



Studies on removal of malachite green from aqueous solution by sorption method using water hyacinth - *Eichornia crassipes* roots

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Abstract

Dye containing waste water can cause serious water pollution problems by hindering light penetration and photo synthesis and toxicity from heavy metals associated with dyes. In this research study, batch experiments were conducted using thermally activated *Eichornia crassipes* roots as an adsorbent for the removal a basic dye, malachite green, from aqueous solutions. Effect of operating variables i.e. pH, sorbent dosage, dye concentration and contact time was studied in an agitated batch adsorber. Results showed that maximum dye uptake was observed at an optimum pH 7. There was no significant difference in dye concentration remaining when the pH increased from 5-10. Dye removal was influenced by initial dye concentration and the sorption process followed first order kinetics. Among the three isotherms tested Redlich Peterson and Langmuir isotherms fitted reasonably well to the data. The negative value of the free energy change indicates the spontaneous nature of biosorption. From the above findings, it was observed that the biosorption process obeyed the first order adsorption kinetics. The negative value of the free energy change calculated indicates the spontaneous nature of the sorption and confirms the affinity between the sorbent and the dye cations.

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Introduction

Dyes are important water pollutants which are generally present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries. They are synthetic aromatic compounds which are embodied with various functional groups (Bhatnagar *et al.*, 2005). These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction. Some dyes are also toxic and even carcinogenic. Therefore, it is highly necessary to reduce dye concentration in the wastewater (Wang *et al.*, 2005). The stability of dyes towards light and oxidizing agents also create a problem for their removal by different waste treatment procedures. Hence, their removal methods are selected with a great deal of care and thoughtfulness. Formerly, conventional method adopted by textile industries for removal of coloration from their disposed waste includes froth flotation, flocculation, coagulation etc. However, all such methods were found inefficient and incompetent (Gupta *et al.*, 2004). Some of the dyes and pigments present in these effluents resist biological oxidation and require tertiary treatment (Bhattacharyya *et al.*, 2005).

Cytoplasmic azo reductases play an important role in the anaerobic biodegradation of azo dyes to produce colourless aromatic amines. Although complete mineralization is difficult, the resulting aromatic amines produced during anaerobic degradation may be toxic and carcinogenic. These amines are resistant to further anaerobic mineralization. During the last 10 years, the attention has been shifted towards adsorption technique, which has emerged as one of the widely accepted methods for the removal of all such contaminants (Gupta *et al.*, 2004). Granular or powdered activated carbon is the most widely used adsorbent because it has an excellent adsorption capability for organic compounds, but its use may be limited due to its high cost (Bhattacharyya *et al.*, 2005). This has led many workers to search for cheaper sources to prepare activated carbons or

cheaper substitutes like fly ash, silica gel, wool wastes, blast furnace sludge, and clay materials (bentonite, kaolinite, montmorillonite, etc.). The ability of water hyacinth (*Eichhornia crassipes*) to remove heavy metals in solution is well documented (Low *et al.*, 1995). It was found that the metals were mostly concentrated at the roots of the plant and translocation appeared to be slow. This means that the root system could act as a biosorbent for various materials, which are soluble in water. This study also aimed to remove the dye malachite green from the aqueous solution using thermally activated water hyacinth roots as adsorbent and to study the effects of process variables like activation temperature, initial pH, sorbent dosage and initial dye concentration on amount of dye uptake with equilibrium and kinetics of sorption mechanism.

Materials and methods

Preparation of adsorbent

The water hyacinth roots used in this study were obtained from a pond situated behind the Department of Chemical engineering, Annamalai University, Annamalai nagar, Tamilnadu, India. The collected plant biomaterial was extensively washed with tap water to remove soil and dust and sliced into pieces manually. The sliced material was dried by exposure to the sunlight for 3 days and subsequently at 80°C for 4 h in a hot air oven. The dried material was milled into fine powder and allowed to pass through a + 65 to -80 mesh opening size sieve. The sieved powder was thermally activated at different temperatures for various times in an inert atmosphere and cooled to room temperature. The activated sorbents were stored in desiccators before use.

