Adsorptive Removal of Malachite Green from Aqueous Solution Using Low Cost Adsorbent

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Abstract

Adsorption capacity of Malachite Green on low cost adsorbent prepared from Hyptissuaveolens (vilaytitulsi) is studied in the present work. Malachite Green adsorption increases with increase in dye concentration and temperature. The optimum phis 9.0 for dye adsorption. The adsorption data was analysed and it was found that pseudo-second order kinetic is most suited for the present study. The spontaneous nature of adsorption is observed from negative value of ΔG and the endothermic nature from positive value of ΔH.

Keywords: Basic Green 4, Adsorption, Hyptissuaveolens, VilaytiTulsi

Introduction:

Synthetic dyes become a part of modern life due to their application in textile and printing industries. Discharging of untreated waste water containing dyes can seriously damage the environment. One of the significant reasons is that dye, even in low concentration, affects the penetration of sunlight [1]. Different technologies are used to remove dye from waste water such as photo catalysis, bio degradation [2], ozonation [3] membrane filtration [4] etc. among these techniques adsorption is most widely used due to operational ease and cost effectiveness [5]. Activated carbon is effective adsorbent for removal of hazardous material by adsorption but its use is not cost effective and regeneration method is costly [6]. Several low cost adsorbent and bioadsobent such as neem saw dust [7], wood apple [8], sand paper waste [9], ginger waste [10], almond gum [11], coffee husk [12] were reported for removal of malachite green. The bio adsorbent, with higher adsorption efficiency, ease of availability and low cost, is still need of present research. Malachite Green belongs to triphenyl methane class, it is used in leather, paper, textile and rubber industries [13]. Malachite green was report to have serious adverse effect on human and due its complicated structure, it is very difficult to remove it from aqueous solution using biological treatment and chemical coagulation [14]. As a continuation of our work to find the adsorptive capacity of bio adsorbent prepared fromHyptissuaveolens [15, 16] in the present study adsorption capacity of the bio adsorbent was determined for Malachite green. To determine the adsorption efficiency various adsorption parameter such as dye concentration, contact time, pH and temperature was investigated in the present study.

Experimental:

Preparation of Adsorbent

The steams and braches of fully grown plants of Hyptissuaveolens (VilaytiTulsi) were collected and cut into small pieces, washed with distilled water, dried under shed. The adsorbent was prepared as per the procedure mentioned in our earlier publication [15].

Preparation of sorbet

Malachite Green (MG), a cationic dye was purchased from Sigma Aldrich India with molecular formula $C_{23}H_{25}ClN_2$ was used for present study. A stock solution of 1000 mg L-1 was prepared by dissolving accurately weigh dye quantity in double distilled water. Dilution with double distilled was carried out to get desired experimental concentration.

Adsorption Studies

For adsorption studies, 0.1 g bio adsorbent was added to 250 mL stoppered glass bottle containing 50 mL dye solution of desired concentration and pH, the solution was stirred by mechanical shaker. After predetermined time interval small fraction were withdrawn and centrifugation at 2,000 rpm to sepaterate the dye solution from adsorbent. The initial pH was achieved using 0. M NaOH and 0.1 M HCl. The solid phase dye concentration was determined using equation 1.

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

WhereC_o is initial dye concentration and C_t is dye concentration at time t in mg L^{-1}, V is volume of solution in L q_t is adsorption amount at time t, and W is weight of adsorbent in g. The Langmuir and Freundlich isotherm used to determine adsorption capacity of adsorbent. The dye concentration remain unadsorbed was determined by measuring the absorption of supernatant solution at 618 nm using Elico double beam spectrophotometer SL-210. Effect of adsorbent dose was deliberateby varying the dosage (0.05 to 0.3 g). To study the effect of temperature on adsorption, 0.1 g adsorbent was added to 50 mL of dye solution of desired concentration at various temperatures.

Results and Discussion:

Effect of pH

The ionization of dyes and surface of adsorbent was affected by pH of the dye solution [17]. The adsorbent capacity mainly affected by initial pH [31]. 0.1 g adsorbent was shaken for 30 min with 50 mL solution of 50mg L^{-1} dye concentration.The adsorption of Malachite Green increases with increase in pH and reaches a maximum value 19.15 mg g^{-1}at pH 9 further increase in pH does not affect the adsorption.

Effect of Adsorbent dose

At optimum pH varying adsorbent amount (0.05 to 0.3 g) was stirred with 50 mg L^{-1} dye concentration for 30 min. It has been observed that due to increase in adsorption site the % removal of dye increases from 73.84 % to 81.31% but unit adsorption was decreased from 36.9 mg g^{-1} to 6.9 mg g^{-1} as amount of adsorbent was increased from 0.05 g to 0.3 g.

