

Biosorption for the Removal of Malachite Green Dye

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Abstract—Removal of Malachite Green (MG) from water using biosorption on dried powdered leaves of *Achyranthes aspera* has been studied. A series of experiments were conducted in a batch system to assess the effects of the system variables such as pH, biosorbent dosage, contact time, initial dye concentration. The extent of dye removal increased with decrease in the initial concentration of the dye and increased with increase in contact time, amount of adsorbent used and the initial pH of the dye solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and pseudo- first and second order kinetic equations. The kinetics of adsorption was found in the pseudo- first order.

1. INTRODUCTION

One of the major causes of environmental pollution are the industrial effluents because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid [1]. The untreated disposal of this colored water into the aquatic environment causes damage to aquatic life as well as human beings by mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons [2,3]. Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation and ozonation [4,5]. However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams.

Biosorption has emerged as an alternative to traditional methods with advantage of being technically easy, and potential for regeneration and sludge free operation, ecofriendly nature, excellent performance, and low cost domestic technique for remediating even heavily metal loaded water [5-7]. The present work investigates the possible use of dried powdered leaves of *Achyranthus aspera* for the removal of Malachite green dye from water.

2. MATERIALS AND METHODS

2.1 Preparation of adsorbent

Leaves of *Achyranthes aspera* are collected and washed several times and dried in shadow. Dried leaves are grounded

and sieved to 50 µm size mesh. Sieved leaves powder is washed with deionised double distilled water and then dried. The prepared biomass was then stored in air tight glass bottles to be protected from moisture. The prepared bio-sorbent is used in the further studies.

2.2 Preparation of dye solution

Malachite green (M.F.: C₂₃H₂₅ClN₂, M.Wt.: 364.911 g/mol), a cationic dye was purchased from Merck. The stock solution of malachite green 1000 mg/L was prepared in distilled water.

2.3 Batch adsorption studies

Batch sorption studies were carried out at desired initial pH, contact time, temperature and sorbate concentration in a 250 mL stoppered conical flask containing 50 mL of test solution. pH of the solution was monitored by adding 0.1 M HCl and 0.1 M NaOH solution as required. Necessary amount of biosorbent was then added and content in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 125 rpm. The time required for reaching equilibrium condition was estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of flask separated from biosorbent by centrifuge at 15000 rpm and was analyzed for remaining Cr(VI) concentration in the sample. The amount of Cr(VI) sorbed per unit mass of the biosorbent (qt in mg/g) was evaluated by using following equations;

$$q_t = (C_i - C_t) \times V / W \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Effect of pH on removal of dye

The effect of pH on dye sorption was studied by adding 0.20 g of adsorbent into Erlenmeyer flasks containing 50 mL of 100 mg/L dye solutions adjusted at different initial pH (2-11). pH of dye solutions was adjusted using 0.1M HCl/NaOH. Flasks were then shaken at 300 rpm and 30°C for 180 min

Fig. 1 shows that adsorption percentage of dye increased with increasing pH and the maximum adsorption was observed at pH 11. At lower initial pH there is competition of H⁺ ion with the cationic dye molecules due to the presence of excess H⁺ also decreased the adsorption. On the other hand, at higher initial pH the surface of the adsorbent becomes negatively charged, which favors the adsorption of the positively charged dye cations through electrostatic force of attraction.

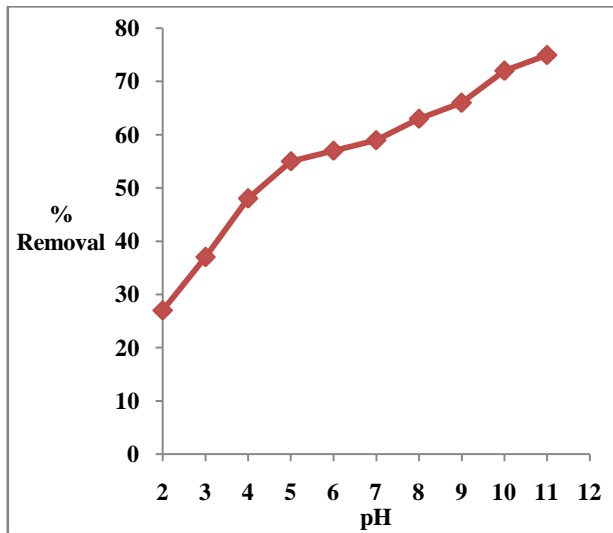


Fig. 1: Effect of pH.

