Malachite Green Dye Removal Using the Seaweed *Enteromorpha*

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Abstract: Malachite green adsorption from an aqueous solution onto activated *Enteromorpha* carbon has been studied experimentally using batch adsorption method. Adsorption kinetics and equilibrium were investigated as a function of initial dye concentration, pH, contact time and adsorbent dosage. Kinetics studies indicated that the adsorption followed pseudo second order reaction. Equilibrium data was analyzed using Langmuir and Freundlich isotherm models. The adsorption capacity of *Enteromorpha* was found to be 94.74%. On the basis of experimental results and the model parameters, it can be inferred that the carbonaceous *Enteromorpha* is effective for the removal of malachite green from aqueous solution.

Keywords: Adsorption, *Enteromorpha*, Activated carbon, Malachite green dye, Kinetics, Equilibrium.

Introduction

Dyes normally have a complex aromatic molecular structure which makes them more stable and more difficult to biodegrade¹. Further dyes have synthetic origin. They are widely used in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceuticals and food industries. At present there are more than 10,000 dyes which are commercially available². Widespread use of dyes often poses pollution problems in the form of coloured waste water discharged into environmental water bodies. It not only affects aesthetic merit but also reduces light penetration and photosynthesis. Also, some dyes are either toxic or mutagenic and carcinogenic³. The conventional methods for treating dyes containing waste waters are coagulation and flocculation⁴, oxidation or ozonation^{5&6}, membrane separation⁷ and activated carbon adsorption⁸. But these technologies do not show considerable efficiency or economic advantage. Though activated carbon is the most popular and widely used dye

sorbent it has certain problems in its usage. The major drawback is its cost. Hence, there is a widespread awareness in using low cost, easily available biomaterials for the adsorption of dye colours. Many botanical materials of a very low price have directly been used as sorbent for dye adsorption from waste water⁹⁻²⁰. Since India is a developing nation and a large producer of synthetic textile dyes, novel and economical treatment technologies of dye waste water are the need of the hour.

In the present study, a marine alga which is commonly and abundantly available in the Bay of Kodyakkarai coast namely, *Enteromorpha* was selected as an adsorbent for the removal of Malachite green from aqueous solution.

Experimental

Enteromorpha was collected from Kodyakkarai coast in south east coast of India and sun dried. Dry biomass was cut with a knife into irregular shaped particles between 1 and 3 mm in size. The biomass was then washed with distilled water, filtered and finally dried overnight at 60 °C and crushed to an average size of 0-63 μ in a mortar and then activated by 0.1 M H₂SO₄ for 24 h and finally carbonized and subsequently used for adsorption experiment.

Adsorbate solution

A 25 ppm solution of malachite green dye was prepared by weighing accurately 25 mg of analar grade malachite green dye and dissolving in 1000 mL standard flask. It was made up to the mark with deionised water. The stock solution was further diluted with deionised water to desired concentration for obtaining the test solution.

Chemicals

Analytical grade reagents were used for malachite green dye solution; ACS reagent grade concentrated hydrochloric acid, NaOH and pH buffer solutions were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

Batch mode adsorption studies

The adsorption of MG dye on the *Enteromorpha* was studied by batch technique. A known weight of adsorbent (for example 50-350 mg of adsorbent) was equilibrated with 50 mL of dye solution of known concentration in a 250 mL reagent bottle in a mechanical shaker for a known period of time (30-180 min). After equilibrium, the suspension of the adsorbent was separated from solution by filtration using Whatman no. 41 filter paper. The concentration of dye remaining in solution was measured. The effect of some parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid, sodium hydroxide and buffer solutions when required. The results of these studies were used to obtain the optimum conditions for maximum dye removal from aqueous solution.

Results and Discussion

The results of the experiments carried out for the removal of malachite green dye from aqueous solution using *Enteromorpha* as adsorbent are discussed below.

Effect of initial concentration of dye

The results for effect of initial concentration on percentage removal of dye using *Enteromorpha* is presented in Table 1. It can be seen from the Figure 1 that the percentage removal decreases with the increase in dye concentration. For *Enteromorpha* the percentage removal is 94.74% at the initial concentration of 25 mg/L for 250 mg of adsorbent dose and a contact time of 3 h.

