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Removal of Malachite Green from Aqueous Solution by *Sargassum wightii*

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In present work, the use of *Sargassum wightii* for the removal of malachite green dye from aqueous solution was studied. Batch adsorption studies were conducted to determine the influence of adsorbent dose, initial dye concentration, pH and temperature. Langmuir, Freundlich and Temkin isotherm models were used to determine the equilibrium isotherm. The adsorption data were fitted on Langmuir isotherm equation. The maximum adsorption capacity was found to be 116.6 mg/g. Thermodynamic analysis of the biosorption proves their spontaneity and endothermic nature. This work reveals that *Sargassum wightii* algae is low cost alternative source for the removal of malachite green dye from aqueous solution.

Keywords: *Sargassum wightii*, Malachite green, Adsorption, Langmuir, Freundlich.

INTRODUCTION

Dyes are used in huge quantities in numerous industries like textile, leather, cosmetics, paper, printing, plastic, prescribed drugs, food, etc. to colour their product that generates wastewater. The fabric manufacturing only accounts for two third of the overall dye stuff production [1,2]. The release of dyes into the rivers not only affect their artistic environment but also affect the transmission of light into rivers and thus affect photosynthetic action. Usual biological treatment processes are not very successful in dye removal [3]. Basic malachite green dye has been extensively used for the colouring of wool, pelt, silk and jute, as in distilleries, as a fungicide and as antiseptic in aquaculture industry [4]. Malachite green has properties that make it striving to remove from aqueous solutions and also harmful to major microorganisms. The removal of malachite green from the aqueous solution is difficult due its properties.

Malachite green (Fig. 1) is environmentally adamant and acutely harmful dye to a wide range of water and terrestrial animals. The exposes of malachite green to rats causes tumor in the breast, ovary and lungs have been reported. Decrease in corpuscle count (dyscrasia), Hb (anemia) and HTC (%) increase in WBC count (leukocytosis) and delay in blood clotting were noticed post-exposure to malachite green [5-7].

Conventional treatment processes to remove colour are electro-coagulation, photo-oxidation, ozonation and adsorption [8]. Activated carbon is used adsorbent with huge success as a result of its high adsorption power, micro-porous structure and

large surface area. The usage of activated carbon is limited due to its high cost [9]. Therefore, it is most important to look for low-cost and efficient alternatives. The utilization of biomass as adsorbents for the treatment of wastewaters can provide a possible alternate and low-cost ways of removing dyes from huge volumes of effluents [10]. Algae are distributed in many parts of the world [8]. Thus, algae are everywhere naturally and serve as one of the biomaterials with high prospective for removing dye from contaminated waters. Marungrueng and Pavasant [11] reported that several functional groups such as carbonyl, phosphoryl, hydroxyl, carboxyl and amide making up the algae cell wall played the crucial roles in dye removal.

The green algae, *Sargassum* are especially helpful in these respects due to its ample distribution and moderately easy structure. *Saragassum* have comparatively huge surface and physiologically active cells [12].

In present work, the removal of malachite green dye from aqueous solution was examined by means of *Saragassum wightii* as an innate, renewable biosorbent. The experimental parameters affecting the biosorption method resembling primary dye concentration, pH, biomass dosage and temperature were studied. The adsorption isotherm and thermodynamic parameters was also studied.

EXPERIMENTAL

Preparation of the adsorbent: *Sargassum wightii* were collected from sea shore near Mandapam coastal region,

Rameswaram. The collected algae were washed with distilled water many times to remove sand and detritus, after that dried in oven at $60 \pm 2^\circ\text{C}$. The dry seaweed was pulverized to make a powdered mass with $100\ \mu$ mesh size.

Preparation of adsorbate solution: The basic dye, malachite green, was used without extra rarefaction. A stock solution of $1000\ \text{mg/dm}^3$ malachite green was prepared using de-ionized water and the solution used for the experiment when required.

Characterization of biosorbent: The exterior functional groups of the loaded and unloaded biosorbent were perceived by Fourier transform infrared (FTIR). Scanning electron microscopy (SEM) was used to study the surface morphology of adsorbent

Biosorption studies: In each Batch adsorption experiment 50 mL of dye solution with known concentration being taken in a 100 mL shaking flask and stirred on magnetic stirrer at 150 rpm. The effect of factors such as adsorbent dose, pH, initial dye concentration and temperature are evaluated in the experiment by varying the factors while other factors maintained constant. After stirring, the mixture were centrifuged and the centrifugate were analyzed for malachite green content at 621 nm with UV-visible spectrophotometer.

The percentage removal of malachite green dye can be calculated by the following equation:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where C_o = Initial concentration of dye, C_e = equilibrium concentrations of dye.

