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Article

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Posted Date: May 8th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-9313150/v1

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Scientific Reports on August 11th, 2026.
See the published version at https://doi.org/10.1038/s41598-026-65458-9.

Sustainable biosorption of Methylene Blue using highly-efficient activated Mediterranean macroalgae: a comparative mechanistic study

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Abstract

Synthetic dyes, for instance methylene blue, are persistent water pollutants that withstand conventional methods applied for water treatment. This poses a high risk to ecosystems and public health. In this study, we investigated the biosorption efficiency of four marine macroalgae species, *Ulva lactuca*, *Ulva prolifera*, *Bryopsis*, and *Corallina*, collected from the Lebanese coastline, as low-cost local adsorbents for the removal of methylene blue from aqueous solutions. The algal biomasses were chemically pretreated with either $CaCl_2$, NaOH, or HCl to enhance their stability and adsorption performance. Batch experiments were conducted to evaluate the influence of pH, initial dye concentrations, biomass dosage, and contact time. Adsorption isotherms, described in terms of Langmuir and Freundlich, and kinetic models (*pseudo*-first-order, *pseudo*-second-order, and intraparticle diffusion) were used to analyze the data. All four algae exhibited efficient dye removal, with the maximum Langmuir adsorption capacity (Q_{max}) reaching an impressive 653 mg/g for *Ulva prolifera*. The optimal conditions were within pH ranges of 5 to 12, biosorbent dosage of 100 mg/L, and contact time of 90 min. Kinetic modeling revealed strong conformity with *pseudo*-first- and *pseudo*-second-order mechanisms of adsorption. Our work further highlights that marine macroalgae, particularly $CaCl_2$–treated *Ulva prolifera*, and to a lesser extent *Ulva lactuca*, demonstrate an outstanding potential as sustainable and low-cost biosorbent material for the removal of cationic dyes. These findings support their application in phycoremediation strategies for industrial wastewater treatment.

Keywords: Phycoremediation, Biosorption, Marine macroalgae, Methylene blue, Water treatment.

1. Introduction

The rapid expansion of industrial activity has led to an alarming increase in the discharge of synthetic dyes into aquatic environments.[1,2] Colored wastewater can absorb and reflect sunlight in ways that alter the solubility of gas concentrations, and hence seriously disturb aquatic life and the food chain.[3] Textiles usually serve as the primary emitter, although such chemicals are heavily used in paper, food, medical, and other industry products.[4] In particular, methylene blue (MB) has emerged as a widely used and persistent pollutant. It is commonly employed in the pharmaceutical, cosmetic, and textile industries, and despite its utility, its toxic and non-biodegradable nature poses significant ecological and health risks.[5] Prolonged exposure to MB disrupts aquatic photosynthesis, alters water chemistry, and negatively affects human and animal health through bioaccumulation.[6],[7] Traditional dye removal methods, such as chemical coagulation, oxidation, and activated carbon adsorption, often suffer from high operational costs, limited selectivity, and secondary pollution problems.[8] These limitations have prompted the exploration of eco-friendly and cost-effective alternatives that align with global environmental targets, such as the United Nations' sustainable development goals (SDG 6: Clean Water and Sanitation, and SDG 14: Life Below Water). In recent years, phycoremediation, the use of algae for pollutant removal—has gained prominence due to algae's high surface area, fast growth rates, and natural biosorption capabilities.[9,10] Macroalgae in particular offer a promising biosorbent matrix owing to their abundance of functional groups (e.g., hydroxyl, carboxyl, sulfate) which can effectively bind cationic dyes such as MB.[11,12] Furthermore, marine algae are widely available, renewable, and do not compete with food crops, making them ideal candidates for large-scale bioremediation systems.[13] The eastern Mediterranean sea, particularly the Lebanese coastal zone, is increasingly burdened by untreated industrial and domestic effluents.[14] However, this region is also home to a diverse population of native macroalgae that remain underexplored for their biotechnological potential and applications.[15] For example, Kanaan et al. identified ninety-four species of algae that grow along the Lebanese coast and established a map of collection sites for these algal species.[16]

This study aimed to evaluate and compare the biosorption efficiency of four marine macroalgae species—*Ulva lactuca*, also known as sea lettuce; *Ulva prolifera*, known as branched string lettuce; *Bryopsis hypnoides* (*Bryopsis*) often referred to as hair algae; and the red alga *Corallina officinalis* (of the *mediterranea* variety)—in the removal of MB dye under varying environmental conditions. By investigating the effects of pH, algal dosage, initial dye concentration, and contact time, and modeling the adsorption behavior using kinetic and isotherm equations, we aim to support and further establish the scientific basis for the deployment of marine algae in wastewater treatment systems. On the other

hand, studies have shown that chemically modified algae, i.e. pretreated biomass, have shown much promising results in terms of adsorption capacities and efficiency,[17] accordingly this study will focus on pretreated algal mass primarily.

2. Experimental

2.1. Collection and Identification of Algal Biomass

Four different species of marine algae, namely *Ulva Lactuca*, *Ulva Prolifera*, *Bryopsis Hypnoides* (i.e. *Bryopsis*), and *Corallina Officinalis* (i.e. *Corallina*), are shown in figure 1. They were collected from the Eastern Mediterranean coastline of the Lebanese capital city Beirut, at the Military Seaside resort, in November 2022. Identification of the species was carried out according to Belous and Kanaan (2016).[18] All samples were thoroughly washed with tap water, followed by deionized water to remove salts, epiphytes, and other debris from the samples. The cleaned algae were then shade-dried at room temperature for 4 months and further dried in an oven at 60°C for 24 h until a constant weight was achieved. The samples were then ground into a fine powder for further use.

Figure 1*: Images of the four different types of algae showing their collection sites at the Lebanese coastline, left to right: Ulva Lactuca, Ulva Prolifera, Bryopsis, and Corallina.*

2.2. Chemical Pretreatment of the Algae

To enhance the biosorption capacity, the dried biomass samples were chemically pretreated as follows. *Ulva lactuca* was divided into three portions and treated separately with 0.1 M sodium hydroxide (NaOH), 0.1 M hydrochloric acid (HCl), and 0.2 M calcium chloride ($CaCl_2$) which was found to be the most effective. All other algae (*Ulva prolifera, Bryopsis, and Corallina*) were pretreated with 0.2 M $CaCl_2$, accordingly. The biomass was soaked in the respective solutions with an agitator for 24 h at room temperature, filtered, washed repeatedly with distilled water, dried in an oven at 60°C for 24 h, ground, and finally stored in a desiccator for later use.

2.3. Preparation of Dye Solution

The stock solution of methylene blue, a cationic dye with a heterocyclic aromatic structure and an absorption maximum at λ_{max} = 664 nm, was prepared at a concentration of 1000 mg/L in distilled water using analytical-grade dye powder (provided by Sigma-Aldrich). Working solutions of different concentrations (1.25–900 mg/L) were prepared by serial dilution with distilled water.

2.4. Batch Biosorption Experiments

Experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of MB dye solution under various conditions: pH (1 to 12, adjusted using 0.1 M NaOH or HCl), algal biomass dose (10 to 400 mg/L), initial dye concentration (1.25 to 900 mg/L), and contact time (0 to 120 min). The flasks were agitated at 180 rpm on a rotary shaker at room temperature (± 25°C). After each experiment, the samples were filtered and analyzed using a UV–visible spectrophotometer at λ_{max} = 664 nm. Detailed steps are provided in the Supporting Information.

