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Bioremoval of toxic dye by using different marine macroalgae

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Abstract: The removal of malachite green dye from aqueous solution by *Ulva lactuca*, *Sargassum crassifolium*, and *Gracilaria corticata* has been demonstrated in order to examine their potential use as low-cost adsorbents. The optimum pH (8.0), temperature (25 °C), contact time (150 min), and biomass (2.0 g) for removal of dye by algae are reported. The maximum removal percentage of the dye ranged between 95.6% and 98.3% by using *Sargassum crassifolium* at the optimal conditions. Minimum removal of dye by algae (69%–77.1%) was observed with the high dye concentration of 35 mg L^{-1} at the optimal conditions. Adsorption of the dye by using the biomass was found to fit well with Langmuir and Freundlich isotherms. The adsorption reaction was spontaneous, exothermic, and highly favorable by the tested algae. The FT-IR analyses confirmed that hydroxyl, carboxyl, amino, and carbonyl groups were responsible for the dye binding process. Scanning electron microscopy showed great porosity on the algal surface, which allows the free passage of dye molecules. The biomass of brown algae was the most effective in the removal of malachite green, followed by green and red algae. The highest affinity of the brown biomass for dye removal may be due to its high binding site affinity, the negative free energy of adsorption, and the great pores on its surface.

Key words: Marine macroalgae, malachite green, equilibrium isotherm, thermodynamic, FT-IR, scanning electron microscope

1. Introduction

Dyes are toxic, mutagenic, and dangerous to aquatic living organisms. They decrease light penetration and photosynthesis, which causes problems to aquatic groups (Hammud, 2011). As synthetic dyes are usually designed to be chemically and thermally stable, dye wastewater needs to be disposed of accordingly and should not be discharged directly into bodies of water (Kooh et al., 2016). Malachite green (MG) is used for the coloring process in leather, wool, cotton, silk, jute, paper, detergent, and anthelmintics; it is also used as food coloring and a food additive (Srivastava et al., 2004). MG is widely used as a stain for cell and tissue samples during microscopic analysis and in aquaculture as a fungicide, bactericide, antiprotozoal, etc. (Hecht and Endemann, 1998). Poe and Wilson (1983) reported MG residue in fish tissue for the first time.

MG is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals (Srivastava et al., 2004). It causes serious public health hazards and poses a potential environmental problem. Both clinical and experimental observations reported so far reveal that MG is a multiorgan toxin. It decreases food intake, growth, and fertility rates; causes damage to the liver, spleen, kidneys, and heart; inflicts lesions on the skin, eyes, lungs, and bones; and produces teratogen effects in rats and mice (Sundarrajan et al., 2000). Apoptosis in the transitional epithelium of the urinary bladder and thyroid follicles has also been observed in MG-fed mice (Culp et al., 1999).

MG is highly cytotoxic to mammalian cells (Fessard et al., 1999) and carcinogenic to the liver, thyroid, and other organs of experimental animals (Mahudawala et al., 1999). Incidences of tumors in the lungs, breast, and ovaries have been reported in rats exposed to MG. In the thyroid gland, leucomalachite green results in a blockade of hormone synthesis, decreases T4 and increases TSH concentrations, and causes tumors in thyroid follicle cells of rats (Doerge et al., 1998). Despite being banned in several countries, the dye is still being used in many parts of the world due to a lack of a proper alternative. Before the discharge

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of dyes into a stream, it is important to remove the dye from the wastewater by using an effective treatment technique. Effluents polluted with dye can be treated by different techniques such as chemical, physical, radiation, electrical, and biological processes. Sun and Yang (2003) reported that the resistance of dyes to heat, oxidizing agents, and aerobic digestion causes some problems in treating colored wastewater. Therefore, removal of the dye by using a nonliving biomass can be used as an alternative method for the treatment of polluted waters (Robinson et al., 2001).

Macroalgae or seaweeds belong to one of several groups of multicellular algae: red algae, green algae, and brown algae. Macroalgae can be used as nonliving biomasses to remove various textile dyes. Hence, macroalgae are nontoxic, low-cost, and easily available biomaterials for the treatment of colored effluents with different degrees of success (McKay et al., 1999). Furthermore, dead cells of algae are easily removed from wastewater after adsorption of the dye by filtration and can be reused by desorption process with 0.1 NaOH that removes 99% of the dye from the algae (Singh and Kaur, 2013). The surface of the algae has the ability to adsorb pollutants from solutions (Miranda et al., 2012). Marungrueng and Pavasant (2007) investigated the adsorption of dye onto the green macroalgal species *Caulerpa lentillifera*. Their results were compared to the sorption performance of a commercial activated carbon. The results revealed that the algae exhibited greater sorption capacities than activated carbon for the dye. The cell wall of marine macroalgae has a good binding affinity due to the presence of proteins, polysaccharides, and lipids on the surface that act as binding sites (Davis et al., 2003). The biosorption depends on the chemical characters of the pollutant, type of material, and environmental conditions (Vijayaraghavan and Yun, 2008).

In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost-effectiveness. If low-cost adsorbents perform well in removing MG at a low cost, they can be adopted and widely used in industries not only to minimize cost-inefficiency but also improve profitability.

The purpose of the present study was to evaluate the efficiency of different marine macroalgae collected from the local habitat for removal of MG dye from an aqueous solution. The effects of pH, temperature, contact time, weight of biomass, and dye concentrations on the removal of the dye were studied. In addition, adsorption isotherms, thermodynamics, infrared spectroscopy, and scanning electron microscopy (SEM) were explored.

2. Materials and methods

2.1. Preparation of biomass

Different marine macroalgae were collected from the coastal area of Jeddah, Saudi Arabia. The algae were identified as *Ulva lactuca* (green), *Sargassum crassifolium* (brown), and *Gracilaria corticata* (red). They were washed thoroughly with distilled water and dried until constant weight at 45 °C. The dry sample was ground with a blender and sieved by using a 1.0-mm standard sieve. A solution of 0.2% calcium chloride in deionized water was prepared. Every 1 g of dry powdered sample was washed with 100 mL of calcium chloride to increase the adsorption capacity of the biomass. The samples were then washed with deionized water several times, dried at 45 °C until constant weight, and kept at room temperature.

2.2. Preparation of dye solution

Malachite green MS dye ($C_{52}H_{54}N_4O_{12}$) was obtained from Merck, Germany, with a purity of 90% (Figure 1). The average molecular weight was 927.02. One gram was dissolved in 1 L of deionized water (1 g L^{-1}) to prepare a stock solution of the dye. The stock solution was diluted to obtain different dye concentrations (5, 10, 15, 20, 25, 30, and 35 mg L^{-1}).