Effect of dye concentration

0.1 g adsorbent was stirred with 50mL dye solution with varying concentration from 50 mg L^{-1} to 125 mg L^{-1}) at optimum pH.From the results as shown in Fig.3, the percentage removal of dye decreases as the initial dye concentration increases, but the unit adsorption increases from 20.05 mg g^{-1} to 54.68 mg g^{-1}.

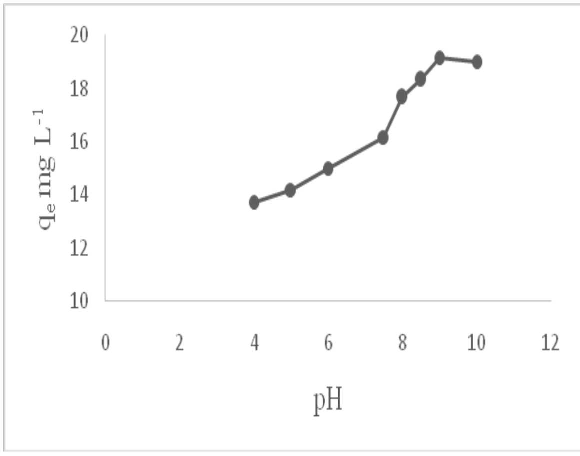

Fig. 1: Effect of pH on dye removal

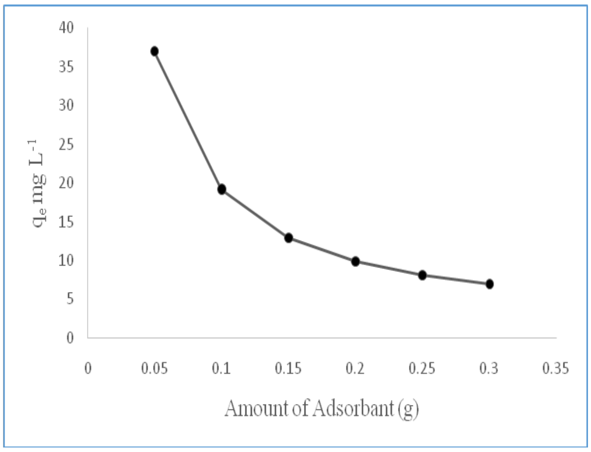

Fig. 2: Effect of Adsorbent dose

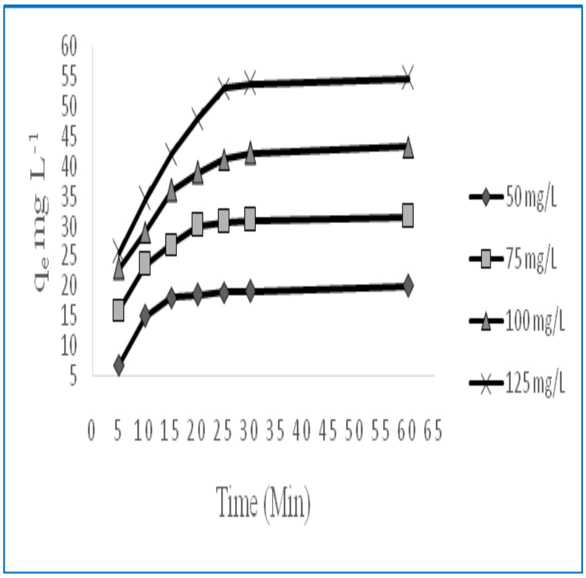

Fig. 3: Effect of initial dye concentration on adsorption

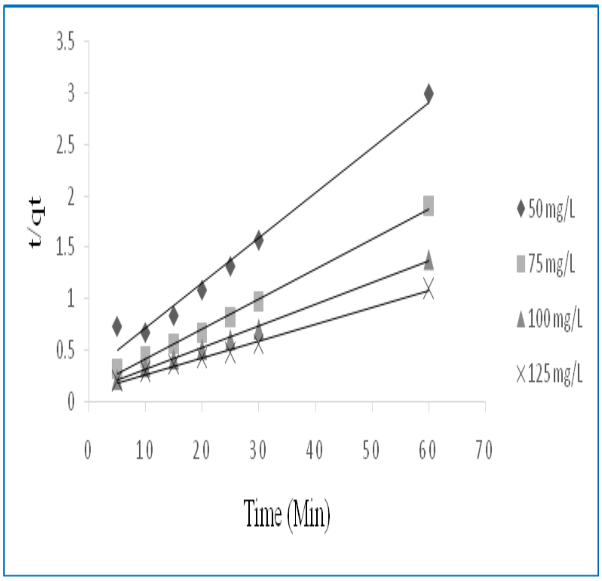

Fig.4: The pseudo second order kinetic

Adsorption dynamics

The pseudo first order kinetic model

The pseudo first order kinetic model expression is given by Lagergren [18] as follows

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

Where q_t and q_e are amount of dye adsorbed at time t and equilibrium, respectively k_1 is the rate constant. Poor correlation coefficient (R^2) for the Lagergren pseudo first order plot shows inapplicability to present study.