2.5. Biosorption Efficiency and Capacity

The dye removal efficiency (%) and adsorption capacity (q_e, mg/g) were calculated using standard equations based on the initial and equilibrium dye concentrations, solution volume, and biomass mass. The equation used to calculate the amount of MB adsorbed on to marine macroalgae: $q_e = \frac{C_i - C_f}{M} V$, where q_e (mg/g) is the amount of dye adsorbed per gram of biosorbent at equilibrium, C_i and C_f are the initial and equilibrium MB concentration in the solution (mg/L), respectively, V is the MB solution volume (L), and m is the algae mass (g). The following equation was used to determine the percentage of MB removal efficiency: $\% \, Removal = \frac{(C_i - C_f)}{C_i} 100$.

2.6. Isotherms and Kinetic Modeling

The Langmuir and Freundlich isotherm models and pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models were used. The model fit was evaluated using the correlation coefficients (R^2).

3. Results and Discussions

FT-IR spectra of the four macroalgal biomasses were highly similar, to near identical, indicating comparable surface chemistries dominated by oxygenated and to a lesser extent, nitrogenated functional groups typical of macroalgal biomass (Figure 2a). The broad band at 3280 cm^{-1} corresponds to O–H stretching (with possible N–H contribution), while the signal at 2932 cm^{-1} is assigned to aliphatic C–H stretching. The bands at 1616 and 1534 cm^{-1} are attributed to amide I and amide II vibrations and/or carboxylate contributions, confirming the presence of proteinaceous and carboxyl-containing groups. The pronounced band at 1408 cm^{-1} is consistent with symmetric stretching of $–COO^-$ groups, supporting the availability of negatively charged sites relevant for binding the cationic methylene blue via electrostatic attraction and/or ion-exchange processes. The region at 1211 cm^{-1} and the strong bands at 1020–979 cm^{-1} are characteristic of C–O/C–O–C vibrations of polysaccharides with possible sulfate-ester contributions typical of marine algal matrices.

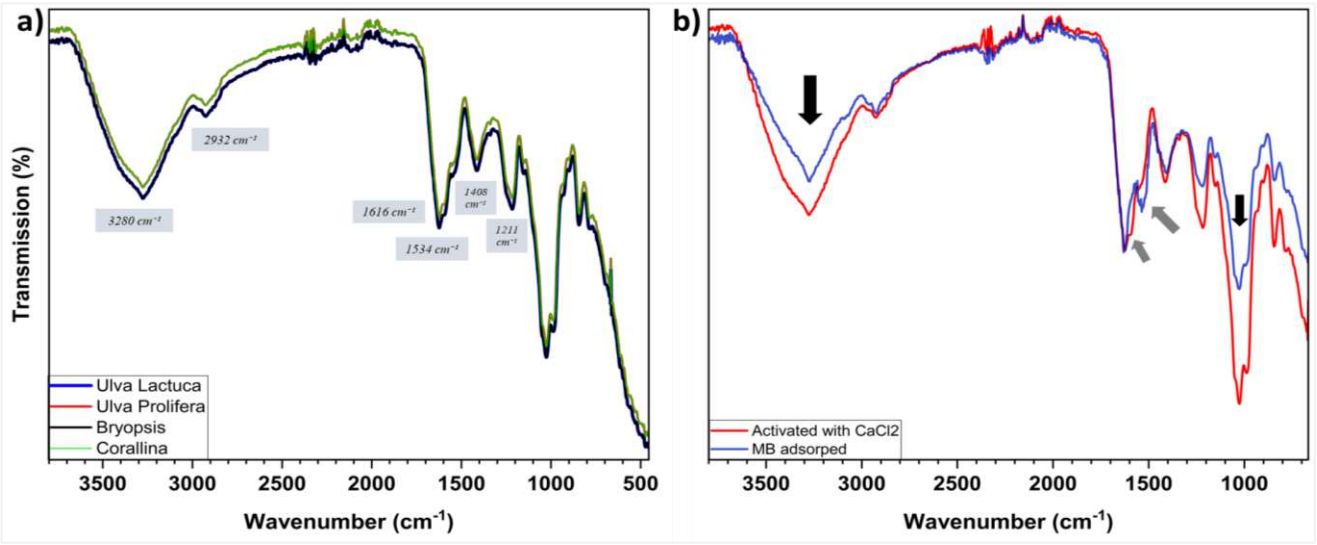


***Figure 2**: Fourier-transform infrared spectra (FT-IR) of **a)** the four samples, and **b)** Ulva Lactuca activated with $CaCl_2$ followed by the adsorption of methylene blue.*

Overall, the near-identical FT-IR profiles suggest that the primary adsorption-active functionalities (hydroxyl and carboxylate groups, and possibly sulfate-containing polysaccharides) are broadly conserved across the tested species; thus, differences in biosorption performance are more likely governed by surface accessibility, charge density, and Ca^{2+}-mediated ion exchange rather than by distinct

functional group chemistry. When MB is adsorbed, evident variations in the FT-IR spectrum of *Ulva Lactuca*, for example, are observed as shown in figure 2b. The broad O–H (N–H) stretching at 3280 cm^{-1} decreases in intensity, vibrations in the 1600–1500 cm^{-1} region show structural variations (marked by arrows), and a sharp decrease in the 1211 cm^{-1} and the 1020–979 cm^{-1} vibrations become evident. The results are further confirmed by microscopic images of the algal leaves before, and after, the biosorption process. The transparent surface of *Ulva Lactuca* becomes highly dyed with blue color upon treatment with MB as shown in figure 3.