2.3. Effect of different parameters on dye removal

The optimal conditions for the highest removal rate of dye from an aqueous solution were studied. For these, 100 mL of aqueous solution of dye (5 mg L^{-1}) was placed in Erlenmeyer flasks and 0.1 g of biomass was added. The influence of pH, temperature, contact time, and algal biomass on the removal of the dye was investigated. The effect of pH (2.0–10) was determined, and the value of pH was amended by using hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). The effect of temperature on the removal of the dye was tested using different temperatures (25, 35, 45, and 50 °C). The influence of contact time was estimated at different times, ranging from 0.0 to 180 min. To study the influence of adsorbent concentrations on dye removal from aqueous solution, varying weights of algae biomass (0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g L^{-1} dye solution) were used. The biomass was discarded by centrifugation

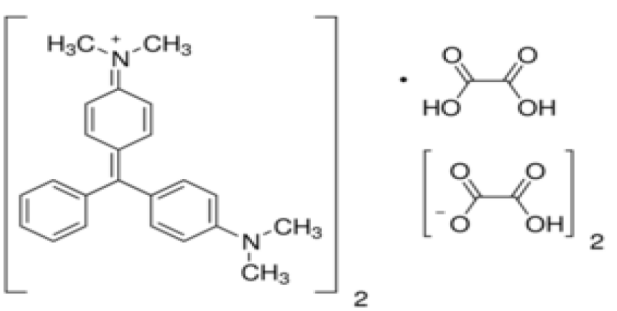

Figure 1. Chemical structure of malachite green dye.

and the dye concentration was determined in the solution before and after removal of the dye by measuring the absorbance at 616 nm using a UV spectrophotometer (Shimadzu, UV-1800, Japan). The percentage removal of dye was estimated by using Eq. (1):

$$\text{Dye removal \%} = (C_i - C_e) / C_i \times 100 \quad (1)$$

Here, C_i is the initial dye concentration in the aqueous solution and C_e is the equilibrium dye concentration expressed as mg L^{-1}.

Values were expressed as means of three replicates determinations ± standard deviation.

2.4. Adsorption isotherms

Adsorption isotherms were estimated at the optimal conditions (pH, temperature, contact time, and adsorbent concentration) for the maximum removal of dye from an aqueous solution by using different concentrations of dye (5–35 mg L^{-1}). The Langmuir (1918), Freundlich (1906), and Temkin (Temkin and Pyzhev, 1940) isotherm models were used. The Langmuir isotherm model is applied to monolayer adsorption and the Freundlich model is used to describe nonideal sorption on heterogeneous surfaces, as well as multilayer sorption. The Temkin isotherm model takes into account all the indirect adsorbent–adsorbate interactions.

The linearized form of the Langmuir model is expressed in Eq. (2):

$$1/q_e = 1/q_m + 1/bq_m (1/C_e) \quad (2)$$

Here, q_e is the value of dye uptake onto biomass in mg g^{-1}, q_m is the constant of Langmuir representing the maximum capacity (mg g^{-1}), and b is the Langmuir constant and belongs to the binding site affinity (L mg^{-1}). C_e is the dye concentration at equilibrium in the solution (mg L^{-1}). The value of intercept $1/bq_m$ and the slope of $1/q_m$ for adsorption of MG onto biomass was obtained from plotting the relation between $1/q_e$ and $1/C_e$.

The linearized form of the Freundlich model is represented in Eq. (3):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (3)$$

Here, q_e is the value of dye adsorbed onto biomass at equilibrium (mg g^{-1}), K_F is an indication of the adsorption ability and represents the relative adsorption ability (mg g^{-1}), n is a constant that belongs to sorption intensity, and C_e is the dye concentration at equilibrium (mg L^{-1}).

The Temkin model is applied using Eq. (4):

$$q_e = \text{RT}/b_T \ln A_T + \text{RT}/b_T \ln C_e \quad (4)$$

Here, R is the universal gas constant, T is the absolute temperature, b_T is the Temkin constant related to heat of sorption (J mol^{-1}), A_T is the Temkin isotherm constant (L g^{-1}), and RT/b_T = B, where B is a constant related to the heat of adsorption (J mol^{-1}). A_T and b_T are constants for adsorption of dye onto the biomass and were estimated from the slope and intercept of the plot obtained by plotting q_e versus ln C_e.

2.5. Thermodynamic study

The free energy of the sorption reaction was represented by Eq. (5):

$$\Delta G° = -\text{RT} \ln K_c \quad (5)$$

Here, $\Delta G°$ is the change in free energy (kJ mol^{-1}), R is the gas constant (8.314 kJ mol^{-1}), T is the absolute temperature, and K_c is the equilibrium constant.

The thermodynamic values including the change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were calculated by the change of temperature with the equilibrium constant as shown in Eq. (6):

$$\ln K_c = -\Delta H°/\text{RT} + \Delta S°/\text{R} \quad (6)$$

2.6. Infrared spectroscopy

An infrared spectrophotometer (Tensor 27, Bruker, the Netherlands) was used to study the functional groups on the surface of the biomass.

2.7. Scanning electron microscopy

The biomass surface was scanned before and after treatment with the dye by using a scanning electron microscope. SEM images were obtained by using a JEOL (JSM-5200 LV, USA) microscope.

3. Results

3.1. Effect of pH

The results showed that the removal of MG dye (5 mg L^{-1}) increased with increasing pH from 2.0 up to 10 by using the tested algal biomasses (0.1 g 100 mL^{-1}) after 1 h of sorption (Figure 2). Maximum removal of dye by the biomass of *S. crassifolium* (95.6%), *U. lactuca* (93.8%), and *G. corticata* (92.5%) was observed at pH 8.0 and the adsorption was approximately constant at a pH of <8.0. However, minimum percentage removal of MG ranged from 80.9% to 89% at pH 2.0 and 4.0.

3.2. Effect of temperature

Figure 3 represents the removal percentage of MG dye by using different biomasses at different temperatures of 25, 35, 45, and 55 °C after 1 h of sorption. The increase in temperature from 25 to 55 °C led to a decrease in the removal efficiency of dye from 94.5% to 91.9%, from 95.7%

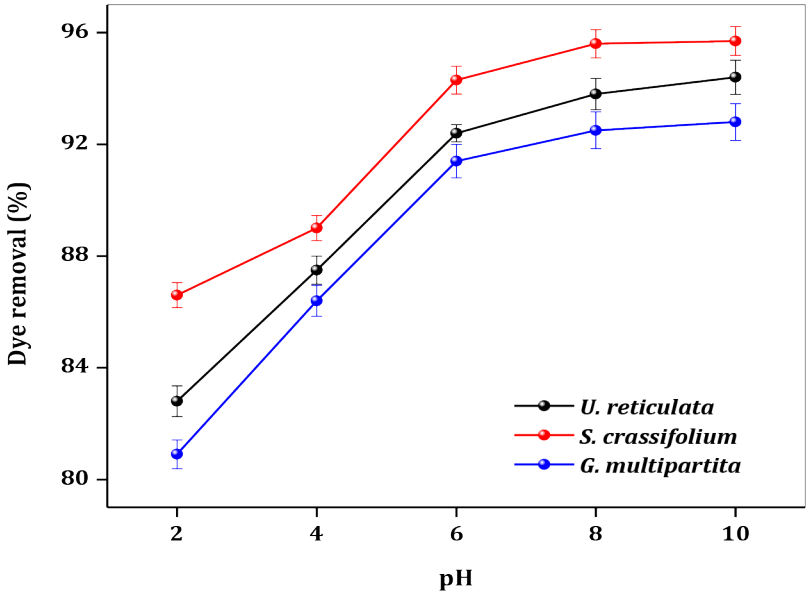

Figure 2. Removal of malachite green dye under the effect of different pH values by using marine macroalgae biomass. Data represented as mean ± SD (n = 3).