Table 1. Effect of initial concentration of MG dye using *Enteromorpha* at 120 min

S.No	Initial concentration mg/L	% removal of MG dye
1.	5	100.0
2.	10	100.0
3.	15	92.60
4.	20	93.95
5.	25	84.2

Figure 1. Effect of initial concentration on removal of MG dye

Effect of adsorbent dose

It is observed that there is a sharp increase in percentage removal with adsorbent dose for *Enteromorpha*. The results for adsorptive removal of MG dye with respect to adsorbent dose over the range of 50 - 350 mg shown Table 2 and Figure 2 indicate that the percentage removal of dye increases with adsorbent dose. The increase in percentage removal is due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of dye adsorption on adsorbent is determined by the adsorption capacity of the adsorbents.

Table 2. Effect of adsorbent dosage on removal of MG dye (Initial concentration: 25 ppm)

S.No	Adsorbent Dosage, mg	Optical Density		MG dye % of adsorption
		Before adsorption	After adsorption	
1.	50	0.38	0.22	42.11
2.	100	0.38	0.18	52.63
3.	150	0.38	0.14	63.16
4.	200	0.38	0.05	86.84
5.	250	0.38	0.02	94.74
6.	300	0.38	0.01	97.37
7.	350	0.38	0.00	100.0

Figure 2. Effect of adsorbent dosage on removal of MG dye

Effect of contact time

Figure 3 shows the variation in the percentage removal of MG dye with contact time on *Enteromorpha*. For varying initial dye concentration ranging from 5-25 mg/L, *Enteromorpha* showed the percentage removal of 94.74% at the contact time of 3 h. For the same concentration it was observed that the percentage removal was not increased with increase in contact time because equilibrium was attained. The optimal contact time to attain equilibrium with *Enteromorpha* was experimentally found to be about 3 h.

Table 3. Effect of contact time on removal of MG dye (15 mg/L)

S. No	Contact time (t) minutes	Optical Density		MG dye % adsorption
		Before adsorption	After adsorption	
1.	30	0.27	92.59	0.02
2.	60	0.27	92.59	0.02
3.	90	0.27	92.59	0.02
4.	120	0.27	92.59	0.02
5.	150	0.27	96.30	0.01

Figure 3. Effect of contact time on removal of MG dye (15 mg/L)

Effect of pH

The pH is one of the most important parameter controlling uptakes of dye from wastewater and aqueous solutions. The effect of pH on adsorption of dye on *Enteromorpha* was studied at room temperature by varying the pH of dye solution from 1- 7. It can be observed from the results shown in Table 4 and Figure 4 that the removal of dye by *Enteromorpha* was maximum at pH 4, other pH shows minimum adsorption.

Table 4. Effect of pH on removal of MG dye (contact time: 180 min)

S.No	pH	Optical Density		MG dye % of adsorption
		Before adsorption	After adsorption	
1.	1	0.38	0.08	78.95
2.	2	0.38	0.07	81.58
3.	3	0.38	0.04	89.47
4.	4	0.38	0.02	94.74
5.	5	0.38	0.05	86.84
6.	6	0.38	0.04	89.47
7.	7	0.38	0.05	86.84

Figure 4. Effect of pH on removal of MG dye

Freundlich Isotherms

Freundlich isotherm is $\log q_e = \log K_f + 1/n \log C_e$

Where q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g), K_f is the measure of sorption capacity and $1/n$ is sorption intensity; C_e is equilibrium concentration of residual dye in solution. Figure 5 shows the Freundlich adsorption isotherms for *Enteromorpha*. The straight line nature of the plots indicates that the process followed was of Freundlich adsorption type.

Table 5. Data for Freundlich plot (150 min)

S. No.	Initial Concentration, mg/L	MG dye eq, C_{eq}	$\log C_{eq}$	MG dye ad, 'x'	$\left(\frac{x}{m}\right), q_e \times 10^{-5}$	$\log_e \left(\frac{x}{m}\right)$	$1 + \log_e \left(\frac{x}{m}\right)$
1.	5	0.00	0.00	5.00	0.500	-0.30	0.70
2.	10	0.00	0.00	10.00	1.000	0.00	1.00
3.	15	0.55	-0.26	14.45	1.445	0.16	1.16
4.	20	1.21	0.08	18.79	1.879	0.27	1.27
5.	25	0.66	-0.18	23.03	2.303	0.32	1.32