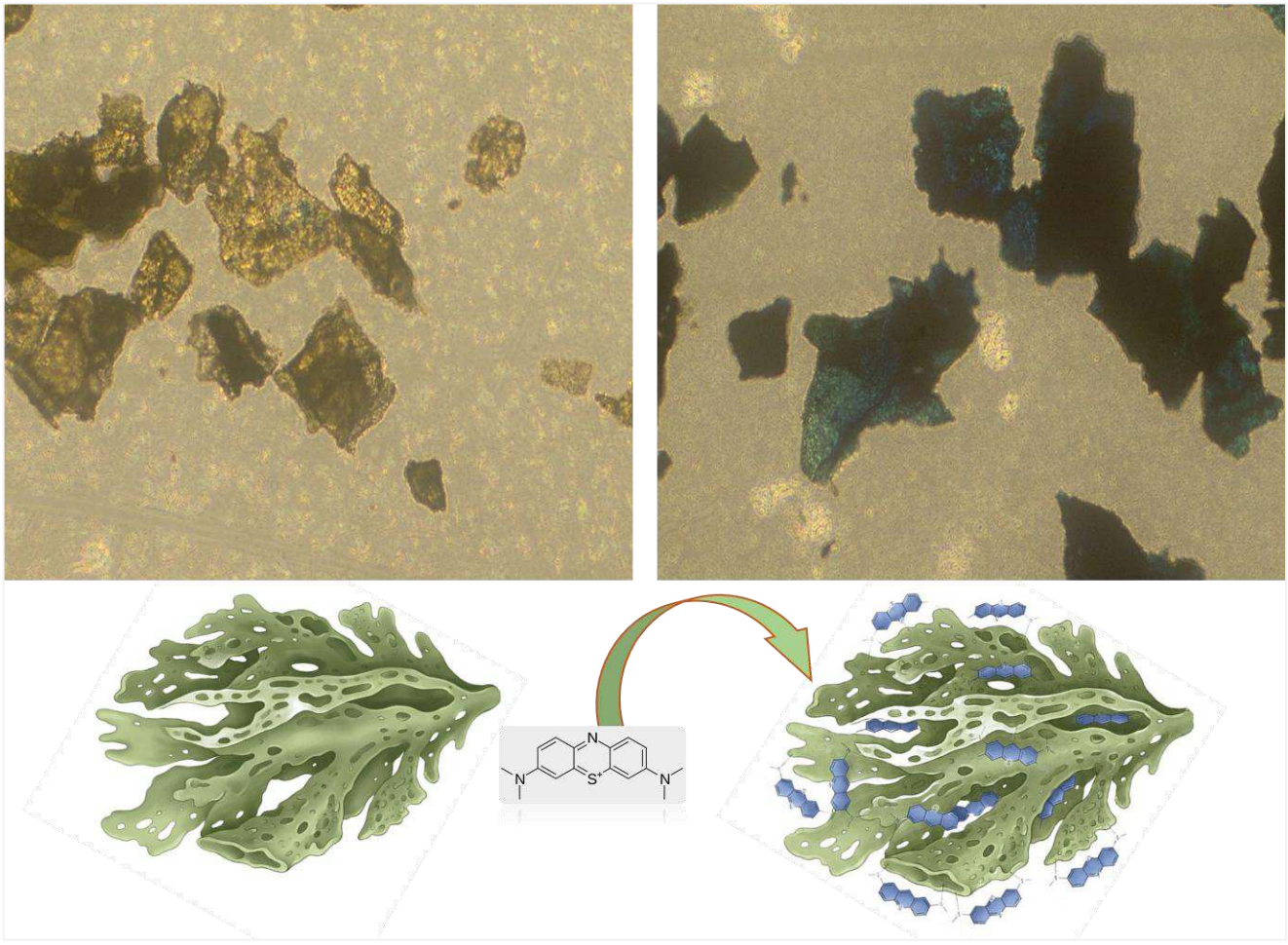


Figure 3*: Microscopic images of Ulva lactuca before (left) and after (right) the biosorption of methylene blue dye.*

3.1. Effects of the initial pH of solution

Adsorption of the MB dye was significantly influenced by the initial pH of the solution as presented in Figure 4. The removal efficiency increased as the pH increased from 1 to 12, with maximum adsorption observed between pH 5 and 12. Lower levels resulted in competition between hydrogen ions and MB molecules for the active sites on the algal surface, thereby reducing the biosorption efficiency. At higher

pH values, the deprotonation of functional groups like the carboxyl and hydroxyl, increased the negative surface charge and enhanced accordingly the electrostatic attraction toward the cationic MB dye. Among the tested species, *Ulva prolifera* exhibited the highest removal at an alkaline pH. Indeed, it is well reported in literature that the pH can generally influence the biosorption performance through different mechanisms; including solute speciation (metal speciation, protonation/deprotonation of dyes and organic compounds, etc.) and bio-sorbent surface properties (acid/base properties, for example).[19] The initial pH of the four different marine algae treated with $CaCl_2$ was determined by adding 0.1 mg/L of *Ulva Lactuca*, *Ulva Prolifera*, *Bryopsis*, and *Corallina* treated with 40 mL of 0.2 $CaCl_2$ and agitated for 90 min. The initial pH of the filtrates were measured and shown in figure 4a. Chemically modified *Ulva Lactuca*, *Ulva Prolifera*, *Bryopsis*, and *Corallina* had slightly basic pH of 7.85, 7.77, 8.06, and 7.88, respectively.

a)

pH				[H_2O +Algae]
Distilled H_2O	Ulva Lactuca + $CaCl_2$	Ulva Prolifera + $CaCl_2$	Bryopsis + $CaCl_2$	Corallina + $CaCl_2$
6.84	7.85	7.77	8.06	7.88

b)

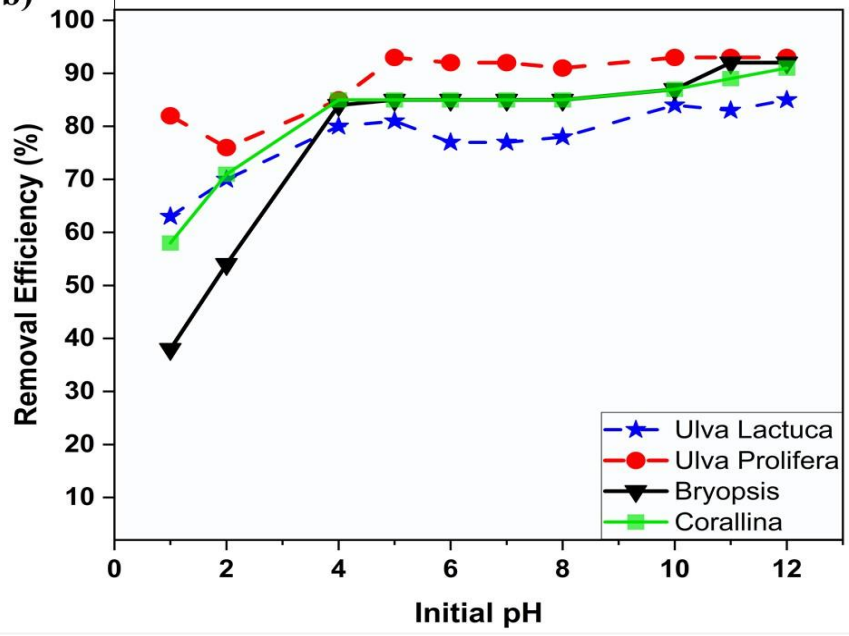


Figure 4. a) *table of the initial pH of the four different marine algae treated with $CaCl_2$ in 40 mL of distilled water with an algae dosage of 0.1 mg/L for 90 min.* ***b)*** *Effect of initial pH on the MB removal efficiency (%) of Ulva Lactuca, Ulva Prolifera, Bryopsis, and Corallina treated with $CaCl_2$: algae dosage: 100 mg/L, MB concentration: 10 mg/L, time: 120 min.*

The biosorption experiments conducted in the initial pH range from 1 to 12, as shown in Figure 4, revealed that the MB biosorption efficiency increased sharply as the solution pH increased from 1.0 to

5.8 for *Ulva Lactuca*, *Ulva Prolifera*, *and Bryopsis*, and for *Corallina* treated with $CaCl_2$. As can be seen from the curves, the increase in pH from 7.0 to 12.0 had no significant influence and maintained the percentage of MB removal at a constant level. According to Figure 4, the appropriate solution pH for MB biosorption on the four different marine macroalgae treated with $CaCl_2$ was in the range of 5–12.

The pH of the point of zero charge (pH_{PZC}) or isoelectric point determines the pH at which the biosorbent surface has net electrical neutrality. In fact, at pH_{PZC}, there are equal amounts of anions and cations on the solid surface.[20] In general, all algal species have an isoelectric point around pH 2–4. At a pH of the initial solution less than the pH_{PZC}, the biosorbent surface is electropositive, whereas at pH greater than pH_{PZC}, the surface is electronegative and favors the biosorption of cations. The low biosorption in the acidic zone of pH can be explained by the electrostatic repulsion of MB with the positively charged surface of the biomass. At higher solution pH (pH> pHpzc), functional groups are deprotonated, and electrostatic attraction can occur between the negatively charged functional groups and the positively charged cationic dye.[21] In addition, as the pH increased, the competition between protons and the basic dye for the same functional groups decreased, resulting in an enhanced removal efficiency.[22] In these graphs, figure 4 shows that the effective zone of pH is in the range of 5-12 for the four pretreated algae, where the percentage of removal efficiency of MB increased from 70% to 85% for *Ulva Lactuca* treated with $CaCl_2$, 76% to 93% for *Ulva Prolifera* treated with $CaCl_2$, 54% to 92% for *Bryopsis* treated with $CaCl_2$, and 71% to 91% for *Corallina* treated with $CaCl_2$. These results showed that the optimum pH for MB removal was approximately 5 for all four types of algae.