The amount of malachite green adsorbed (q_e) can be calculated by the following equation:

$$q_e = (C_o - C_e) \times \left(\frac{V}{m} \right) \quad (2)$$

where q_e = amount of dye adsorbed. C_o = initial concentration of dye, C_e = equilibrium concentrations of dye. V = volume of the dye solution and m = amount of the adsorbent used. Repeated all the experiments and the average values were calculated.

RESULTS AND DISCUSSION

FTIR spectroscopy is used to evaluate qualitatively the chemical structure of *Sargassum wightii*. Fig. 1, shows that the FTIR spectrum of *Sargassum wightii*. The peaks present in between 1100 and $1000\ \text{cm}^{-1}$ indicates the C–H bending or C–O or C–C stretching vibrations of carbohydrates [13] and polysaccharides [14]. The broad and strong absorption peaks at $3371\ \text{cm}^{-1}$ as assign to the free O–H and N–H stretching of amino acids [15]. The peaks at $1654\ \text{cm}^{-1}$ indicates the C–O stretching and N–O asymmetric stretching of the ester group [16]. Comparing Fig. 1(a) and 1(b), we can conclude that some peaks are shifted or disappeared and new peaks are detected. The result indicates the possibility of involvement of those functional group on the surface of *Sargassum wightii* in biosorption.

Fig. 1. FT-IR spectrum of *Sargassum wightii*: (a) raw biosorbent (b) malachite green dye loaded biosorbent

Fig. 2 shows the surface morphology of the *Sargassum wightii* before and after dye biosorption studied by SEM. It is obvious that *Sargassum wightii* was found to be irregular and porous. Which facilitate biosorption.

Fig. 2. SEM micrographs: (a) raw biosorbent (b) malachite green dye loaded biosorbent

Effect of initial dye concentration: The influence of initial concentration of malachite green on *Sargassum wightii* shown in Fig. 3. An increase the initial dye concentration from 10 to 60 mg/L the percentage removal decreased from 90 to 87 %. At lower concentration, increases of dye removal caused by higher adsorbent site ratio. Due to the saturation dye removal is decreased in higher concentration [17].

Effect of biosorbent dosage: The result of biosorbent dose on the removal of malachite green by *Sargassum wightii* is shown in the Fig. 4. It shows percentage removal increases and then reaches a constant value. The percentage removal was increased with the increase of biosorbent dose, This may be due to increase in the number of available adsorption sites and the surface area [18].

Effect of pH: Adsorption on the surface of the algae is highly pH dependent. It was already proved by many researchers [19-21]. Fig. 5 shows that the effect of pH on the removal of malachite green on *Sargassum wightii*. It shows

Fig. 3. Effect of initial concentration on the removal of malachite green by *Sargassum wightii*

Fig. 4. Effect of dose on the removal of malachite green by *Sargassum wightii*

Fig. 5. Effect of pH on the removal of malachite green by *Sargassum wightii*

that the percentage of removal of malachite green increases with increase of pH. This is due to the electrostatic forces of attraction between the positively charged malachite green and surface of the *Sargassum wightii* is increases and hence percentage removal increases [22]. The obtained results similar to the reported results [23-27].

Adsorption isotherm: The parameter obtained from different adsorption isotherm model provide important information about surface properties of adsorbent and adsorbent affinity to the adsorbate. The accepted adsorption isotherm model for single solute system is Langmuir, Freundlich and Temkin isotherm. Analyzed isotherm data were used to determine the best fitting isotherm models.

Langmuir isotherm: The Langmuir adsorption isotherm was used for adsorption as a monolayer sorption on a surface

with a finite number of identical sites. Assumes adsorption on the surface with the uniform energy [28].

Langmuir equation [29] is:

$$C_e/q_e = (1/K_L q_m) + (1/q_m) C_e \quad (3)$$

where q_m = monolayer adsorption capacity, K_L = Langmuir isotherm constant. Adsorption capacity and isotherm constant value can be calculated by plotting C_e/q_e vs. C_e Fig. 6. The shape of the Langmuir isotherm model was predicted by a dimensionless constant separation factor, R_L [30], R_L is defined as follows

$$R_L = 1/(1 + K_L C_e)$$

The influence of isotherm shape on “favourable” or “unfavourable” adsorption has been considered [31]. The R_L values indicate the type of the isotherm is to be either favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). In this study, The R_L value is found to be 0.458, showing the favourable adsorption of malachite green on *Sargassum wightii*.

Fig. 6. Langmuir isotherm for the removal of malachite green by *Sargassum wightii*

Freundlich isotherm: The adsorption process takes place on heterogeneous surfaces, Freundlich isotherm gives the relationship between adsorption capacity and concentration of malachite green at equilibrium [32].