3.2 Effect of adsorbent dose

Effect of adsorbent dose was studied by adding different adsorbent doses (0.05-0.20 g) in Erlenmeyer flasks containing 50 mL of 100 mg/L malachite green solutions. The pH of the solutions was kept original without any adjustment. Flasks were shaken at 300 rpm and 30°C for 180 min. Fig. 2 shows that the percentage removal of malachite green increased with the increase in sorbent dose. This can be attributed to the increase in surface area with a high dosage of the adsorbent.

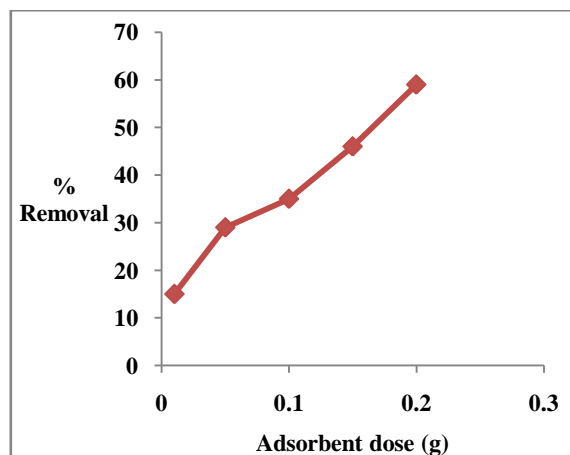


Fig. 2: Effect of Adsorbent dose.

3.3 Effect of contact time & initial dye concentration

In order to study the effect of contact time and initial concentration on removal of dye, 50 mL of dye solutions with initial concentration of 100-300 mg/L were prepared in a series of 250 mL Erlenmeyer flasks. 0.20 g of sorbent was added into each flask. The flasks were then placed in an isothermal water bath shaker at constant temperature of 30°C at 300 rpm, until equilibrium point was reached. In this case, the solution pH was kept original without any pH adjustment.

It can be seen from Fig. 3 that percentage removal of dye initially increased with the increase in contact time rapidly and thereafter it proceeded at a lower rate and finally attained equilibrium. This suggests that, in the initial stage adsorption takes place rapidly on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate determining step. The rapid sorption at the initial stage can be explained by the fact that a large number of surface sites are available for adsorption but with the lapse of time, the remaining surface sites are occupied with difficulty. This is because of the repulsion between the solute molecules of the solid and bulk phases, thus, make it take long time to reach equilibrium.

It can also be seen from this Fig. that the percentage removal of dye decreased with increase in initial dye concentration and showed little decrease by increasing concentrations. This can be explained that all adsorbents have a limited number of active sites, which become saturated after certain concentration

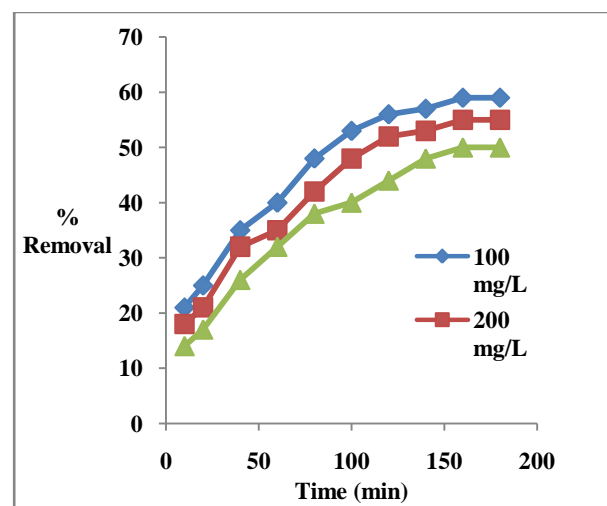


Fig. 3: Effect of contact time and initial dye concentration.