3.2. Effect of Algal Mass

The biosorbent dosage on MB removal is another essential factor that influences the biosorption efficiency. Optimizing this factor can help improve the removal efficiency and prevent further expenses. We investigated doses varying from 10 to 400 mg/L of the pre-treated macroalgae, at an optimized pH of 5.0 with an initial MB concentration of 10 mg/L, and shaking at 180 rpm for 120 min and at room temperature (± 25 °C). As shown in Figure 5a, the MB removal efficiency increased as the algae dose increased from 10 to 100 mg/L. For the same concentration of MB dye, more binding sites were available at higher biomass dosages.[23] However, increasing the biosorbent dosage above 100 mg/L did not significantly increase the dye removal efficiency of the biosorbent. This indicates that the effective surface area needed for the dye biosorption was achieved at 100 mg/L biomass dosages, at which the removal efficiency of MB reached 79%, 97 %, 93%, and 92% for *Ulva Lactuca*, *Ulva Prolifera*, *Bryopsis*, and *Corallina*, respectively.

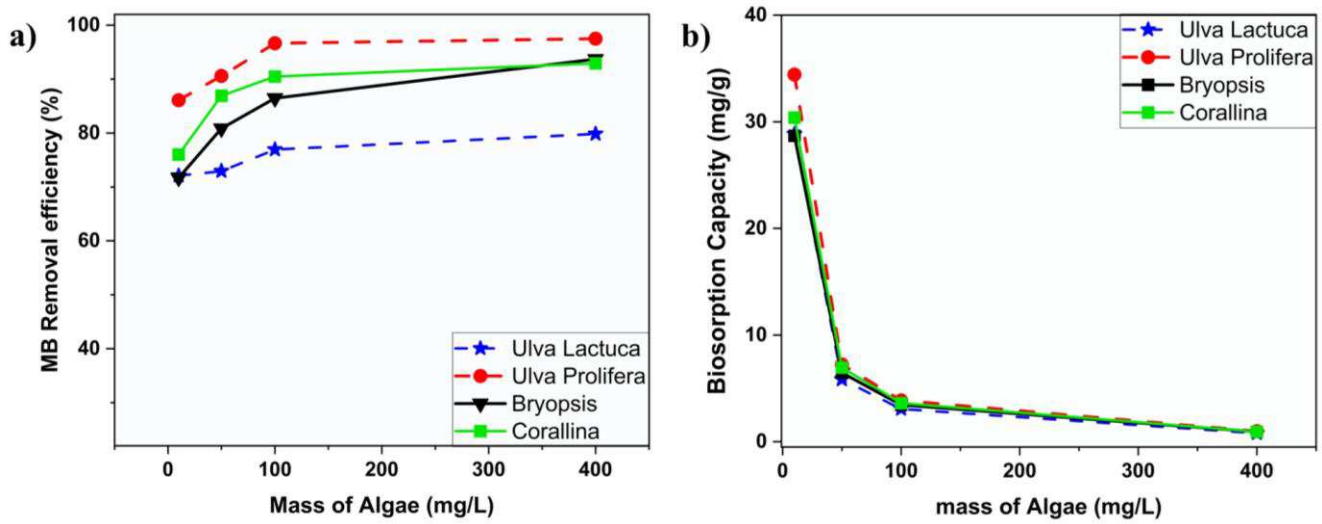
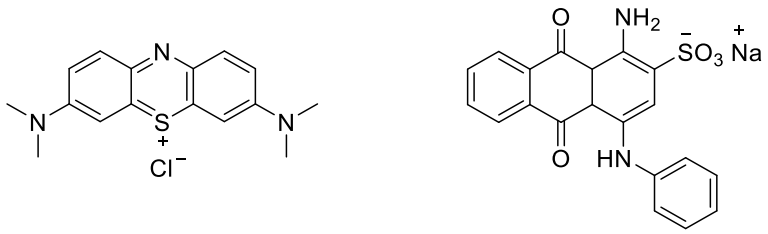


***Figure 5**. Effect of algae mass for Ulva Lactuca, Ulva Prolifera, Bryopsis, and Corallina treated with $CaCl_2$ on the MB a) removal efficiency % and b) biosorption capacity mg/g at pH 5.0. Initial MB concentration 10 mg/L, time 120 min, T: 25 °C.*

Figure 5b depicts the biosorption capacity (mg/g) dramatically decreasing within alga mass of 50 mg/L, after that the decrease flattens to reach eventually a plateau. At lower biomass dosages, algae particles have a higher chance of being covered by the dye, therefore, the amount of mg dye biosorption onto g biosorbent decreased as the algae concentration increased. These results are consistent with the biosorption of anthraquinone-based dye Acid Blue 25 (Scheme 1) by aquatic biomass.[24]



***Scheme 1.** Chemical Structures of Methylene Blue (left) and Acid Blue 25 (right)*

3.3. Effects of the initial MB concentration and the contact time

The optimized initial dye concentration is important for determining the maximum biosorption capacity (Q_{max}) of the biosorbent. A dose of 100 mg/L of algal mass was used based on the previous result. Evidently, there will be little or no dye removal from the aqueous solution after Q_{max} because of biomass saturation. At lower concentrations however, the unsaturated binding sites of the biosorbent would remain unused. While effluents with high dye concentrations can be treated economically using physical/chemical methods, the treatment of low-cost adsorbents is required for dye wastewater treatment. The effect of the initial MB concentration was investigated at a wide span: 1.25–900 mg/L (see S.I., table S1). Results are shown in Figure 6, left. The graph illustrates that the

biosorption capacity of marine macroalgae significantly increasing to ~ 341, 345, 110, and 153 mg/g for *Ulva Lactuca*, *Ulva Prolifera*, *Bryopsis*, and *Corallina* treated with $CaCl_2$, respectively. This suggests that a higher MB concentration gradient provides an important driving force to overcome the transfer resistance of the dye molecules between the aqueous and solid phases.[25] It is worth noting that *Byropsis* and *Corallina* started reaching a form of plateau beyond an initial MB concentration of 300 mg/L, showing a biosorbent saturation. In the case of *Ulva Lactuca* and *Ulva Prolifera*, the curve continues linear, indicating the presence of unsaturated sites on the surfaces of the algal particles at this range. Similar results were reported by other researchers for the biosorption of methylene blue dye on three different marine macroalgae.[26] Removal efficiencies of MB by the macroalgae reached 95 and 98% in *Ulva Lactuca* and *Ulva Prolifera* respectively, while increasing the initial dye concentration to 900 mg/L, showing the promising possible application of these material as sustainable and low-cost biosorbents.