Freundlich equation is:

$$\ln q_e = \ln K_F + \ln C_e \quad (4)$$

where K_F [mg/g (L/mg) $^{1/n}$] is the Freundlich constant related to the adsorption capacity and $1/n$ is the intensity of adsorption. The favourability of adsorption can be measured by the magnitude of the Freundlich constant n . These values calculated from intercept and slope of the plot of $\log q_e$ vs. $\log C_e$ (Fig. 7).

Fig. 7. Freundlich isotherm for the removal of malachite green by *Sargassum wightii*

Temkin isotherm: Temkin isotherm comprises a determinant that unequally assessing adsorbent – adsorbate interaction. This isotherm characterized by uniform allocation of binding energies by plotting q_e vs. $\log C_e$. The value of constants (A & B) was determined from the slope and intercept (Fig. 8). Temkin equation is given as [33].

$$q_e = (RT/b) \ln AC_e$$

$$q_e = B_1 \ln A + B_1 \ln C_e \quad (5)$$

where A = equilibrium binding, $B_1 = RT/b$, T = temperature, R = gas constant. q_e = amount of dye adsorbed dye and C_e = concentration of dye at equilibrium. The value of B and A have been calculated from the slopes and intercepts of the plots, respectively, from graph q_e vs. $\ln C_e$ (Fig. 8), b = related with heat of adsorption. The values of constants (A & B) and correlation coefficient value are given in Table-1.

Fig. 8. Temkin isotherm for the removal of malachite green by *Sargassum wightii*

Adsorption isotherm constant values are obtained by Langmuir, Freundlich, Temkin isotherm are examined in Table-1. According to correlation coefficients, the adsorption data of Langmuir isotherm are better fit while compared to other two isotherms. Already researchers proved similar results on adsorption of methylene blue dye [34]. Homogeneity in the surface of *Sargassum wightii* adsorbent suggested by the experimental data of Langmuir isotherm model. In this work, the adsorption capacity value is larger than those in many of earlier studies. The results show that the malachite green can be easily adsorbed on *Sargassum wightii*.

Effect of temperature: Temperature is an important factor that indicates whether the adsorption process is an endothermic or exothermic. Fig. 9 shows that the effect of temperature on adsorption on malachite green with *Sargassum wightii* and the adsorption capacity increases with increasing of temperature. This is caused by the increase in the mobility of dye increases with the increase of temperature. The results suggest that the adsorption is an endothermic process.

Thermodynamic studies: Spontaneity of a process could be concluded by thermodynamic parameters like ΔH°

Fig. 9. Effect of temperature on the removal of malachite green by *Sargassum wightii*

(enthalpy change), ΔG° (free energy change) and ΔS° (entropy change). Decreasing values of ΔG° and ΔH° with increasing temperature indicates the adsorption process is spontaneous [35]. The temperatures used in the thermodynamic study were 298, 303, 308, 313 and 323 K. The thermodynamic parameters were calculated based on the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$\ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where k is the equilibrium constant, R is the universal gas constant (8.314 J/mol K) and T is the temperature (K).

Plotting the linear plot $\ln K$ against $1/T$ (Fig. 10), ΔH° and ΔS° values can be calculated from the slope and intercept. Table-2 shows the thermodynamic parameter values. The positive values of ΔH° indicates the adsorption process of malachite green by *Sargassum wightii* are endothermic and the negative values of ΔG° indicates the adsorption process is spontaneous. The positive values of ΔS° indicates the increase of disorder of solid-liquid interface during the sorption process [36]. Similar results have been reported in the literature for the adsorption of malachite green by activated carbon [37].

Fig. 10. Van't Hoff plot for the removal of malachite green by *Sargassum wightii*

TABLE-1
ADSORPTION ISOTHERM CONSTANT FOR THE REMOVAL OF MALACHITE GREEN BY *Sargassum wightii* ADSORBENT

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q_m (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n	R^2	b_T (kJ/mol)	A_T (dm ³ /mol)	R^2
116.6	0.03	0.994	5.68	0.767	0.987	132.51	0.499	0.947

TABLE-2
THERMODYNAMIC PARAMETERS FOR THE REMOVAL OF
MALACHITE GREEN ONTO *Sargassum wightii*

Temperature (K)	Thermodynamic parameters		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
298	-19.52		
303	-19.92		
308	-20.29	22.85	73.31
313	-20.66		
323	-21.39		

Conclusion

The present work signifies that *Sargassum wightii* algae is a good biosorbent for the removal of malachite green from aqueous solution. The adsorption of malachite green was increases with increase of adsorbent dose and the adsorption was maximum in basic condition. Equilibrium analysis shows that the adsorption of malachite green on *Sargassum wightii* are well fitted in the Langmuir isotherm model and the adsorption capacity of malachite green was found to be 116.6 mg/g. Thermodynamic results indicate spontaneous and endothermic process. Finally, it is concluded that *Sargassum wightii* has the great potential biosorbent for the removal of malachite green.

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