3.4 Effect of solution temperature

The effect of solution temperature on percentage dye removal was examined at various temperatures i.e. 20°C, 30°C and 40°C by adjusting the temperature controller of the water bath shaker, while other operating parameters such as volume of dye, sorbent dosage and rotation speed were kept constant.

Initial pH was kept constant without any adjustment. The results are shown in Fig. 4 from which it can be seen the removal of dye was increased with the increase in solution temperature from 20 to 40°C. This increase is due to an increase in kinetic energy with increasing temperature, and this situation leads to more adsorption on the surfaces of sorbent.

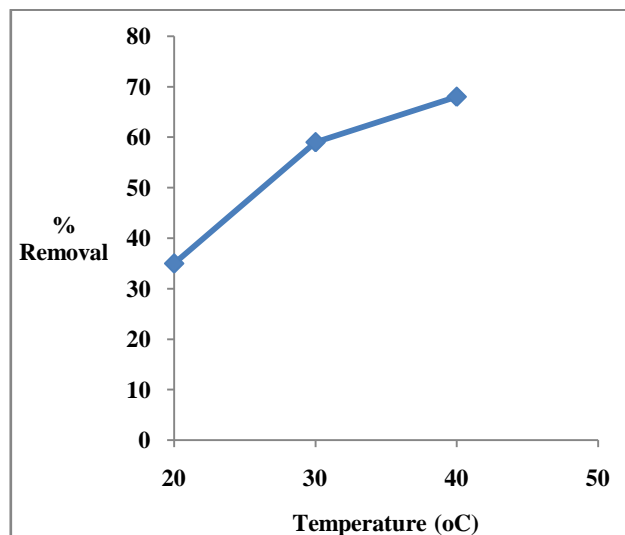


Fig. 4: Effect of temperature.

3.5 Adsorption isotherms

Langmuir and Freundlich isotherm models have been utilized for describing sorption equilibrium for wastewater treatment. The study of isotherm was carried out by varying initial metal ion concentration from 100 to 500 mg/L at various temperatures (20, 30 and 40 °C).

The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules.²⁰ The linear form of the Langmuir isotherms may be represented as:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (1)$$

where, C_e is the equilibrium concentration of solute in bulk solution (mg/L), q_e amount of solute adsorbed per unit weight of sorbent at equilibrium (mg/g), b and Q_0 are the Langmuir constants related to the free sorption energy (L/mg) and monolayer sorption capacity of (mg/g) respectively.

The Freundlich sorption isotherm which describes the equilibrium on heterogeneous surfaces and the linear form of the isotherm can be represented as²¹:

$$\log q_e = \log K_F + 1/n \log C_e \quad (2)$$

where, n and K_F are the Freundlich constants indicative of the intensity of sorption and the relative sorption capacity of the sorbent (mg/g) respectively.

The Langmuir isotherm constants Q_0 and b were calculated from the slope and intercept of plot between C_e/q_e and C_e (Fig. 5) and are presented in Table 1. The isotherm showed good fit to the experimental data with good correlation coefficients. The sorption capacity of dried powdered leaves of *Achyranthes aspera* was found to be 97.05 mg/g at 20 °C. The values of Q_0 show a decrease with the increase in temperature.

Freundlich isotherm constants n and K_F were calculated from the slope and intercept of plot between $\log C_e$ and $\log q_e$ (Fig. 6) and are also presented in Table 1. The relative sorption capacity (K_F) was found to decrease with increase in temperature. The values of n (intensity of sorption) between 1 and 10 (i.e., $1/n$ less than 1) represents a favourable sorption. For the present study the value of n also presented the same trend representing a beneficial sorption.