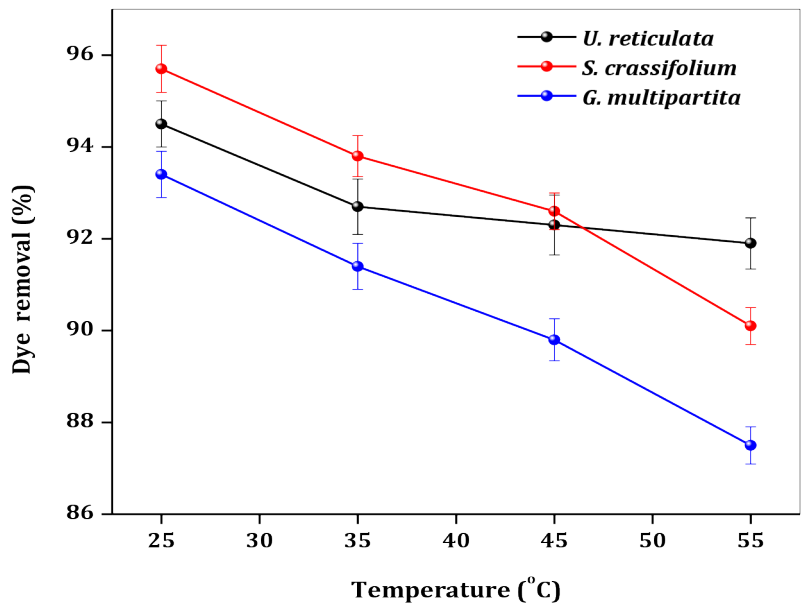

Figure 3. Removal of malachite green dye under the effect of different temperatures by using marine macroalgae biomass. Data represented as mean ± SD (n = 3).

to 90.1%, and from 93.3% to 87.5% by using the biomass of *U. lactuca*, *S. crassifolium*, and *G. corticata*, respectively. The removal of dye was found to be maximum at 25 °C and minimum at 55 °C by using the algal biomasses.

3.3. Contact time

The effect of contact time (0.0–180 min) between the algal biomass and MG dye on removal efficiency is shown in Figure 4. The removal of dye by *U. lactuca*, *S. crassifolium*, and *G. corticata* increased quickly during the first 10 min (67%, 75%, and 62%, respectively), then increased moderately at 45 min (91%, 93%, and 89%) and finally reached equilibrium (97%, 98%, and 96%) after 150 min.

3.4. Weight of biomass

The effect of different weights of algal biomasses (0.5–3.0 g) on the uptake of dye from the solution was tested (Figure 5). The results showed that the removal of dye

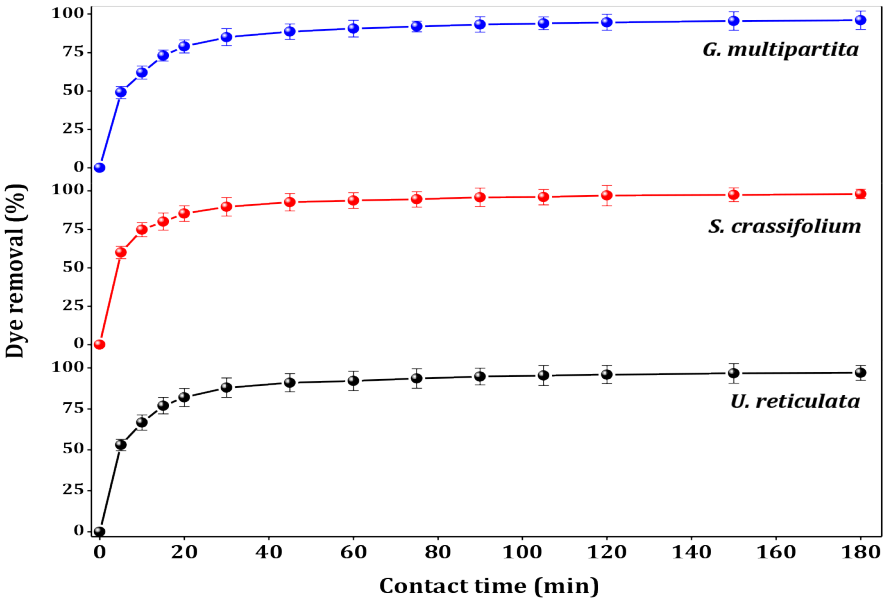

Figure 4. Removal of malachite green dye under the effect of contact time by using marine macroalgae biomass. Data represented as mean ± SD (n = 3).

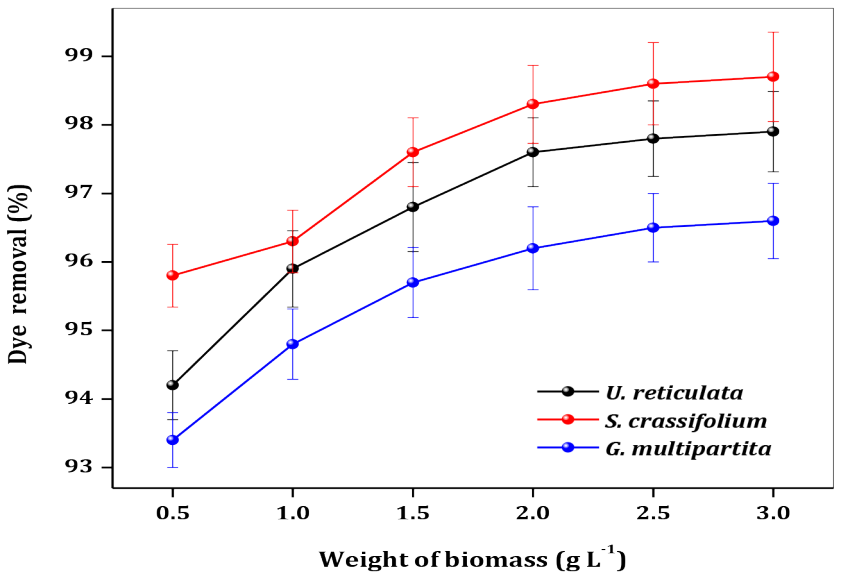

Figure 5. Removal of malachite green dye under the effect of different weights of marine macroalgae biomasses. Data represented as mean ± SD (n = 3).

increased with increasing weight of biomass up to 2.0 g. The maximum removal of dye (97.8%, 98.3%, and 96.2%) was obtained by 2.0 g of *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively. Further increase in biomass weight did not increase the rate of dye removal.

3.5. Dye concentration

The effect of different dye concentrations (5–35 mg L^{-1}) on the removal of MG dye at the optimum conditions of pH (8.0), temperature (25 °C), weight of biomass (2.0 g), and contact time (150 min) is illustrated in Figure 6. The results showed that the removal percentage of dye by algae decreased with increasing dye concentration. The minimum dye removal rates were 73.0%, 77.1%, and 69.0% by using *U. lactuca*, *S. crassifolium*, and *G. corticata*, respectively.