Preparation of Malachite green solution

The cationic dye malachite green was obtained from CDH Chemicals, New Delhi and used without further purification. The dye stock solution of 100 mg/L was prepared using distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

Effect of thermal activation

The effect of thermal activation on the equilibrium uptake of malachite green was estimated at maximum concentration of stock solution (100 mg/L). In the present study water hyacinth roots were subjected to four different temperatures and time like 500°C for 2 hr , 400 °C for 3 hr, 300°C for 3.5 hr and 200 °C for 4hr. In the preliminary studies, it was showed that the higher activation temperature decreased the amount of dye adsorbed by the adsorbent and the adsorption capacity of the untreated water hyacinth roots was also reported. During this study, the dye solution was used as such and no pH alterations were made. The equilibrium uptake capacity was determined by agitating 50mL of aqueous solution with 0.1 g of sorbent dosage at the constant speed of 200rpm, before starting the experiments all the beakers were covered with aluminum foil in order to prevent heat loss due to evaporation. Agitation was performed using magnetic stirrers for 6 hrs , which is more than sufficient to reach the equilibrium. Samples were then centrifuged and dye concentrations in the supernatant were analyzed using UV spectrophotometer by monitoring the absorbance changes at a wave length of maximum absorbance.

Effect of pH

The effect of pH on the dye uptake was studied by agitating 100mg/L Malachite green solution with 0.1g of water hyacinth roots in the pH range of 2- 10. The dye solutions were adjusted to the required initial pH values by adding HCl or NaOH.

Effect of sorbent dosage

In order to find out the effect of sorbent dosage on the dye uptake a set of trials were carried out with thermally activated water hyacinth roots, whose dosage ranges from 0.1 to 0.5 g per 50 mL of aqueous dye solution through out this set of experiments, dye concentration was maintained constant at 100 mg/L. After shaking, the samples were analyzed for color reduction in the UV spectrophotometer.

Effect of contact time

Thermally activated water hyacinth roots were shaken with 50 mL of aqueous dye solution whose concentration varied in the range of 25 to 100 mg/L. Twelve magnetic stirrers running at different contact time intervals were used to perform kinetic studies. Each stirrer was switched off at regular time intervals and dye concentrations in samples were analyzed using UV spectrophotometer.

Results and discussion

Effect of thermal activation

Fig.1. shows the amount of dye adsorbed q_e (mg/g) at different thermal activation temperatures. q_e was obtained from a simple mass balance Eq (1) as shown below;

$$q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

q_e (mg/g) is the amount of dye adsorbed at equilibrium, V (L) is the volume of the solution treated, C_o (mg/L) is the initial dye concentration, and M (g) is the adsorbent dosage. It was observed that the water hyacinth roots activated at 200°C for 4 hrs showed the maximum uptake capacity of malachite green. The uptake capacity of sorbent was found to decrease with increase in temperature above 200°C. As a result, 200°C was found as the suitable activation temperature. The effect of thermal activation was proved to be vital as allow dye uptake capacity of 18.36 mg/g was attained with 100mg/L malachite green solution when the water hyacinth roots were used without any activation.

Table 1. Equilibrium isotherm constants at 30°C.

Freundlich isotherm			Langmuir isotherm			
K_F	$1/n$	R^2	k_L	q_o	h	R^2
(mg/g)			L/mg	mg/g	L/g	
(L/g) ⁿ						
7.62	0.2047	0.9651	0.19109	34.36	6.566	0.9827

Table 2. Redlich- Peterson equilibrium isotherm constants at 30°C.

Redlich-Peterson isotherm			
k_R	a_R	b_R	R^2
10.62	2.049	0.2014	0.9997

Effect of pH

Because initial pH of solution can significantly influence sorption of dyes, the effect of pH on dye sorption by the water hyacinth roots was studied. The value of pH used range from 2 to 11.As elucidated in Fig.2, the maximum dye uptake was at the initial pH 5.0. The dye adsorbed increased as the initial pH was increased from 2 to 5.When the pH varied from 5 to 10 the amount of dye adsorbed remained nearly constant. Previously, a number of studies have reported that there exist a linear relation between pH and the amount of dye (basic) adsorbed (Vasanth Kumar *et al*, 2005).At lower pH, the sorbent surface might have become negatively charged attracting more of the basic dye molecules. It is likely that charges develop on the surface of an adsorbent in an acidic medium, resulting in a higher adsorption of anionic dyes than in cationic dyes. If this is the case, the sorption of cationic dye should decrease at a lower pH (Low *et al*, 1990). As result of this study, the optimal pH was shown to be 7.

