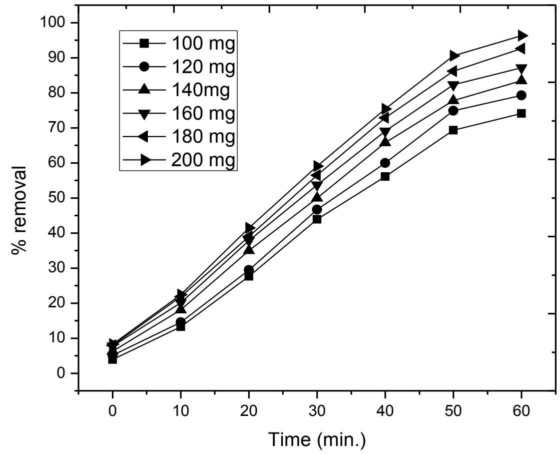

Fig. 3: Effect of adsorbent dosage on adsorption (C_0: 120 ppm)

3.4. Adsorption Isotherms

The equilibrium adsorption isotherms are the important parameters to study the mechanisms of the adsorption systems. Various adsorption isotherm models are available, but in this study the Langmuir, Freundlich isotherm and Temkin equations were used to interpret the experimental data.

3.4.1.Langmuir Adsorption Isotherm

The most widely used isotherm equation for modeling of the adsorption equilibrium data is Langmuir adsorption isotherm. This isotherm consider the adsorption as homogeneous and monolayer. The linear form of the Langmuir adsorption equation is[17]

$$C_e/q_e = 1/q_mK_L + C_e/q_m$$

where qeis the equilibrium dye concentration on the adsorbent (mg/g); C_e is the equilibrium dye concentration in the solution (mg/L); K_L is the Langmuir constant related to the energy of adsorption (L/g), q_m is the monolayer adsorption capacity (mg/g).The values of q_m and K_L were calculated from the slopes ($1/q_m$) and intercepts ($1/K_Lq_m$) of the linear plots of Ce/qe vs. Ce (Fig.4)and are given in the Table. The characteristics of Langmuir isotherm can be expressed by a parameter called equilibrium parameter R_L.

R_L= 1/ 1+ K_L C_0

$C_0$is the initial dye concentration (mg/L). The R_L values shows whether the isotherm is favourable ($0<R_L<1$), linear ($R_L=1$), unfavourable ($R_L>1$)) or irreversible ($R_L=0$).[17]

All the values of R_L for the adsorption of MG on the activated carbon at various temperatures found to be between0 and 1. This shows that the adsorption behaviour of the EOC was favourable for malachite green.

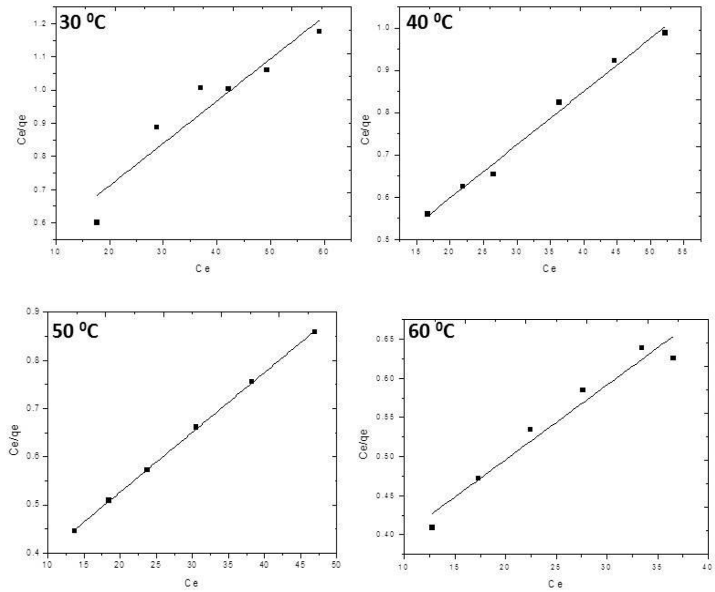

Fig. 4: Langmuir plots for the adsorption of MG dye on EOC at various temperatures

3.4.2.Freundlich Adsorption Isotherm

Freundlich Isotherm is given by

$$q_e = K_F\, C_e^{1/n}$$

K_F and n are the Freundlich constants that relates to relative capacity and adsorption intensity respectively. This is an empirical equation which considers adsorption as heterogeneous. It is based on the assumption of a heterogeneous surface with interactions between adsorbed molecules and a non-uniform distribution of adsorption heat on the surface[12].