3.6. Adsorption isotherms

As shown in Table 1, the Langmuir isotherm data revealed that maximum capacities (q_m) were 42.30, 43.40, and 41.22

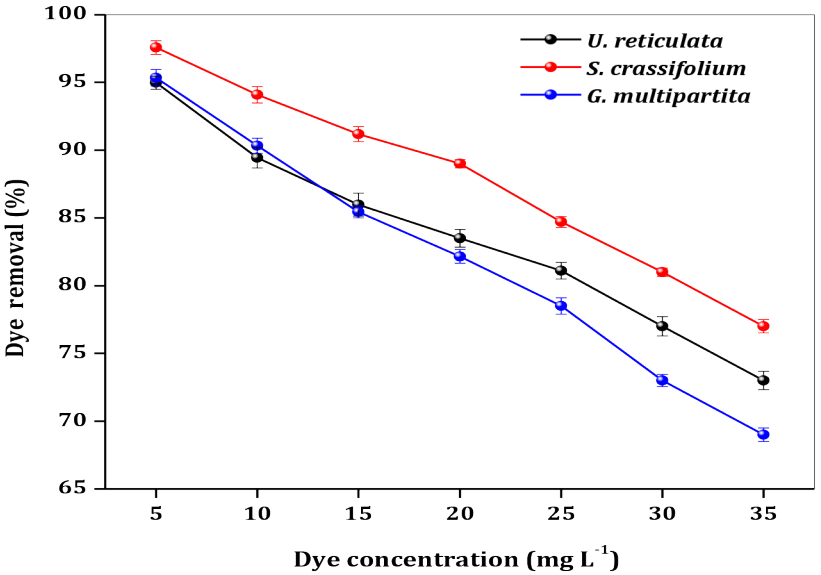

Figure 6. Removal of different concentrations of malachite green dye by using marine macroalgae biomass. Data represented as mean ± SD (n = 3).

Table 1. Langmuir, Freundlich, and Temkin isotherm parameters for removal of malachite green dye by using marine macroalgae biomasses.

Algae	Langmuir				Freundlich			Temkin			
	q_m (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_F (mg g^{-1})	n	R^2	A_T (L mg^{-1})	b_T	B (J mol^{-1})	R^2
U. reticulata	42.30	0.220	0.115	0.995	9.24	1.83	0.990	1.76	232	10.68	0.984
S. crassifolium	43.40	0.228	0.111	0.998	9.43	1.88	0.996	1.77	243	10.19	0.985
G. corticata	41.22	0.150	0.161	0.992	8.22	1.65	0.985	1.35	211	11.74	0.980

mg g^{-1} for *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively. Affinity with the binding site (b) was 0.220, 0.228, and 0.150 L mg^{-1}, respectively. The Langmuir constant (b) was used to show the affinity of adsorbent to adsorbate through R_L (dimensionless separation factor). R_L was expressed as follows (Malik, 2004):

$$R_L = 1/(1 + bC_o)$$

R_L indicates that the shape of the isotherm may be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).

The values of R_L for *U. reticulata*, *S. crassifolium*, and *G. corticata* were 0.115, 0.111, and 0.161, respectively, clarifying that the removal process of MG dye by using algal biomasses is favorable (Table 1). As seen from the results, the brown alga *S. crassifolium* was found to be more favorable for MG removal than the other tested algae.

The Freundlich isotherm showed that the plot of ln q_e versus ln C_e gives a straight line with a slope of 1/n and intercept of ln K_F for adsorption of MG dye by using algae. The values of n were found as 1.83, 1.88, and 1.65 for *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively (Table 1). The adsorption capacities (K_F) were 9.24, 9.43, and 8.22 mg g^{-1} for *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively. K_F for *S. crassifolium* was highest as compared with the other tested biomasses.

The results in Table 1 show that A_T was 1.76, 1.77, and 1.35 L mg^{-1} for *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively, according to the Temkin isotherm. The b_T values were 232, 243, and 211 for *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively. B values for these algae were 10.68, 10.19, and 11.74 J mol^{-1}, respectively.

According to the Langmuir, Freundlich, and Temkin isotherms (Table 1), the correlation coefficients (R^2) of

the *S. crassifolium* biomass have the highest values (0.998, 0.996, and 0.985, respectively), followed by *U. reticulata* (0.995, 0.990, and 0.984, respectively) and *G. corticata* (0.992, 0.985, and 0.980, respectively). It can be observed that the presented algae possess a great ability for removal of dye and consequently decrease the toxic effect of the dye in solution.

3.7. Thermodynamic study

Thermodynamic values are given in Table 2. $\Delta G°$ was estimated as –6.1 kJ mol^{-1}, –6.4 kJ mol^{-1}, and –5.9 kJ mol^{-1} for the biomasses of *U. reticulata*, *S. crassifolium*, and *G. corticata*, respectively. The values of $\Delta H°$ and $\Delta S°$ for *U. reticulata* (–8.75 kJ mol^{-1} and –8.04 kJ mol^{-1}), *S. crassifolium* (–7.20 kJ mol^{-1} and –2.50 kJ mol^{-1}), and *G. corticata* (–19.73 kJ mol^{-1} and –43.82 kJ mol^{-1}) are presented in Table 2.

3.8. IR spectral analysis

The IR spectral analysis of the *U. reticulata* cell wall (Figure 7a) showed different functional groups at 3422 cm^{-1} (υOH and υNH), 2924 cm^{-1} (υCH), 1638 and 1428 cm^{-1} (υCOO$^-$), 1638 and 1531 cm^{-1} (amide I and amide II), 1241 cm^{-1} (υSO$_3$), 1156 cm^{-1} [υC-O (ether)], and 1027 cm^{-1} [υC-O (alcohol)]. The IR spectra after dye removal (Figure 7b) showed changes in the position of the adsorption peak at 1638 cm^{-1}, 1428 cm^{-1}, and 1531 cm^{-1} due to υCOO$^-$, amide I, and amide II.

The IR spectral analysis of *S. crassifolium* biomass before dye treatment (Figure 8a) clarified the presence of adsorption bands on the cell wall at 3447 cm^{-1} (υOH and υNH), 2927 cm^{-1} (υCH), 1634 and 1442 cm^{-1} (υCOO$^-$), 1250 cm^{-1} (υSO$_3$), 1161 cm^{-1} [υC-O (ether)], and 1027 cm^{-1} [υC-O (alcohol)]. The position of adsorption peaks at υOH and υC = O of the algae changed after dye treatments (Figure 8b), which confirms the involvement of these groups in dye removal.

On the other hand, IR spectra for *G. corticata* (Figure 9a) revealed the appearance of adsorption bands on the cell surface at 3424 cm^{-1} (υOH and υNH), 1649 cm^{-1} (υC = O), 1458 cm^{-1} (υNH amide I), 1381 cm^{-1} (amide II), 1256 cm^{-1} (υSO$_3$), 1157 cm^{-1} [υC-O (ether)], and 1067 cm^{-1} [υC-

Table 2. Thermodynamic parameters and activation energy for removal of malachite green dye by using marine macroalgae biomasses.

Algae	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1})
U. reticulata	–6.1	–8.75	–8.04
S. crassifolium	–6.4	–7.20	–2.50
G. corticata	–5.9	–19.73	–43.82

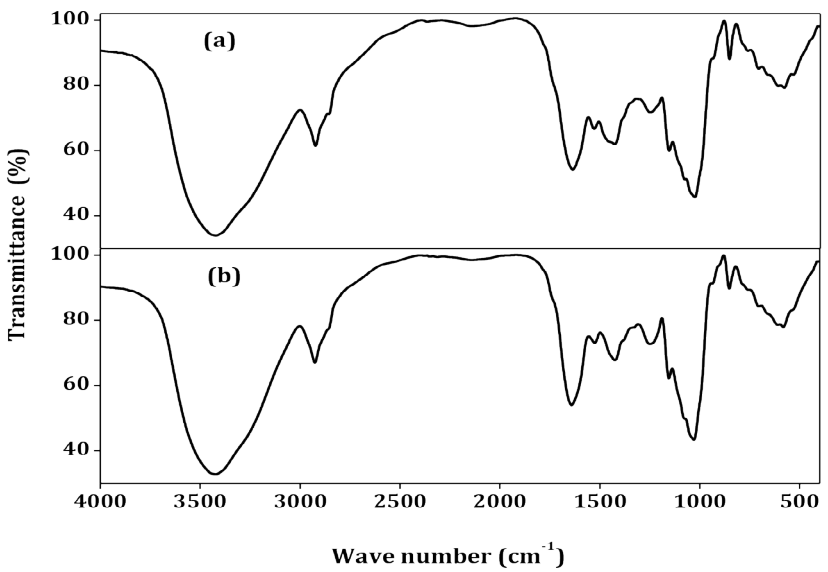

Figure 7. FT-IR spectrum of *U. reticulata* before (a) and after (b) malachite green dye treatment.