Table 3. Kinetic constants for sorption of Malachite green onto water hyacinth roots.

C_0 mg/L	k_1 min-1	R_1^2	k_d mg/g. min ^{1/2}
25	0.1432	0.9016	0.7619
50	0.0829	0.9742	1.8933
75	0.1077	0.9245	3.1855
100	0.247	0.9308	3.257

Effect of sorbent dosage

From Fig 3., it was observed that the dye uptake on the water hyacinth roots was decreased with increasing amount of sorbent dosage whereas, the effect of sorbent dosage on the % color removal increases with increasing sorbent dosage. This may be due to the fact that the amount of solute sorbed

onto unit weight of sorbent gets splitted with increasing sorbent concentration (Waranusantigul *et al*, 2003). The relation between q_e and sorbent dosage was found to fit the equation with the higher correlation coefficient of 0.9999.

$$q_e = 45.488C_e^{-0.968} \tag{2}$$

Biosorption equilibrium

The Langmuir, Freundlich and Redlich and Peterson isotherms are the most frequently used two parameter models in the literature describing the non-linear equilibrium between amount of dye adsorbed on the acid treated water hyacinth roots (q_e) and equilibrium concentration of solution (C_e) at a constant temperature(30°C). The Langmuir equation, which is valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites, is given by Eq. (3).

$$q_e = \frac{q_o k_L C_e}{1 + k_L C_e} \tag{3}$$

where parameters q_o and k_L are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time . The values of q_o and k_L can be determined from the linear plot of C_e/q_e versus C_e . The Langmuir equation used for homogeneous surfaces is,

$$h = k_L q_o \tag{4}$$

$$\frac{C_e}{q_e} = \frac{1}{h} + \frac{C_e}{q_o} \tag{5}$$

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness. The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known relationship describing the sorption equilibrium and is expressed by the below mentioned Eq (6):

$$q_e = K_F C_e^{1/n} \quad (6)$$

Where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity. Eq (6) can be linearized in logarithmic form and Freundlich constants can be determined.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

The Freundlich equation predicts that the dye concentration on the adsorbent will increase so long as there is an increase in the dye concentration in the liquid. Jossens and co-workers modified the three-parameter isotherm first proposed by Redlich and Peterson to incorporate features of both the Langmuir and Freundlich equations. It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \quad (8)$$

At low concentrations the Redlich-Peterson isotherm approximates to Henry's law and at high concentrations its behavior approaches that of the Freundlich isotherm. The linearized form of the Eq (8):

$$\ln \left(\frac{K_R C_e}{q_e} - 1 \right) = b_R \ln C_e + \ln a_R \quad (9)$$

The Redlich-Peterson isotherm constants K_R, a_R and b_R the coefficients of correlation are presented in Table 2. The best fit equilibrium model was determined based on the correlation coefficient. Redlich-Peterson isotherms exhibit extremely high value of correlation coefficient (0.9997) followed by the Langmuir and Freundlich isotherms with correlation coefficient of 0.9827 and 0.9651 respectively. Also the higher values of adsorption capacity, q_o (45.75) indicate the presence of strong electrostatic force of attraction (Vasanth Kumar *et al*, 2005). The value of Freundlich exponent ($n = 4.94$) lying in the range of 1-10, indicates favourable adsorption.

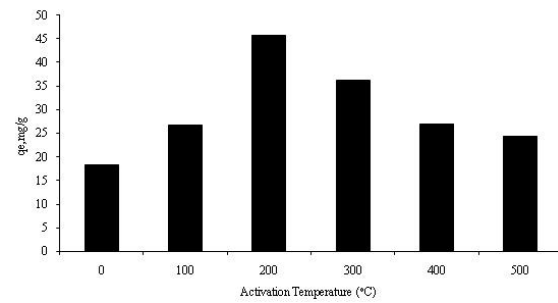


Fig 1. Effect of ph on equilibrium on uptake of malachite green (M:0.1G;V:50ML;CO:100MG/L;TEMP:30OC).