The linear form of Freundlich equation is

$$\log q_e = \log K_F + 1/n \log C_e$$

The constants K_F and n can be determined from the slope (1/n) and intercept (log K_F) (Fig.5) and they are shown in the Table. The values of n are greater than 1, shows that the adsorption of malachite green dye on activated carbon was favourable

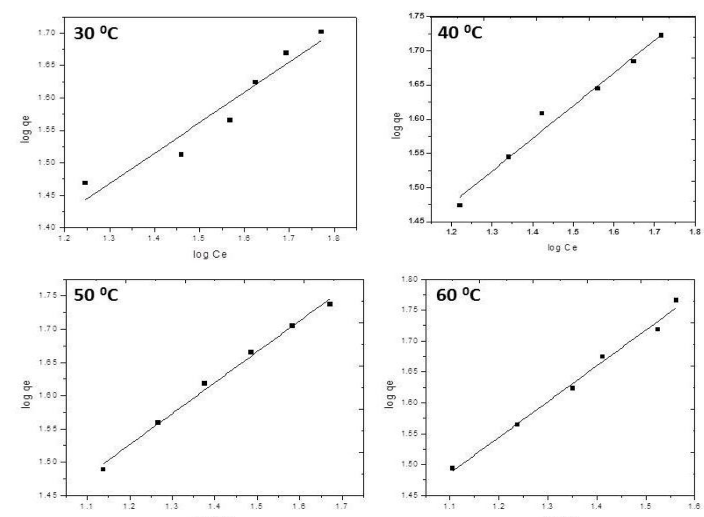

Fig. 5: Freundlich plots for the adsorption of MG dye on EOC at various temperatures

3.4.3.Temkin Adsorption Isotherm

Temkin isotherm is based on the heat of adsorption that arises because of the interactions between adsorbate and adsorbent.

The linear form of the Temkin isotherm is given by

$$q_e = B \ln A + B \ln C_e$$

B = RT/b. A is the equilibrium binding constant; it corresponds to the maximum binding energy. Constant B is related to the heat of adsorption[9].

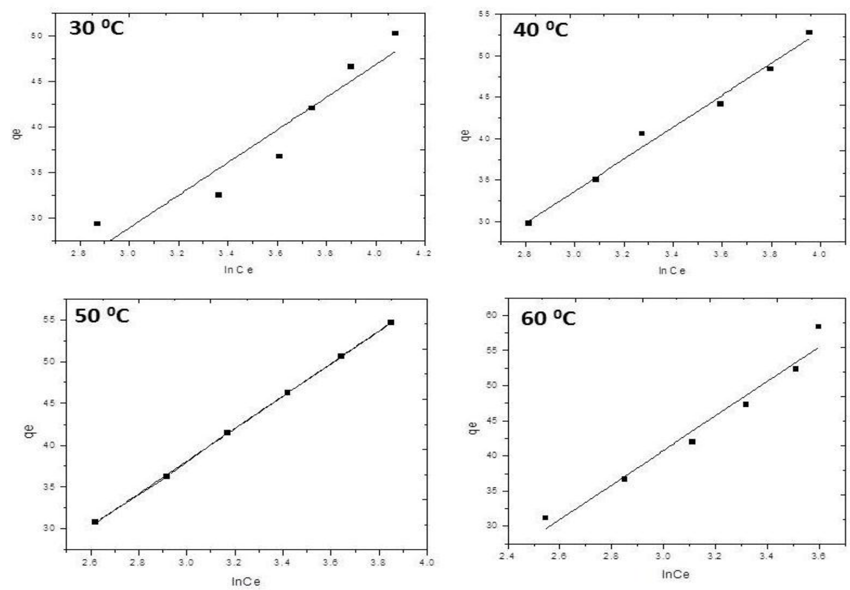

Fig. 6: **Temkin plots for the adsorption of MG dye on EOC at various temperatures**

From the adsorption isotherm results from figures 4 to 6 and from the Table, it was found that Freundlich isotherm equation give the higher values of correlation coefficients (R^2) than those for Langmuir and Temkin. So the empirical Freundlich equation better describes the behaviour of adsorption of MG dye on the surfaces EOC, implying that the adsorption process involved multilayer coverage[11].

Moreover, the values of 1/n are less than one in all cases shows that the adsorption process is favourable. The maximum adsorption capacity calculated from Langmuir isotherm was 104.7120 mg/g., suggest that EOC was an effective adsorbent for MG dye.

Table. Langmuir, Freundlich and Temkin isotherm constants for the adsorption of MG by EOC at different temperatures

T.^{0}C	Langmuir				Freundlich				Temkin		
	q_{max}(mg/g)	K_L	R_L	R^2	K_F	1/n	n	R^2	A(L/mg)	B	R^2
30	78.7402	0.0277	0.2313	0.8813	7.2350	0.4682	2.1359	0.91521	4.0098	17.9648	0.87866
40	79.3021	0.0365	0.1860	0.98737	7.9675	0.4791	2.0872	0.97476	3.5104	19.2991	0.98376
50	80.3859	0.0448	0.1860	0.99966	9.2905	0.4654	2.1486	0.99199	2.8346	19.4572	0.99980
60	104.7120	0.0313	0.2103	0.94434	7.0719	0.5789	1.7274	0.98807	2.8135	24.5534	0.95994

CONCLUSIONS

The present study reveals that the activated carbon prepared from *Eupatorium Odoratum* is an effective adsorbent for the removal of malachite green from aqueous solutions. The adsorption was found to be dependent of pH, initial dye concentration, adsorbent dosage and temperature. The optimum pH range for adsorption is 5 – 6, which is closer to neutral pH. The adsorption increases with increasing temperature. It equilibrium of adsorption process reaches after 60 minutes which is relatively a faster one. The Freundlich isotherm fits better the experimental results which indicate multilayer adsorption. Overall, the leaves of Eupatorium Odoratum can be used as precursor for preparing activated carbon for the effective adsorption of dyes such as Malachite Green from waste water.

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