The pseudo second order kinetic model

The pseudo second order Lagergren equation is expressed as [18]

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_t} \qquad (3)$$

The Fig.4 shows Plot of t/q_tversus t. Values of equilibrium adsorption capacity (q_e) and second order rate constant (k_2) were determined from the slopes and intercepts and represented in table 1.The present system follows pseudo second order Lagergren model. The adsorption process was affected by adsorbent and adsorbate concentration.

Table 1: Rate constants for pseudo first-order and pseudo second-order adsorption

Conc.	pseudo first-order			pseudo second-order		
C_0 (mg L^{-1})	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (min^{-1})	R^2
50	15.30	0.1061	0.9094	22.72	0.007073	0.9788
75	30.63	0.1381	0.9767	34.24	0.007250	0.9961
100	44.03	0.1229	0.9897	47.39	0.004339	0.9969
125	83.71	0.1473	0.9525	61.72	0.002591	0.9928

Adsorption equilibrium study

Two isotherm, Langmuir isotherm and Freundlich isotherm was used for present study.

Langmuir isotherm

Langmuir isotherm is represented by following equation [19]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \qquad (4)$$

Where Ce is the equilibrium dye solution concentration (mg L^{-1}),q_m is Langmuir constant (related to adsorption capacity) (mg g^{-1}), b is Langmuir constant (related to energy of adsorption) (L mg^{-1})and q_e is the amount adsorbed at equilibrium (mg g^{-1}).

Freundlich isotherm

Freundlich isotherm is represented by following equation [19, 20]

$$\log q_e = (1/n) log C_e + \log k_f \qquad (5)$$

Where n is adsorption intensity, k_f is adsorption capacity, q_e is equilibrium dye concentration in solid and C_e is equilibrium dye concentration in solution. The isotherm parameters are given in table 2.

Table 2: Langmuir and Freundlich isotherm parameter

Temp (^{0} K)	Langmuir isotherm parameter			Freundlich isotherm parameter		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	n	k_f (mg g^{-1})	R^2
313	151.515	0.01093	0.9487	0.3512	0.0293	0.9980
323	161.29	0.01099	0.9468	0.3420	0.0291	0.9957
333	163.934	0.01094	0.9439	0.3359	0.027	0.9986

Effect of temperature

From the present study it has been observed that the percentage removal increases with increase in the temperature. The equation 7 was used to determine thermodynamic parameter.

$$K_0 = \frac{C_{solid}}{C_{liquid}} \qquad (7)$$

Where K_0 is equilibrium constant, C_{liquid} is equilibrium liquid phase concentration (mg L^{-1}) and C_{solid} is equilibrium solid phase concentration (mg L^{-1}).

Gibb's free energy (ΔG) is represented by following equation [21]

$$\Delta G = -RT lnK_0 \qquad (8)$$

Where R is gas constant, T is temperature in Kelvin and K_0 is equilibrium constant.

The Van't Hoff equation is represented by following equation.

$$\log K_0 = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (9)$$

From the Van't Hoff plot the values of ΔH and ΔS were determined and represented in table 3.

Table 3: Thermodynamic parameter of adsorption

Temp (^{0} K)	ΔG (kJ $mole^{-1}$)	ΔH (kJ $mole^{-1}$)	ΔS (J K^{-1} $mole^{-1}$)
313	-35.54	9.74	57.48
323	-38.91		
333	-40.49		

Conclusion:

Adsorptive removal of Malachite Green was studied on Bio adsorbent prepared from *Hyptissuaveolens (VilaytiTulsi)*. The kinetic process follows the pseudo second order kinetic model. The Freundlichisothermmodel was best suited for the adsorption equilibrium data. The presents study shows that the maximum adsorption capacity is 61.72 mg g^{-1}. Negative value of ΔG and positive values of ΔH and ΔS represent aendothermic and spontaneous adsorption. The bio adsorbent prepared from *Hyptissuaveolens (VilaytiTulsi)* can be used as a low cost adsorbent for the removal of Malachite Green.

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Conflict of Interest:

The authors declared that they have no conflict of interest.

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