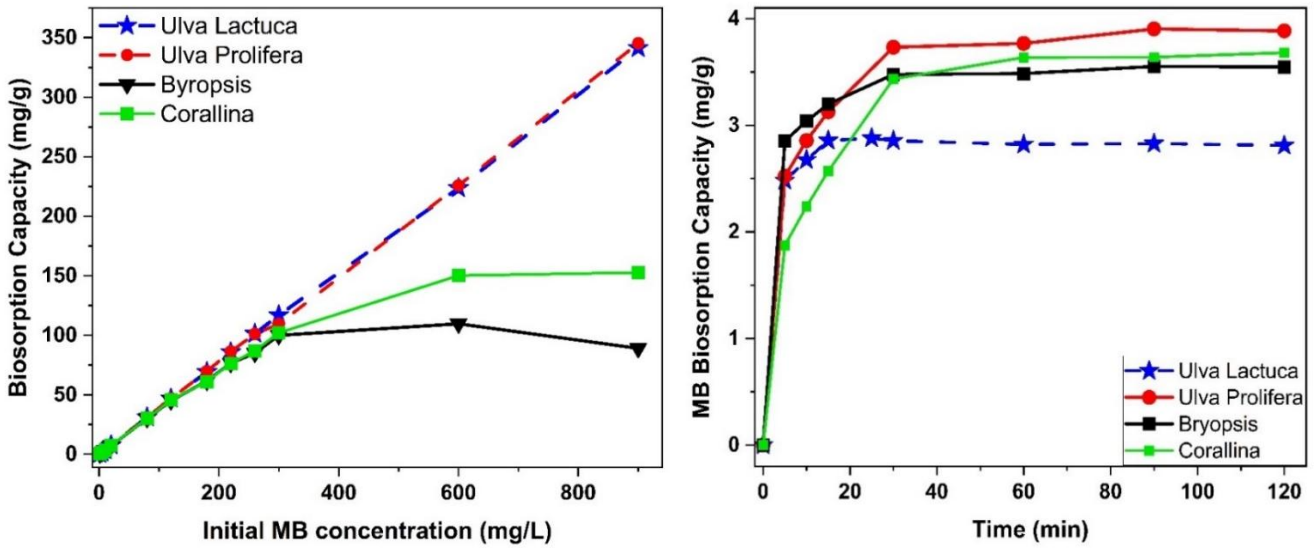


Figure 6. *Left) effect of initial MB concentration on the biosorption capacity at pH 5.0 and mass dosage of 100 mg/L. Right) effect of contact time on the biosorption capacity of MB, initial pH of solution: 5.0, MB concentration:10 mg/L.*

To determine the time required for the maximum biosorption capacity, an algal mass of 100 mg/L was equilibrated with 40 mL of MB dye solution having an initial concentration of 10 mg/L at pH 5.0, while recordings were made between 5 min and 2 hours as depicted in figure 6 right (also see S.I., table S2). According to the results three phases for the MB biosorption process are identified: fast, slow, and stationary. A rapid biosorption rate occurred at the beginning, followed by the dye molecules gradually being biosorbed, until finally the maximum capacity of the biosorbents was reached. The initial rapid increase is due to the availability of a large surface area and many vacant macropores for the accumulation of MB, while the subsequent deceleration is due to the saturation of most of the available

sites and the repulsive forces among adsorbed dye molecules and those present in the solution.[27] In the third stage, the algal particles were saturated, and the biosorption process reached equilibrium. The same dye biosorption behavior was observed for the four different types of algae. Clearly, a contact time of 30 min only is sufficient for biosorption to attain most of its equilibrium.

3.4. Chemical pretreatment of the algae

Treatment of the algae by different types of chemicals was applied in order to increase the maximum capacity of sorption on the biomass and thus improve the removal of dyes from aqueous solution. The four samples were pretreated with $CaCl_2$ (0.2 mol/L) as described earlier; other samples of *Ulva Lactuca* had been treated with diluted HCl (0.1 mol/L) or NaOH (0.1 mol/L) for comparison. Table 1 shows the effect on the biosorption capacity and % of removal efficiency of MB accordingly.

Table 1. *Effect of the pretreatment by $CaCl_2$, NaOH and HCL on the biosorption capacity of Ulva Lactuca and its % removal efficiency of MB.*

[MB] mg/L	*Ulva Lactuca* + $CaCl_2$		*Ulva Lactuca* + NaOH		*Ulva Lactuca* + HCl	
	q_e (mg/g)	% R	q_e (mg/g)	% R	q_e (mg/g)	% R
1.25	0.365	73.1	0.33	66.67	0.36	72.1
5	1.64	82.45	1.61	80.37	1.71	85.45
10	3.51	87.76	3.43	85.98	3.54	88.525
20	7.22	94.53	7.39	92.41	7.52	94.01
80	31.122	97.25	31.1	97.14	31.18	97.43
120	46.9	97.72	47.01	97.94	47.1	98.12

Results indicate that pretreatment with $CaCl_2$, NaOH or HCl does not show a significant change or effect on the amount adsorbed at equilibrium. However, the maximum adsorption capacity is enhanced for $CaCl_2$. During the treatment with salt, Ca cations get adsorbed on the algal surface, subsequently during the MB sorption process, these cations will be exchanged with that of the dye as MB is cationic.[28]

3.5. Biosorption Isotherms

In adsorption studies, the *Langmuir* isotherm model assumes a monolayer adsorption on a homogeneous surface with a finite number of identical sites. Once a dye molecule occupies a site, no further adsorption can occur at that site, and there are no interactions between adsorbed molecules. The Langmuir model is represented (in nonlinear form) by: $q_e = \frac{Q_0\, b\, C_e}{1+b\, C_e}$ where qe (mg/g) is the amount adsorbed at equilibrium, Ce (mg/L) is the equilibrium solute concentration, Q_0 (mg/g) is the maximum monolayer adsorption

capacity, and b (L/mg) is the Langmuir constant related to the affinity or binding energy of adsorption. A higher Q_0 indicates a greater sorbent capacity, while a higher b value reflects stronger affinity of the sorbent for the dye. The quality of the model fit is often evaluated by the correlation coefficient (R^2). By contrast, the Freundlich isotherm model is an empirical model that assumes a heterogeneous adsorption surface with non-uniform distribution of heat of adsorption over the surface. Unlike Langmuir, it does not presuppose a monolayer limit; instead, it allows for multilayer adsorption and interaction between adsorbed molecules. The Freundlich model is expressed as: $q_e = K_F\, C_e^{1/n}$ where KF is the Freundlich adsorption constant (capacity factor) and n is the Freundlich intensity exponent (dimensionless). KF empirically indicates the adsorption capacity of the sorbent; higher KF implies a greater adsorption at a given equilibrium concentration.

3.5.1. Isotherm Parameter Determination and Fitting Method

In this study, the equilibrium biosorption data were fitted to both models using non-linear regression. The non-linear forms of the Langmuir and Freundlich equations were directly solved to obtain the best-fit parameters Q_0 and b, and KF and n, respectively. This approach avoids biases introduced by linearizing the isotherm equations. For clarity, the model parameters can also be obtained from linearized plots in classical analysis. Here we relied on non-linear fitting of qe vs. Ce data to determine the parameters, and the resulting Langmuir and Freundlich constants are summarized in Tables 2 and 3, for each alga (see also S.I., Figure S1). The regression correlation coefficients (R^2) for each fit were used to assess which model better represents the biosorption isotherm.