Figure 5. Data for Freundlich plot (150 min)

Langmuir isotherm

It is represented experimentally by the expression, $\frac{P}{x/m} = \frac{1}{K_1 K_2} + \frac{P}{K_2}$ where K_1 and K_2 are proportionality constants, P - initial concentration (C_{eq}), x/m - amount of dye adsorbed at equilibrium (mg/g), q_e . A plot of C_e/q_e versus C_e will give a straight line. The slope of this is $1/K_2$ and intercept on the y - axis will give $1/K_1 K_2$. Figure 6 indicates adsorption of dye on *Enteromorpha* is best fit with Langmuir model and so we infer that it followed Langmuir adsorption isotherms.

Table 6. Data for Langmuir plot (120 min)

S. No.	MG dye eq	$\left(\frac{x}{m}\right), q_e \times 10^{-5}$	$\frac{C_e}{q_e}$
1.	0.00	0.500	0.00
2.	0.00	1.000	0.00
3.	1.11	1.389	0.80
4.	1.21	1.879	0.64
5.	2.64	2.105	1.25

Figure 6. Data for Langmuir plot (120 min)

Lagergren kinetics

Lagergren also proposed kinetics for the adsorption. According to him, if a plot of time in minutes *versus* $\log_{10} (q_e - q)$ gives a straight line and it follows the first order kinetics. If a plot of time in minutes *versus* t/q gives a straight line and it follows the pseudo second order kinetics.

Where,

- q_e –Maximum x/m value at maximum time
- q –minimum x/m value at minimum time
- x –amount of dye adsorbed
- m –Mass of the adsorbent

Figure 7 indicated adsorption of dye on *Enteromorpha* gave the straight line, so it followed the pseudo second order.

Table 7. Data for Lagergren plot (20 mg/L)

S. No	Contact time (t) minutes	MG dye ad 'X' μg	$\left(\frac{x}{m}\right)q \times 10^{-5}$	$q_e - q$	t/q
1.	30	16.36	1.636	0.364	18.34
2.	60	17.58	1.758	0.242	34.13
3.	90	18.18	1.818	0.182	49.50
4.	120	18.79	1.879	0.121	63.86
5.	150	18.79	1.879	0.121	79.83
6.	180	20.00	2.000	0.000	90.00

Figure 7. Data for Lagergren plot (20 mg/L)

XRD study

Further, the x-ray diffraction studies of the carbon prepared from the marine algae *Enteromorpha* were carried out using Rotoflux x-ray diffractometer 20KW / 20A, Model 10.61 with a microprocessor record. The XRD pattern of the carbonized marine algae is shown in the Figure 8.

Figure 8. XRD Pattern of *Enteromorpha*

IR study

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency changes in the functional groups of carbons. The spectra of carbon were measured within the range of 400-4000/cm wave number. Some fundamental FTIR frequencies of *Enteromorpha* observed for before and after adsorption are presented in Table 8. As can be inferred from Figure 8 that the adsorption frequencies are shifted to higher wave numbers with the adsorption of MG dye in *Enteromorpha*. From these findings it is presumed that the dye is incorporated within the adsorbent through interaction with the active functional groups.

Table 8. Some fundamental FTIR frequencies of *Enteromorpha* before and after adsorption

Possible assignments	Before adsorption of <i>Enteromorpha</i>	After adsorption of <i>Enteromorpha</i>
O-H stretching	3412.08	3500
C-H stretching	2924.09	3000
Quadrant & semi-circle stretching	1597.06	1600
C-H in plane ring bending	1099.43	1100
N-H bending	796.60	800
C-I Stretching	468.70	500

Figure 9. FTIR Spectrum of *Enteromorpha* before and after MG dye adsorption

Conclusion

The present study showed that *Enteromorpha* can be used as an effective adsorbent for the removal of Malachite green dye from aqueous solution. The maximum adsorption capacity was obtained (94.74%) by using carbonaceous *Enteromorpha* at pH 4 with adsorbent dose of 250 mg and with agitation time of 180 minutes. The adsorption followed pseudo second order kinetics and data fitted the Langmuir and Freundlich adsorption isotherms. The data may be useful in designing and fabrication of an economic treatment plant for the removal of Malachite green dye from wastewaters.

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