Kinetic modeling

Pseudo-First order model

In order to investigate the mechanism of biosorption and potential rate controlling steps, such as mass transport and chemical reaction processes, kinetic models have been used to test the experimental data. When the biomass is employed as a free and small-sized thermally treated water hyacinth roots suspension in a well-agitated batch system, all the water hyacinth roots binding sites are made readily available for metal uptake. Hence, the effects of external film diffusion and intraparticle diffusion on biosorption rate can be assumed not significant and ignored in any engineering analysis. The kinetic models including the pseudo first-order, pseudo second-order and saturation type can be used in this case assuming that measured concentrations are equal to adsorbent surface concentrations. The first-order rate expression of Lagergren is based on

$$\frac{dq}{dt} = k_1(q_e - q) \quad (10)$$

where q_e and q are the amounts of adsorbed dye on the biosorbent at equilibrium and at time t respectively, and k_1 is the rate constant of first-order biosorption. After integration and applying boundary conditions, $t=0$ to $t = t$ and $q=0$ to $q = q$; the integrated form of Eq. (9) becomes:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (11)$$

A straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model. The first order rate

constant k_1 values were calculated from the slope of the line in Fig.5. The calculated k_1 values and their corresponding linear regression correlation coefficient values were shown in the Table 2. The correlation coefficients were found to exist in the range of 0.9424 to 0.9762 with an average of 0.9611, which shows that this model can be applied to predict the sorption kinetics.

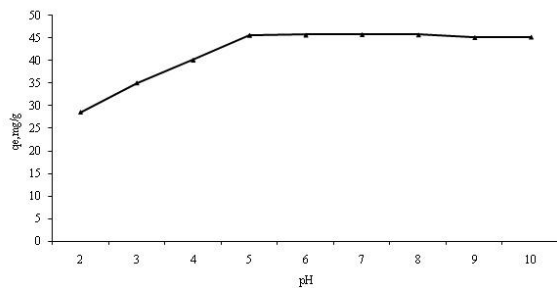


Fig 2. Effect of pH on equilibrium uptake of Malachite green (M:0.1g;V:50ml;Co:100mg/L;Temp:30oC).

Diffusion model

The intraparticle diffusion model presented here refers to the theory proposed by Weber and Morris who concluded that the uptake is proportional to the square root of contact time during the course of adsorption. The amount of dye sorbed at different initial concentrations on water hyacinth roots was plotted against the square root of time of uptake ($t^{1/2}$).

$$q_e = k_d t^{0.5} \tag{12}$$

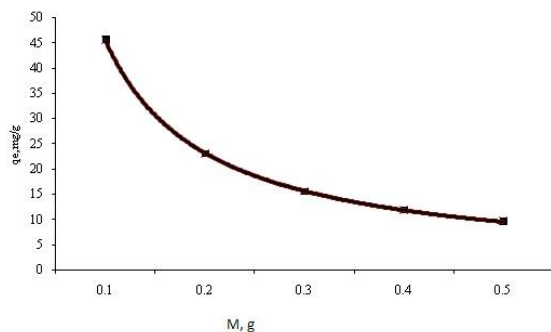


Fig 3. Effect of sorbent dosage on uptake of Malachite green (Co:100mg/L;V:50mL;pH:7).

All the plots had the same general features, an initial curve portion followed by linear portion. The rate constants for intraparticle diffusion (k_d) are

obtained from the slopes of the linear portion of the plots q_e versus $t^{1/2}$ from Fig.7. Various values of k_d at different initial dye concentration are listed in Table 3. From Fig.7,it, may be seen that there are two separate regions. The initial portion is attributing to the bulk diffusion and the linear portion to intra particle diffusion (Allen *et al*, 1989). The deviation of straight line from the origin indicates that the pore diffusion is not the sole rate controlling step (Mall *et al*, 2005). It is observed the rate constant for intraparticle diffusion increased with increasing dye concentration. Similar result was obtained by Low K.S., and Lee. C.K, 1995 in their study on removal of methelene blue by sorption on water hyacinth roots.

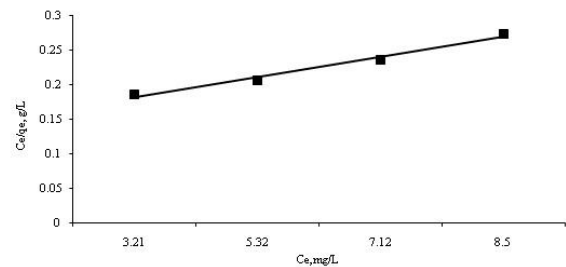


Fig 4. Langmuir plot for sorption of Malachite green onto waterhyacinth roots (M:0.1g;V:50mL;pH:7.0;Temp:30oC).