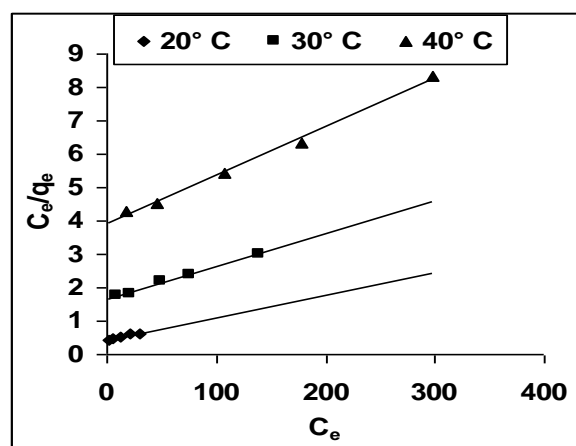


Fig. 5: Langmuir Isotherm plot.

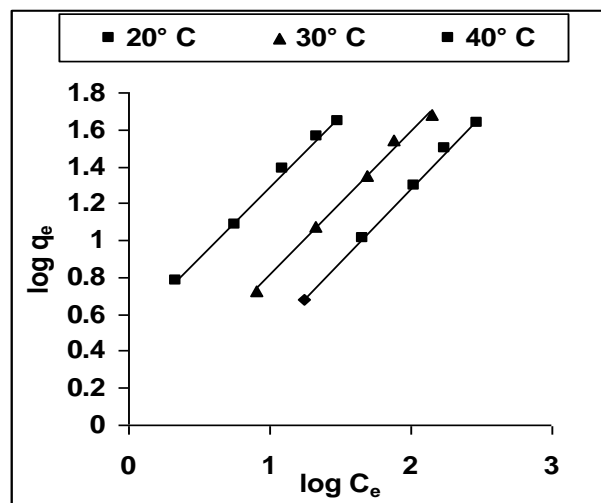


Fig. 6: Freundlich Isotherm plot.

Table 1: Parameters of Langmuir, Freundlich isotherm at various temperatures

Temp. (°C)	Langmuir constants			Freundlich constants		
	Q ^o (mg/g)	b (L/mg)	r ²	n	K _F	r ²
20	97.05	0.0156	0.9976	1.297	3.288	0.9872
30	85.01	0.0060	0.9959	1.280	1.082	0.9862
40	68.49	0.0037	0.9989	1.263	0.494	0.9882

3.6 Dynamic modelling

Pseudo-first-order equation can be given as:

$$\log (q_e - q_t) = \log (q_e) - k_s \times t / 2.303 \tag{3}$$

where, k_s the equilibrium rate constant (min⁻¹) is calculated by the slope of log (q_e - q_t) against time (min) plots. Approximately, linear fits were observed for all temperatures. The correlation coefficient and constant k_s have been calculated and summarized in Table 2.

Pseudo-second order kinetic model is presented as follows:

$$t / q_t = 1 / k_2' q_e'^2 + t / q_e \tag{4}$$

$$h = k_2' q_e'^2 \tag{5}$$

The equation constant (g/mg/min) and h (initial sorption rate, mg/g/ min) can be determined by plotting t/ q_t against t and given in Table 2. Good correlation coefficients were observed for pseudo-first order kinetic model in comparison to pseudo-second order model indicating that dye uptake process can be approximated with the pseudo-first order kinetics model. Thus the pseudo first order kinetics was pathway to reach the equilibrium.

Table 2: Kinetic parameters obtained under different temperatures

Temp. (°C)	Pseudo-first order			Pseudo-second order			
	k _s (X 10 ⁻²)	q _e (cal)	r ²	k' ₂ (X 10 ⁻⁴)	h	q _e (cal)	r ²
20	11.07	80.891	0.9971	6.88	3.72	73.52	0.9713
30	10.50	80.223	0.9933	4.29	2.16	70.92	0.9867
40	7.81	61.673	0.9940	2.52	1.25	70.42	0.9752

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