3.5.2. Biosorption Isotherm Results and Model Comparison

Langmuir Isotherm Results:

The MB uptake capacities obtained from the Langmuir model (Q_0) differed markedly among the $CaCl_2$-treated algae. *Ulva prolifera* showed the highest monolayer capacity, $Q_{max} \approx 652.5$ mg/g, followed by *Ulva lactuca* with $Q_{max} \approx 489.8$ mg/g. In contrast, the red alga *Corallina* and the green filamentous alga *Bryopsis* had lower capacities of ~164.5 mg/g and 105.0 mg/g, respectively (Table 2). These values suggest that the *Ulva* species (especially *prolifera*) can accumulate far more MB per unit mass at saturation than the other algae, possibly due to greater abundance of binding sites or higher surface area. The Langmuir affinity constant b also varied: *Bryopsis* exhibited the largest b, 0.0871 L/mg, indicating a very strong affinity for MB at low concentrations, whereas *Ulva prolifera* had the smallest b, 0.0179 L/mg, with *Ulva lactuca* and *Corallina* in between, 0.0322 and 0.0312 L/mg respectively. The higher b for Bryopsis suggests that although its capacity is limited, it binds MB very strongly at the

initial uptake stage (steep initial isotherm slope). This trend is reflected in the separation factor values explained thereafter.

Table 2. *The non-linear Langmuir Isotherm values of the four algal species pre-treated with $CaCl_2$.*

model/non-linear	parameter (units)	*Ulva Lactuca*	*Ulva prolifera*	*Bryopsis*	*Corallina*
Langmuir Model $q_e = \frac{Q_0.b.C_e}{(1+bC_e)}$	Q_0 (mg/g)	489.789	652.536	105.014	164.451
	b (dm^3/mg)	0.0322	0.0179	0.0871	0.0312
	R^2	0.9372	0.8221	0.9611	0.9763

Freundlich Isotherm Results:

The Freundlich model parameters (Table 3) provide additional insight into the adsorption characteristics of each alga. The Freundlich capacity constant KF was on the order of 10 for all four materials, but interestingly did not follow the same ranking as Langmuir Q_0. *Corallina* showed the highest KF ≈ 29.2, and *Bryopsis* was next with KF ≈ 26.3, while *Ulva lactuca* and *Ulva prolifera* had slightly lower values (~21.4 and 21.2, respectively). This suggests that at an equilibrium concentration of 1 mg/L MB (a typical reference point for KF), *Corallina* and *Bryopsis* would uptake slightly more dye than the *Ulva* species. This can be rationalized by their high affinity –*Bryopsis*, for example, despite a low Langmuir capacity, has a high affinity leading to strong uptake at low concentrations (thus a high KF).

Table 3*. Non-linear Freundlich isotherm model values for the four different algae pretreated with $CaCl_2$.*

model/non-linear	parameter (units)	*Ulva Lactuca*	*Ulva prolifera*	*Bryopsis*	*Corallina*
Freundlich model $q_e = K_F.C_e^{1/n}$	K_F (mg/g)$(dm^3/g)^n$	21.458	21.242	26.336	29.212
	N	1.4527	1.4423	4.3043	4.0847
	R^2	0.93401	0.8423	0.7405	0.8404

The Freundlich intensity parameter n showed a clear distinction between the two *Ulva* species and the other two algae. *Ulva lactuca* and *Ulva prolifera* had n ≈ 1.45, while *Bryopsis* and *Corallina* had n values in the range 4.08–4.30. All n values are > 1, confirming favorable adsorption in the Freundlich sense.

Moreover, the much larger n for *Bryopsis* and *Corallina* (around 4) corresponds to a very small 1/n (≈0.23–0.24), indicating a highly intense adsorption that is strongly skewed toward the lower concentration range. In other words, these algae have a set of "strong" binding sites that get saturated at relatively low MB concentrations, leading to an isotherm that rises sharply and then plateaus (reflecting heterogeneous site energies). The *Ulva* species, with n ~1.4 (1/n ~0.69), exhibit a more moderate increase in uptake with concentration – their adsorption is less intensive initially and perhaps more uniform, suggesting a more homogenous distribution of binding sites or a tendency toward linear partitioning behavior at the tested concentrations. This difference in n aligns with the notion that *Bryopsis* and *Corallina* surfaces are more energetically heterogeneous, whereas the *Ulva* biomass might have more evenly matched binding sites. We also note that the $CaCl_2$ pretreatment could influence these parameters by altering surface functional groups and charge properties, potentially creating very strong binding sites in some algae.

Model Fit and Applicability

All experimental isotherm data were reasonably well described by both models (see R^2 values in Tables 2–3), but there were notable differences in the goodness of fit. The Langmuir model provided an excellent fit for *Bryopsis* and *Corallina* biosorption, with R^2 = 0.9611 and 0.9763, respectively, significantly higher than the Freundlich R^2 for those species (0.7405 and 0.8404). This indicates that MB adsorption on *Bryopsis* and *Corallina* conforms closely to Langmuir assumptions of a monolayer, homogeneous surface – likely these algae have a relatively uniform set of high-energy sites and reach a clear saturation plateau. In contrast, the *Ulva lactuca* data were fitted almost equally well by Langmuir (R^2 = 0.9372) and Freundlich (R^2 = 0.9340) models. This dual fit suggests that it has aspects of both homogeneous and heterogeneous adsorption; it does attain a high capacity (nearly 490 mg/g) indicative of monolayer saturation, but it may also possess a range of binding site strengths or some multilayer uptake at higher concentrations. For *Ulva prolifera*, the Freundlich model yielded a slightly better fit (R^2 = 0.8423) than Langmuir (R^2 = 0.8221), although both R^2 values are somewhat lower than for the other algae. The relatively poorer Langmuir fit for *Ulva prolifera* could be due to its extremely high capacity not being fully reached within the experimental concentration range, or due to a greater heterogeneity introduced by Ca^{2+} treatment and the very high driving forces (up to 900 mg/L MB) used. The slight preference for the Freundlich model suggests *Ulva prolifera* may have a broader distribution of binding sites or multilayer adsorption tendencies when loaded with large amounts of MB.

In summary, *Bryopsis* and *Corallina* are best described by the Langmuir isotherm, reinforcing the idea of monolayer coverage on fairly uniform sites for these biosorbents. *Ulva lactuca* fits both models well, implying a mixed adsorption behavior that still achieves a definable monolayer capacity. *Ulva prolifera*, with its exceptional capacity, shows better conformity to the Freundlich model, hinting at a more heterogeneous sorption process (perhaps due to its high porosity or diverse functional groups after $CaCl_2$ activation). Nevertheless, even for *Ulva prolifera* the Langmuir model is not far off – both models yield correlation coefficients in the 0.82–0.84 range – so a Langmuir-type monolayer limit exists but with some deviation. The choice of a *more appropriate* model for each algal species thus, rests on these fits.