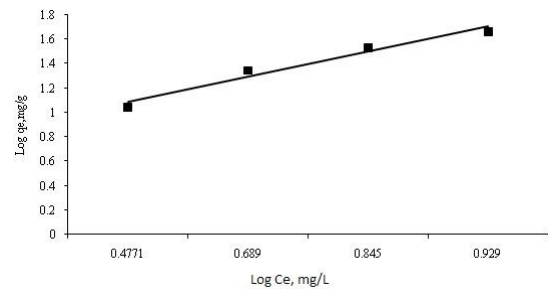


Fig 5. Freundlich plot for sorption of Malachite green onto water hyacinth roots (M:0.1g;V:50mL;pH:7.0;Temp:30oC)

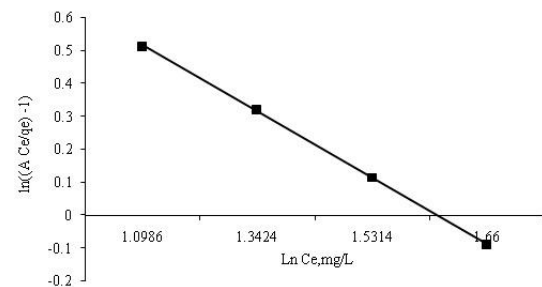


Fig 6. Redlich-Peterson plot for sorption of Malachite green onto water hyacinth roots (M:0.1g;V:50mL;pH:7;Temp:30oC).

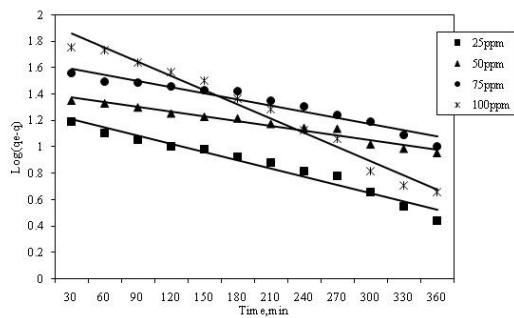


Fig 7. Lagergren plot for sorption of malachite green onto water hyacinth roots (M:0.1g;V:50mL;pH:7.0;Temp:30°C).

Thermodynamic study

Thermodynamic data such as adsorption energy can be evaluated from Langmuir equation (Alam, 2004 and Vasanth Kumar *et al*, 2005).

$$-\Delta G_{ads}^* = RT \ln k_L \quad (13)$$

Where, ΔG_{ads}^* is the free energy change (KJ/mol), T is the absolute temperature (K), R is universal gas constant 8.314(J mol/K) and k_L is the Langmuir constant. Using Langmuir isotherm, the free energy value was evaluated as - 4.16 KJ/mol. Therefore adsorption will be most favored on water hyacinth roots.

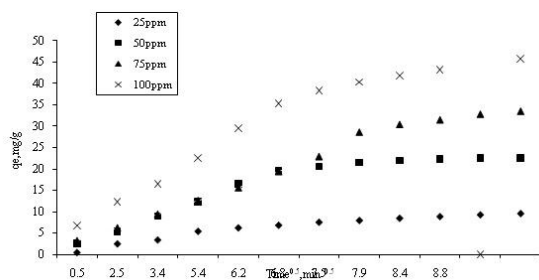


Fig. 8. Intraparticle diffusion plot (M:0.1g;V:50mL;pH:7.0;rpm:200;Temp:30°).

Conclusion

The present study shows that the thermally activated water hyacinth root is a potential adsorbent for the removal of malachite green from aqueous solution, since the raw material is easily available in large quantity. Water hyacinth roots activated thermally at 200°C possessed a higher sorption capacity of 45.75 mg/g confirming that the roots activated under these conditions can be effectively used as biosorbent. The

raw water hyacinth roots possess some capacity to uptake 18.36 mg/g at the dye concentration of 100 mg/l. The optimal pH for better sorption of the dye was found to be 7. The isothermal data of biosorption fitted very well to both Redlich Peterson and Langmuir models. The biosorption process obeyed the first order adsorption kinetics. The negative value of the free energy change calculated indicates the spontaneous nature of the sorption and confirms the affinity between the sorbent and the dye cations.

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