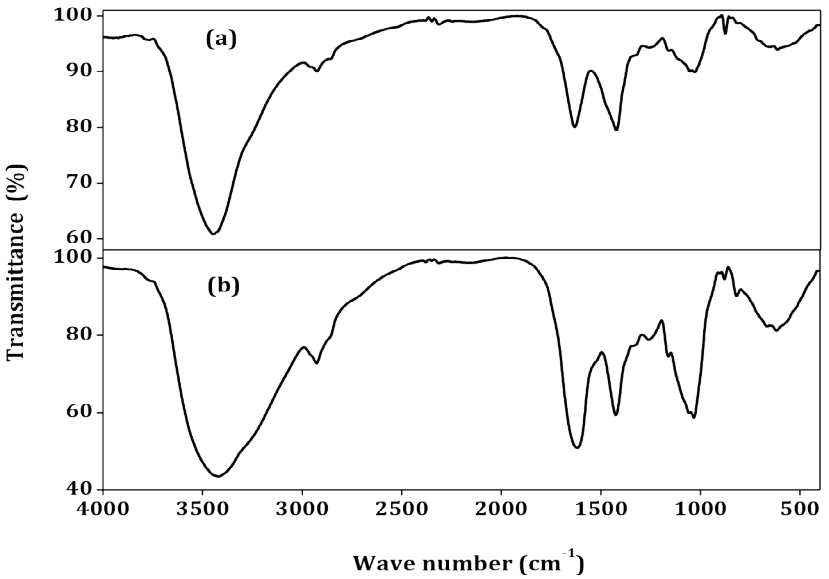

Figure 8. FT-IR spectrum of *S. crassifolium* before (a) and after (b) malachite green dye treatment.

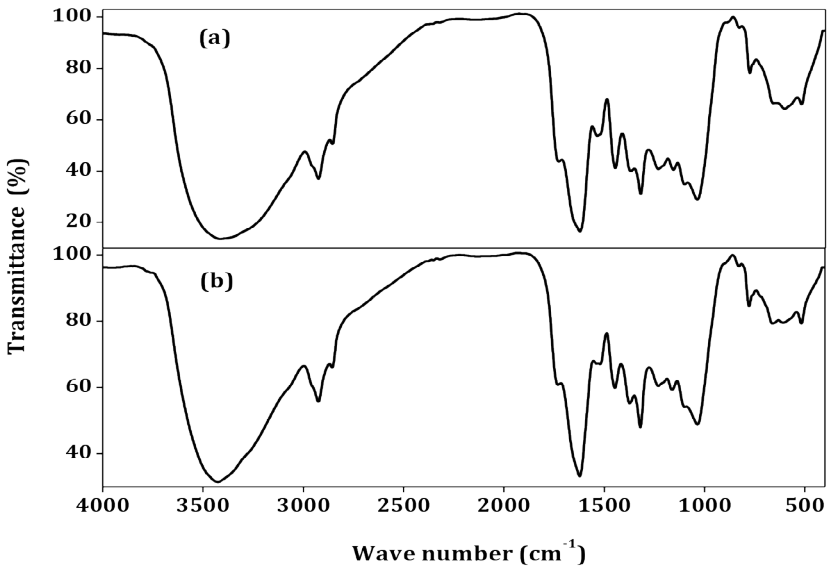

Figure 9. FT-IR spectrum of *G. corticata* before (a) and after (b) malachite green dye treatment.

O (alcohol)]. The change in adsorption position for υC = O of an amide group was observed after biosorption of MG onto the tested biomass (Figure 9b), which indicates the involvement of these groups in dye biosorption.

The results of IR analysis clarified that intermolecular interactions between MG and the tested algae were as follows: 1) ionic between the negative charge on the carboxylate group and MG as a cationic dye, 2) the coordinate bond between the lone pair of electrons on the OH group or NH_2 group and MG, 3) van der Waals forces between nonpolar groups of both MG and algae, and 4) ion–dipole bond between the negative dipole end of the carbonyl group and MG.

3.9. Scanning electron microscopy

An assessment of the morphological changes in cells of *U. lactuca*, *S. crassifolium*, and *G. corticata* biomasses in response to dye adsorption was performed by SEM (Figure 10). The cells of algae were smooth with a highly porous