3.5.3. Separation Factor (RL) Analysis

An important characteristic of the Langmuir model is the separation factor *RL*, a dimensionless indicator of isotherm favorability defined as $RL = 1/(1 + b\ C_0)$, where C_0 is the initial adsorbate concentration. For a given adsorbent–adsorbate system, $0 < R\ L < 1$ signifies favorable adsorption, $RL = 1$ linear adsorption, $RL > 1$ unfavorable adsorption, and $RL = 0$ irreversible adsorption. The ranges obtained were as follows, *Ulva lactuca*: 0.033–0.961; *Ulva prolifera*: 0.058–0.978; *Bryopsis*: 0.013–0.902; and *Corallina*: 0.034–0.962. All four algae yielded *RL* values between 0 and 1 across the initial MB concentration range of 1.25–900 mg/L, confirming that MB biosorption by these $CaCl_2$-treated biomasses is favorable at all conditions tested. At the lowest MB concentrations, *RL* was close to 1 (e.g. 0.96–0.98), indicating that although adsorption is favorable, a significant fraction of MB remains in solution at equilibrium. At the highest concentration (900 mg/L), *RL* dropped to very low values (0.01–0.06 depending on the algae), reflecting that the biosorbents approach their saturation capacity and remove a large proportion of the dye. For example, *Ulva lactuca* had $RL = 0.961$ at 1.25 mg/L and 0.033 at 900 mg/L, while *Bryopsis* showed *RL* decreasing from 0.902 to 0.013 over the same range. Such low *RL* at high concentration suggests an extremely favorable uptake (nearly irreversible binding) when MB loading is high. The consistently favorable *RL* values corroborate the suitability of the Langmuir model for these systems and underscore the strong affinity (especially in the case of *Bryopsis* and *Corallina* which had the lowest *RL min* values) of the algae for cationic MB dye.

Based upon, table 4 shows the maximum adsorption capacities of the various adsorbents related to Langmuir isotherm model. In this study, when compared to the other materials, Lebanese Mediterranean macroalgae adsorbents most specifically *Ulva Prolifera* pretreated with $CaCl_2$, can be used as an alternative adsorbent due to its high adsorption capacity reaching 652 mg/g.

***Table 4**. Different maximum adsorption capacities of various biomaterials for MB reported in literature.*

Adsorbent	Q_{max} (mg/g)	Reference
Ulva fasciata (untreated)	244	[29]
Scenedesmus obliquus (untreated)	132	[30]
***Ulva Prolifera* treated by $CaCl_2$**	**653**	**This study**
Papaya seeds	556	[31]
Periwinkle shells	500	[32]
Ulva Lactuca treated by $CaCl_2$	490	This study
Caulerpa lentillifera	417	[33]
Activated Carbon	374	[34]
Cotton waste	240	[35]
Corallina treated by $CaCl_2$	165	This study
Moss	158	[36]
Spirodela polyrrhiza	145	[37]
Water hyacinth root	129	35
Bryopsis treated by $CaCl_2$	105	This study
Date pits	80	[38]
Rice husk	41	[39]

3.6. Kinetics of the Biosorption

The kinetic data for the biosorption of MB on the different algae were fitted with the Lagergren pseudo-first-order (PFO) and Ho–McKay pseudo-second-order (PSO) models (see S.I., table S3a-b). In all cases, the PSO model yielded a markedly superior fit, with correlation coefficients R^2 exceeding 0.99. It also predicted equilibrium uptake (q_e) values very close to the experimentally observed capacities (see S.I., Figure S2.a–d). This trend indicates that the sorption of MB is not controlled solely by instantaneous diffusion; instead, it follows a second-order rate behavior, suggesting involvement of chemisorptive interactions (e.g. surface complexation or electron sharing) rather than sole mass transport, consistent with a chemical binding or valence force-controlled sorption process.[30] The fact that all four algae follow PSO kinetics strongly suggests the involvement of surface functional groups like $–COO^–$, –OH, $–SO3^–$ on the algal cell wall, forming strong interactions with the cationic dye. The findings align with numerous studies on dye biosorption by marine algae, which report PSO as the best-fitting kinetic model, often

attributing it to chemisorption as the rate-limiting step. Turp *et al.* found that MB adsorption on *Ulva lactuca* conformed to PSO kinetics with R^2=1.000, indicative of a chemical adsorption process.[40] Likewise, Al-Fawwaz *et al.* observed MB removal by a green alga (*Bracteacoccus sp*.) to follow PSO kinetics ($R^2 > 0.999$) rather than PFO.[41]

To elucidate the rate-limiting steps, the intraparticle diffusion (IPD) model (Weber–Morris plot) was applied (see S.I., table S3c). This model considers whether adsorption is controlled by diffusion of dye molecules inside the pores/particles of the biosorbent. If intraparticle diffusion is the sole rate-limiting step, a plot of adsorbed amount qt versus $t^{0.5}$ would yield a straight line through the origin (zero intercept). In this study, the IPD plots for all four algae were multi-linear and exhibited non-zero intercepts (parameter $C > 0$), indicating that adsorption proceeded in multiple stages and that intraparticle diffusion was involved but not the only controlling mechanism (see S.I., Figure S2–e). Typically, three kinetic phases were observed for MB biosorption onto these algae.[42] *Stage 1* is a rapid initial uptake phase, attributed to immediate utilization of readily accessible surface sites and external film diffusion of MB to the algal surface (boundary-layer mass transfer). In this phase, the high concentration gradient drives MB molecules quickly to the biosorbent, resulting in a steep rise in qt at early times. *Stage 2* is a slower, gradual adsorption phase, which is governed by intraparticle (pore) diffusion of MB into the internal structure of the algae (within cell wall matrices or pores). MB molecules migrate from the external surface into deeper binding sites, causing the adsorption rate to slow down. This stage is often diffusion-controlled and can be the rate-limiting step of the overall process once surface sites are initially occupied. *Stage 3* is a final equilibrium phase, where the uptake approaches a plateau and the adsorption rate significantly diminishes. At this stage, remaining vacant sites are few and/or difficult to access, and the system reaches dynamic equilibrium with no significant further MB removal.

In our results, none of the IPD lines passed through the origin ($C > 0$) confirming that intraparticle pore diffusion was not the only rate-limiting step; rather, MB transport occurred via a combination of external film diffusion and internal diffusion. Among the four algae, the magnitude of k_{id} and C differed slightly, likely reflecting variations in their morphology and porosity. For instance, *Ulva* and *Bryopsis* (soft, porous green algae) showed higher k_{id} values, consistent with relatively faster intraparticle diffusion, whereas *Corallina* (a calcified red alga) exhibited a larger intercept C, indicating a more pronounced boundary layer effect (possibly due to its rigid structure reducing the immediate accessibility of dye). Overall, IPD analysis suggests that while MB molecules rapidly attach to algae surfaces initially, the slower diffusion into internal binding sites governs the later uptake, making intraparticle diffusion the predominant rate-limiting step as the system nears equilibrium. This multi-step diffusion behavior is

characteristic for biosorption of dyes onto biomaterials and has been noted by other researchers for algae–dye systems.[43] It is worth mentioning however, that the IPD model produced significantly lower correlation coefficients ($R^2 \approx 0.825–0.829$) indicating that intraparticle diffusion alone does not adequately describe the overall biosorption rate of methylene blue onto the $CaCl_2$–treated macroalgae.

3.7. Mechanistic summary for the biosorption process

Pretreatment of the algae with $CaCl_2$ saturates the biomass with Ca^{2+} ions bound to negatively charged sites (such as carboxylate groups in algal polysaccharides). This Ca^{2+} activation would stabilize and neutralize the sorbents acidic functional groups, ensuring the surface is in a deprotonated (negatively charged) form at the working pH, and would increase surface charge density, rigidity, and accessibility, while also introducing exchangeable cations onto the binding sites. When MB is introduced, an ion-exchange mechanism can occur: two monovalent dye cations can compete with and displace one Ca^{2+} ion to maintain charge balance on each site. The exchange is thermodynamically favorable given MB's high affinity for the negatively charged sites, while Ca^{2+} is released into solution (Figure 7).