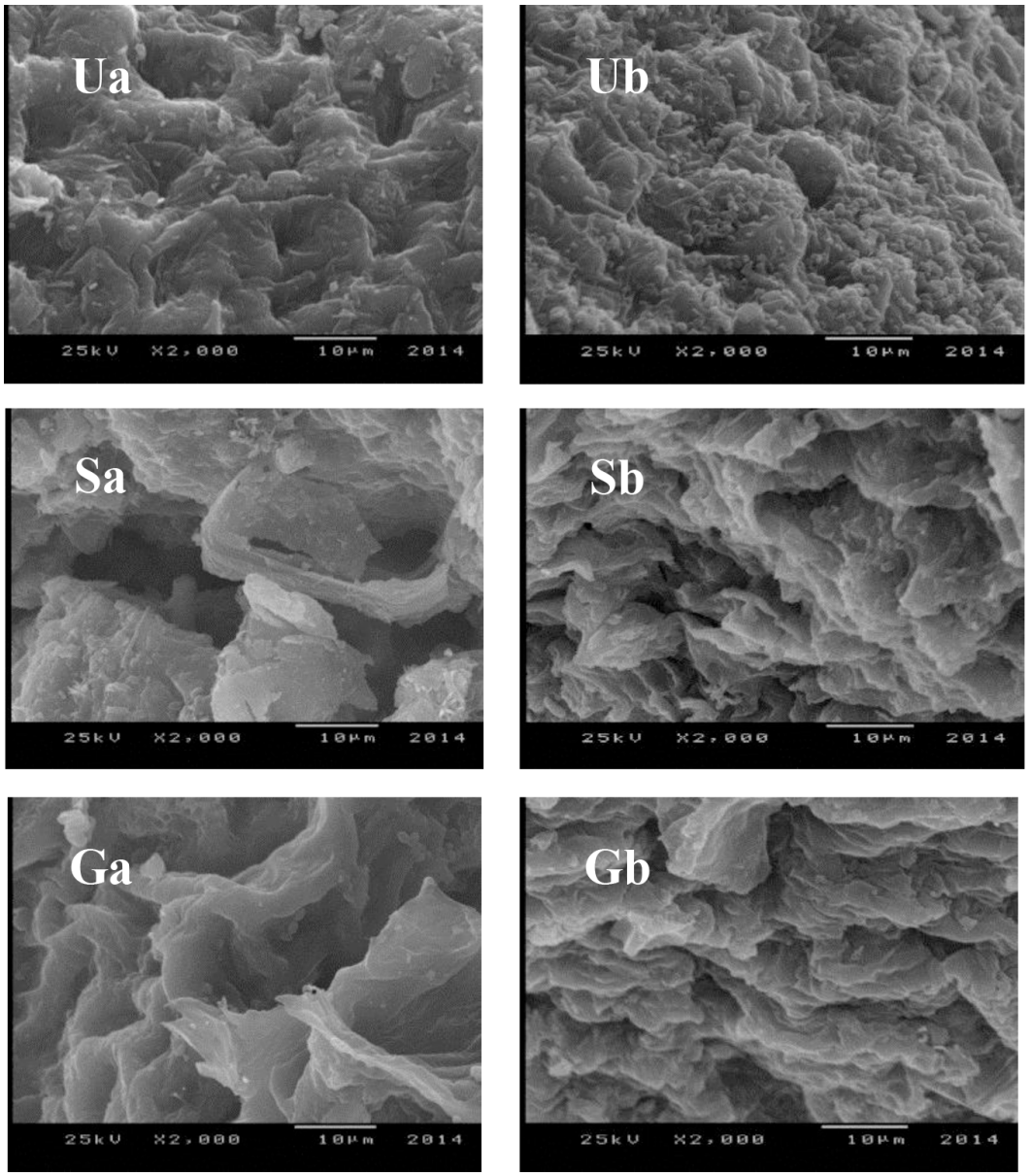

Figure 10. Scanning electron microscopy of the surface of *U. lactuca* (U), *S. crassifolium* (S) and *G. corticata* (G) before (a) and after (b) malachite green dye treatment.

structure that was hole-like before exposure to MG dye (Figure 10, Ua, Sa, and Ga). After exposure of the biomass cells to the dye ions, the surface became rough and meandrous due to precipitation of dye ions around the cell surface (Figure 10, Ub, Sb, and Gb).

4. Discussion

The present study clarified that the removal of MG dye by using algal biomass is affected by pH. The removal of dye was increased to some extent by increasing the pH. Maximum removal of the dye was observed at pH 8.0. Anbia and Ghaffari (2011) found that the removal of dye by adsorbent mass decreased at low pH and increased at pH 8.0–10. Belloa et al. (2014) showed that 95.06% of MG was removed at pH 8.0 by using *Citrus grandis*. The pH of the solution affects the removal process; this is related to the disintegration of functional groups, the degree of ionization of the dye, and the active sites of the biomass (Nandi et al., 2009). The high rate of removal of the dye at pH 8–10 may be due to changes in the structure of MG molecules, as mentioned by Sun and Tomkinson (2001). Maurya et al. (2006) found that the increase in dye

removal by using dead biomass was due to deprotonating of the different functional groups. At acidic pH, the low adsorption of MG by the tested algal biomass may be related to the competition between the abundant hydrogen ions and dye cations for the adsorption sites of the algae (Punjongharn et al., 2008).

The removal rate of the dye from an aqueous solution by using the algal biomass decreased with increasing temperature. A similar result was obtained by Chiou and Li (2002), who concluded that the removal of the dye decreased with increasing temperature in solution. Deokar (2016) showed that the greatest removal of the dye by green algae (*Enteromorpha intestinalis*) was observed at room temperature. This result may be due to the weak linkage between active sites of the biomass and dye molecules at high temperatures. In addition, the active binding sites of the biomass may be damaged by raising the temperature.

The removal rate of MG dye was found to increase with increasing contact time and reached equilibrium at 150 min. Daneshvar et al. (2012) showed that the removal of dye by algae rapidly increased during the first 10 min and approached equilibrium within 90 min. The differences in removal rates between the algal biomasses may be due to the differences in the structure and properties of the algal cell wall, surface area, and density of surface charge (Gupta and Rastogi, 2009). The initial rapid phase may include ion exchange or physical adsorption at the cell surface. However, the slower phase may involve other mechanisms such as saturation of binding sites and complexity or microprecipitation (Gupta and Rastogi, 2009). The results suggest that there is high affinity and a strong electrostatic force of attraction between the functional groups on the surface wall of algae and the MG dye (Cengiz and Cavas, 2008).

From the results, it can be observed that the removal efficiency of the dye generally improved with increasing algal biomass and reached equilibrium at 2.0 g of biomass. Ruangsomboon et al. (2013) reported that the removal of MG decreased from 8.60 to 0.77 mg g^{-1} when the *Padina* sp. biomass was increased from 0.5 to 6 g L^{-1}. Biosorption of MG by freshwater alga *Pithophora* sp. decreased from 42.2 mg g^{-1} to 9.2 mg g^{-1} with an increase in biomass concentration from 0.02 g to 0.06 g, whereas the percentage of MG removal increased from 57.8% to 90.8% (Kumar et al., 2006). Kannan et al. (2010) reported that the amount of dye adsorbed varied with initial adsorbent (*Turbinaria conoides*) dosage. The amount of dye adsorbed decreased from 41.5 to 28.46 mg g^{-1} with an increase in biomass dosage from 0.25 to 0.55 g. Jayaraj et al. (2011) showed that the percentage removal of MG dye by using the marine alga *Enteromorpha* (50–350 mg) increased with adsorbent dose. Cengiz and Cavas (2008) recorded a sharp increase in the adsorbed dye by increasing the dose of *Caulerpa racemosa* var. *cylindracea*. Similar results were obtained for dye removal using *Cystoseira barbatula* (Caparkaya and Cavas, 2008) and *Chaetophora* sp. (El Jamal and Ncibi, 2012). At lower biomass doses, the removal efficiency decreased due to the rapid saturation of adsorption sites with ions of the dye. Deokar (2016) reported that when the biomass concentration is lower, the active sites are effectively utilized. Indhumathi et al. (2014) observed that the removal percentage increases rapidly with the increase in the dose of adsorbents. This is due to a greater availability of surface area with increased amount of biomass; some of the available active sites may remain uncovered leading to a lower specific uptake. Moreover, the percentage of adsorption of the adsorbent is determined by the adsorption capacity of the adsorbents (Ponnusami et al., 2009).

The removal percentage of MG dye by using algal biomass decreased with increasing dye concentration. Khaled et al. (2005) showed an increase in the removal of the dye by *Ulva lactuca* with increasing dye concentration. Tahir et al. (2008) showed an improvement in the removal of the dye by *Ulva lactuca* and *Sargassum* species. They also observed that the adsorption was dependent on initial dye concentration; as the concentration increased, the uptake increased. This result may be due to the increase in the mass gradient pressure between the biomass and the solution (Hameed, 2009). The gradient acts as the force that drives the dye molecules from the solution to the surface of the biomass. The reduction in adsorption capacity with increasing dye concentration may be due to the high concentration of the dye compared to the biomass dosage (Chen and Zhao, 2009). The available sites of adsorption decrease at high dye concentrations, and consequently the removal of dye is related to the initial dye concentration.

The adsorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of adsorbate that remained in the solution at equilibrium time. The Langmuir isotherm refers to homogeneous monolayer adsorption. According to the results of the Langmuir isotherm, the biomass of *S. crassifolium* had the highest affinity of the binding site (b) towards MG dye.

At the same time, the low values of R_L clarified that the removal process of MG dye by using algal biomasses was favorable. The lowest value of R_L means high adsorbent to adsorbate affinity (Jelínek et al., 2015).

The Freundlich isotherm discusses the heterogeneous surfaces of multilayer adsorption. Generally, $n > 1$ means that the MG dye is favorably adsorbed onto the biomass. Accordingly, the biomass of *S. crassifolium* could have the maximum adsorption capacity and the highest binding affinity with MG dye, followed by *U. reticulata* and *G. corticata*.

The Temkin isotherm investigated the influence of some indirect interactions of sorbate (biomass)/adsorbate (dye) on the isotherm of adsorption and proposed that the heat of molecule adsorption decreased linearly in the layer. The low values of B (constant related to the heat of adsorption) indicated the presence of a weak interaction between sorbent and adsorbate.

The values of R^2 were used as the fitting criteria for comparing the Langmuir, Freundlich, and Temkin isotherms. Based on the high correlation coefficient values (R^2), the Langmuir and Freundlich models were found to be more favorable for explaining the adsorption behavior of MG dye onto the tested biomass. On the other hand, both homogeneous and heterogeneous adsorption energies occurred during the process. In agreement with our results, Jayaraj et al. (2011) showed that the adsorption of MG dye onto *Ulva lactuca* and *Enteromorpha* was fitted with the Langmuir and Freundlich adsorption isotherms. However, Ramya et al. (2016) found that the adsorption of MG dye onto the mass follows the Langmuir adsorption isotherm model only. At the same time, Hii et al. (2011) confirmed that the high values of the correlation coefficient of both the Langmuir and Freundlich models ($R^2 > 0.95$) are favorable for characterization of the sorption of the dye by red alga *Aristaeomorpha foliacea*. The application of both the Langmuir and Freundlich isotherms to the sorption study indicated that the *A. foliacea* biomass might exhibit both monolayer adsorption and heterogeneous surface conditions (Kumari and Abraham, 2007).

Thermodynamic study can be used to predict the feasibility of the adsorption process. The negative values of $\Delta G°$ showed that MG adsorption onto the tested algae was a spontaneous and highly favorable process. The highest affinity of the brown alga *S. crassifolium* for removal of the dye may be attributed to the highest negative $\Delta G°$ value recorded for the sorption reaction of *S. crassifolium* compared to the corresponding $\Delta G°$ values for *U. reticulata* and *G. corticata*. The negative values of $\Delta H°$ indicated that biosorption is an exothermic process, and the negative $\Delta S°$ values represent the decreasing randomness during the removal process of the solid/liquid interface. These results may explain the greatest ability of *S. crassifolium* biomass for removal of MG dye. The negative value of $\Delta G°$ for all temperatures suggested that adsorption was a spontaneous process (Fil, 2016). The negative value of $\Delta S°$ clarified a tendency to lower disorder at the solid–solution interface during the adsorption process (Nethaji et al., 2010). Also, the negative value of $\Delta H°$ in the present study indicated that dye adsorption by using the tested algae was exothermic. Boundary layer thicknesses decreased at a very high temperature due to the increase in dye molecules getting away from the adsorbent surface to the solution (Saha et al., 2010).

According to IR spectral analysis the changes in the position of functional groups of algal biomasses after dye treatment establish the participation of these groups in MG removal. The algal cell walls contain a high amount of polysaccharides; some of them are associated with proteins and other components (Williams and Edyvean, 1997; Tüzün et al., 2005). These molecules on the algal cell surface have several functional groups such as carboxyl, amino, phosphate, thiol, and sulfhydryl groups (Tüzün et al., 2005). From the present results, it is assumed that the dye was integrated with the adsorbent through interaction with the active functional groups, as supposed by Jayaraj et al. (2011).

The morphological changes of the tested algal surface after dye adsorption may be attributed to the differences in pores, morphology, and structure of the cell walls of algae. The cell wall of *S. crassifolium* was very porous and easily permeable to ions. This may explain the highest affinity of *S. crassifolium* biomass for removal of MG dye. Deokar (2016) and Fakhry (2013) recorded changes in surface porosity of algae due to dye adsorption.

It can be concluded that the biomass of green, brown, and red marine algae may facilitate the removal of MG from polluted water. The removal of dye is dependent on the dye concentration, algal concentration, temperature, and pH. The experimental data correlated well with the Langmuir and Freundlich adsorption isotherms. The negative $\Delta G°$ values indicated that the algae employed have noticeable potential as adsorbents for the removal of MG dye. Undoubtedly, marine macroalgae perform well and offer many promising benefits for commercial purposes in the future.

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References

Anbia M, Ghaffari A (2011). Removal of malachite green from dye wastewater using mesoporous carbon adsorbent. J Iran Chem Soc 8: 67-76.

Belloa OS, Azmier M, Semire B (2014). Scavenging malachite green dye from aqueous solutions using pomelo (*Citrus grandis*) peels: kinetic, equilibrium and thermodynamic studies. Desalination and Water Treatment 56: 1-15.

Caparkaya D, Cavas L (2008). Biosorption of methylene blue by a brown alga *Cystoseira barbatula* Kützing. Acta Chim Slov 55: 547-553.

Cengiz S, Cavas L (2008). Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. *cylindracea*. Bioresource Technol 99: 2357-2363.

Chen H, Zhao J (2009). Adsorption study for removal of Congo red anionic dye using organo-attapulgite. Adsorption 15: 381-389.

Chiou MS, Li HY (2002). Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. J Hazard Mater 93: 233-348.

Culp SJ, Blankenship LR, Kusewitt DF, Doerge DR, Mulligan LT, Beland FA (1999). Toxicity and metabolism of malachite green and leucomalachite green during short-term feeding to Fischer 344 rats and B6C3F1 mice. Chem-Biol Interact 122: 153-170.

Daneshvar E, Kousha M, Jokar M, Koutahzadeh N, Guibal E (2012). Acidic dye biosorption onto marine brown macroalgae: Isotherms, kinetic and thermodynamic studies. Chem Eng J 204: 225-234.

Daneshvar N, Ayazloo M, Khataee AR, Pourhassan M (2007). Biological decolorization of dye solution containing malachite green by microalgae *Cosmarium* sp. Bioresource Technol 98: 1176-1182.

Davis TA, Volesky B, Mucci A (2003). A review of the biochemistry of heavy metal biosorption by brown algae. Water Res 37: 4311-4330.

Deokar RR (2016). *Enteromorpha intestinalis*: low cost biosorbents for biosorption methylene blue. International Journal of Recent Scientific Research 7: 9291-9297.

Doerge DR, Chang HC, Divi RL, Churchewell MI (1998). Mechanism for inhibition of thyroid peroxidase by leucomalachite green. Chem Res Toxicol 11: 1098-1104.

El Jamal MM, Ncibi MC (2012). Biosorption of methylene blue by *Chaetophora Elegans* algae: kinetics, equilibrium and thermodynamic studies. Acta Chim Slov 59: 24-31.

Fakhry EM (2013). *Padina pavonica* for the removal of dye from polluted water. American Journal of Plant Sciences 4: 1983-1989.

Fessard V, Godard T, Huet S, Mourot A, Poul JM (1999). Mutagenicity of malachite green and leucomalachite green in in vitro tests. J Appl Toxicol 19: 421-430.