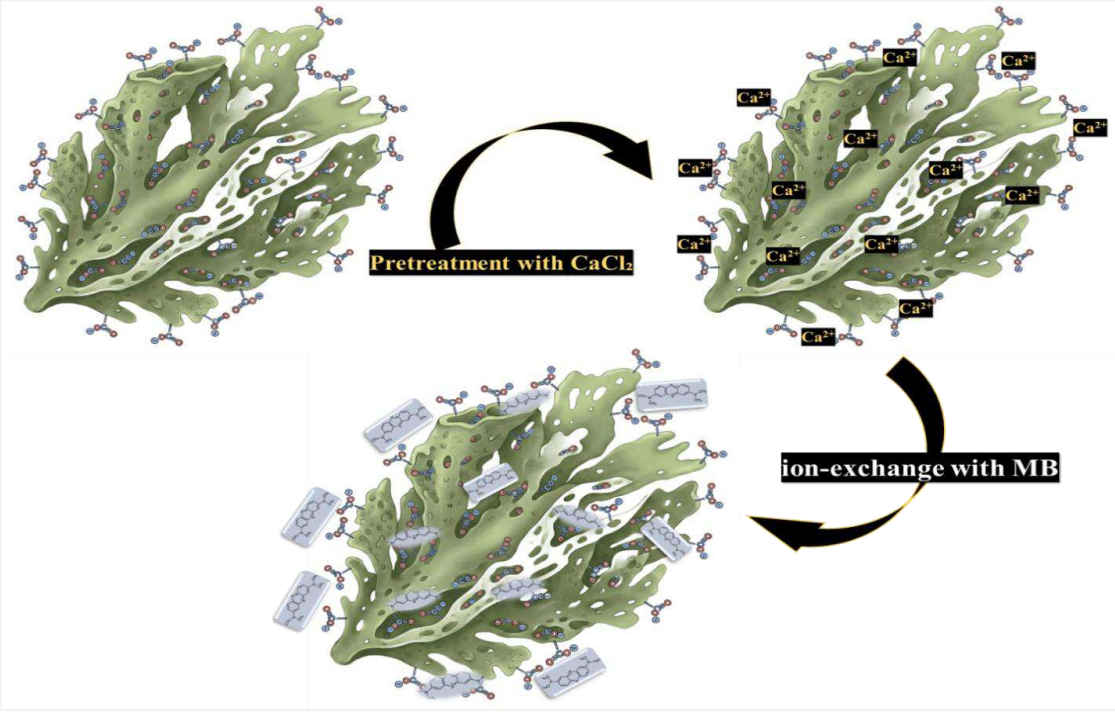


Figure 7. *Illustration of the biosorption process of methylene blue on the surface of the pretreated marine macroalgae.*

The kinetic behavior reflects a multi-step uptake mechanism in which boundary-layer (film) diffusion and rapid surface adsorption control the early stage, followed by a shorter intraparticle diffusion phase before equilibrium is reached. This interpretation is consistent with the observed fast initial uptake within the first 30 min and subsequent plateau toward equilibrium around 90 min. Therefore, the relatively low

IPD R^2 values support the conclusion that MB biosorption on these $CaCl_2$-activated biomasses is governed by combined film diffusion and surface interaction mechanisms, rather than by pore diffusion alone. The cell walls of these macroalgae are rich in polar and ionizable functional groups originating from polysaccharides, proteins, and other biopolymers. Key functional groups include hydroxyl (–OH) and carboxylates ($–COO^-$), rendering the algal surface negatively charged and highly reactive toward cationic species via electrostatic interactions. The initial binding of MB is likely dominated by Columbic attraction between the dye's positively charged amine center and deprotonated acidic groups on the biomass. This is consistent with known biosorption behavior where algae exhibit high capacity for cationic pollutants due to abundant anionic functional groups.[44] In this work, kinetic data for MB uptake suggest that chemisorption is the rate-limiting step. The excellent fit to the pseudo-second-order model implies strong binding at the active sites, consistent with the involvement of specific functional groups and exchange reactions (rather than mere diffusion control). Notably, a good correlation with PSO kinetics often correlates with monolayer adsorption, and aligns with the Langmuir mechanism assumptions, reinforcing that MB attachment is largely to specific sites on the surface (at least in the initial phase of uptake). The overall uptake follows a multi-step pathway consisting of (i) film diffusion, (ii) surface adsorption, and (iii) intraparticle diffusion. First, MB molecules migrate from the bulk solution through the liquid boundary layer to the biomass surface. Once at the surface, MB rapidly binds to available functional sites through electrostatic attraction and ion-exchange interactions. After initial surface coverage, dye molecules continue to penetrate into internal pores and cell-wall matrices via intraparticle diffusion, which governs the later stage of uptake. The resulting kinetics therefore show a two-stage behavior: fast initial adsorption followed by slower equilibration. Multilinear Weber–Morris plots indicate that intraparticle diffusion contributes but is not the sole rate-controlling step.

4. Conclusion

The current study examined four different macroalgae obtained from the local Lebanese coastal shore, and pretreated with $CaCl_2$, as sustainable and low-cost biosorbents for the removal of the cationic methylene blue dye from water. Different parameters, including the initial pH of solution, algal mass, initial dye concentration, contact time, and chemical pretreatment have been thoroughly analyzed. Results suggest that these algal biomasses can be used as highly effective nonconventional biosorbents for MB. The biosorption capacities were mainly influenced by the initial pH solution found to be optimum at $pH \geq 5$. The process was very fast during the first 30 min, after which the sorption quickly reaches equilibrium. Pretreatment of *Ulva Lactuca*, as a model, with HCl and NaOH did not show any

significant change in capacity or % removal of the dye compared with its treatment with $CaCl_2$. Rather, the determination of the Q_{max} biosorption in Langmuir isotherm results indicates that the latter pretreatment is more favorable. Langmuir and Freundlich non-linear models were found to fit well with experimental data results, suggesting that the process in both models was favorable. In addition, kinetic studies show the high correlation coefficients of the four samples in the pseudo-first-order and pseudo-second-order models indicating a substantial fit. Effectiveness of biosorption of the different treated macroalgae in terms of Q_{max} were shown to reach an impressive 653 mg/g for *Ulva Prolifera*. Our study concludes that this local algal biomass could be used as a sustainable and eco-friendly biosorbent with respect to other alternative methods of dye removal.

On the other side, we note that the performed experiments included single-solute MB solutions only, and under controlled laboratory batch conditions, which is a major limitation when considering practical industrial wastewater treatment which contains mixed-dye systems and salt-rich matrices as competing ions. Our future work will focus on real wastewater obtained from factory sites along the Lebanese coastline, with further emphasis on the possible regeneration and reuse of the algal mass to prove its sustainability and practical recyclability through scale-up studies.

Data availability:

All data supporting the findings of this study are available within the paper and its Supplementary Information.

Conflicts of Interest:

The authors declare they have no known competing financial and/or non-financial interests in relation to the work described.

Acknowledgements

The authors would like to thank Prof. Hussein Kanaan for botanically identifying and certifying the different algal species using the voucher specimens (No. 260401, 260402, and 260403) deposited at the herbarium of the Faculty of Pharmacy, Department of Pharmacognosy, at the Lebanese University.

Statement:

The guidelines for collection of the marine algae used in this study were followed and complied with national guidelines. NO specific local permissions or licenses are required for the collection process.

Funding:

This work was funded by the Lebanese American University, Research Grant #SRRC-R-2025-622.

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