Fil BA (2016). Isotherm, kinetic, and thermodynamic studies on the adsorption behavior of malachite green dye onto montmorillonite clay. Particul Sci Technol 34: 118-126.

Freundlich HMF (1906). Over the adsorption in solution. J Phys Chem 57: 358-371.

Gupta VK, Rastogi A (2009). Biosorption of hexavalent chromium by raw and acid treated green alga *Oedogonium hatei* from aqueous solutions. J Hazard Mater 163: 396-402.

Hameed BH (2009). Spent tea leaves: a new nonconventional and low-cost adsorbent for removal of basic dye from aqueous solutions. J Hazard Mater 161: 753-759.

Hammud HH (2011). Biosorption studies of methylene blue by Mediterranean algae *Carolina* and its chemically modified forms. Linear and nonlinear models' prediction based on statistical error calculation. International Journal of Chemistry 3: 147-163.

Hecht T, Endemann F (1998). The impact of parasites, infections and disease on the development of aquaculture in sub-Saharan Africa. J Appl Ichthyol 14: 213-221.

Hii SL, Estrop LL, Wong CL (2011). Adsorption of reactive blue 4 onto the chemically modified red seaweed *Amphiroa foliacea*: equilibrium, kinetics and modeling studies. Int J Phys Sci 6: 7171-7182.

Indhumathi P, Syed Shabudeen PS, Shoba US, Saraswathy CP (2014). The removal of chromium from aqueous solution by using green micro algae. Journal of Chemical and Pharmaceutical Research 6: 799-808.

Jayaraj R, Mohan MC, Prasath PMD, Khan TH (2011). Malachite green dye removal using the seaweed *Enteromorpha*. E-Journal of Chemistry 8: 649-656.

Jelínek L, Procházková G, Quintelas C, Beldíková E, Brányik T (2015). *Chlorella vulgaris* biomass enriched by biosorption of polyphenols. Algal Research 10: 1-7.

Kannan RR, Rajasimman M, Rajamohan N, Siaprakash B (2010). Brown marine algae *Turbinaria conoides* as biosorbent for malachite green removal: equilibrium and kinetic modeling. Frontiers of Environmental Science & Engineering in China 4: 116-122.

Khaled A, Sikaily AE, Abelwahab O, Nemr AE (2005). Biosorption of basic blue nine from water solution by marine algae *Ulva lactuca*. Egyptian Journal of Aquatic Research 31: 130-141.

Kooh MRR, Dahri MK, Lim LBL (2016). The removal of rhodamine B dye from aqueous solution using *Casuarina equisetifolia* needles as adsorbent. Cogent Environmental Science 2: 1-14.

Kumar KV, Ramamurthi V, Sivanesan S (2006). Biosorption of malachite green, a cationic dye onto *Pithophora* sp., a fresh water algae. Dyes Pigments 69: 102-107.

Kumari K, Abraham TE (2007). Biosorption of anionic textile dyes by nonviable biomass of fungi and yeast. Bioresource Technol 98: 1704-1710.

Langmuir I (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40: 1361-1403.

Mahudawala DM, Redkar AA, Wagh A, Gladstone B, Rao KV (1999). Malignant transformation of Syrian hamster embryo (SHE) cells in culture by malachite green: an agent of environmental importance. Indian J Exp Biol 37: 904-918.

Malik PK (2004). Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. J Hazard Mater 113: 81-88.

Marungrueng K, Pavasant P (2007). High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal. Bioresource Technol 98: 1567-1572.

Maurya NS, Mittal AK, Cornel P, Rother E (2006). Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. Bioresource Technol 97: 512-521.

McKay G, Porter JF, Prasad GR (1999). The removal of dye colour from aqueous solutions by adsorption on low-cost materials. Water Air Soil Poll 114: 423-438.

Miranda RM, Gomes EB, Gouveia ER, Machad KG, Gusmao NB (2012). Decolorization of laundry effluent by filamentous fungi. Afr J Biotechnol 11: 4216-4224.

Nandi B, Goswami A, Purkait M (2009). Removal of cationic dyes from aqueous solutions by kaolin: kinetic and equilibrium studies. Appl Clay Sci 42: 583-590.

Nethaji S, Sivasamy A, Thennarasu G, Saravanan S (2010). Adsorption of malachite green dye onto activated carbon derived from *Borassus aethiopum* flower biomass. J Hazard Mater 181: 271-280.

Poe WE, Wilson RP (1983). Absorption of malachite green by channel catfish. Prog Fish Cult 45: 228-229.

Ponnusami V, Gunasekar V, Srivastava SN (2009). Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: multivariate regression analysis. J Hazard Mater 169: 119-127.

Punjongharn P, Meevasana K, Pavasant P (2008). Influence of particle size and salinity on adsorption of basic dyes by agricultural waste: dried sea grape (*Caulerpa lentillifera*). J Environ Sci 20: 760-768.

Ramya V, Vinayagam M, Murugan D, Lajapathirai C, Saravanan P, Sivasamy A (2016). Adsorption of malachite green onto chemically activated carbon prepared from waste biomass. International Journal of Innovative Research in Science, Engineering and Technology 5: 115-123.

Robinson T, McMullan G, Marchant R, Nigam P (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technol 77: 247-255.

Ruangsomboon S, Aue-Umneoy D, Saparnklang A (2013). Biosorption of basic dye, malachite green by brown alga *Padina* sp. International Conference on Information Science and Technology 56/96: 491-501.

Saha P, Chowdhury S, Gupta S, Kumar I (2010). Insight into adsorption equilibrium kinetics and thermodynamics of malachite green onto clayey soil of Indian origin. Chem Eng J 165: 874-882.

Singh J, Kaur G (2013). Freundlich, Langmuir adsorption isotherms and kinetics for the removal of malachite green from aqueous solutions using agricultural waste rice straw. International Journal of Environmental Sciences 4: 250-258.

Srivastava S, Sinha R, Roy D (2004). Toxicological effects of malachite green. Aquat Toxicol 66: 319-329.

Sun Q, Yang L (2003). The adsorption of basic dyes from aqueous solution on modified peat-resin particle. Water Res 37: 1535-1544.

Sun R, Tomkinson J (2001). Fractional separation and physicochemical analysis of lignins from the black liquor of oil palm trunk fiber pulping. Sep Purif Technol 24: 529-539.

Sundarrajan M, Frenandis AZ, Subrahmanyam G, Prabhudesai S, Krishnamurthy SC, Rao KV (2000). Overexpression of G1/S cyclins and PCNA and their relationship to tyrosine phosphorylation and dephosphorylation during tumor promotion by metanil yellow and malachite green. Toxicol Lett 116: 119-130.

Tahir H, Sultan M, Qazi J (2008). Removal of basic dye methylene blue by using bioabsorbents *Ulva lactuca* and *Sargassum*. Afr J Biotechnol 7: 2649-2655.

Temkin MJ, Pyzhev V (1940). Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physicochim URS 12: 217-222.

Tüzün İ, Bayramoğlu G, Yalçın E, Başaran G, Çelik G, Arıca MY (2005). Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto micro algae *Chlamydomonas reinhardtii*. J Environ Manage 77: 85-92.

Vijayaraghavan K, Yun YS (2008). Biosorption of C.I. reactive black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria* sp. Dyes Pigments 76: 726-732.

Williams CJ, Edyvean RGJ (1997). Ion exchange in nickel biosorption by seaweed materials. Biotechnol Progr 13: 424-428.