

# Methylene blue dye removal utilizing biomass of the macroalgae (*Padina* sp.): Adsorption, kinetic studies and mechanism

## Makroalg (*Padina* sp.) biyokütlesi kullanılarak metilen mavisi boyasının uzaklaştırılması: Adsorpsiyon, kinetik çalışmalar ve mekanizma

Hasan Türe<sup>1\*</sup> • Pınar Akdoğan Şirin<sup>2</sup>

<sup>1</sup>Ordu University, Fatsa Faculty of Marine Science, Department of Marine Science and Technology Engineering, 52400, Ordu, Türkiye

<sup>2</sup>Ordu University, Fatsa Faculty of Marine Science, Department of Fisheries Technology Engineering, 52400, Ordu, Türkiye

\*Corresponding author: [hasanture@odu.edu.tr](mailto:hasanture@odu.edu.tr)

Received date: 20.01.2025

Accepted date: 24.03.2025

### How to cite this paper:

Türe, H., & Akdoğan Şirin, P. (2025). Methylene blue dye removal utilizing biomass of the macroalgae (*Padina* sp.): Adsorption, kinetic studies and mechanism. *Ege Journal of Fisheries and Aquatic Sciences*, 42(2), 122-130. <https://doi.org/10.12714/egejfas.42.2.04>

**Abstract:** Macroalgae, which are abundant in marine ecosystems, are promising natural adsorbents for water purification because of their high surface area, rich functional groups, and natural adsorption capabilities. In this study, the adsorption capacity of *Padina* sp., a brown macroalgae in dried powdered form, was evaluated for the removal of toxic methylene blue (MB) dye from water. A series of batch adsorption tests were conducted to investigate the effects of several operational parameters, as initial MB concentrations (2, 5, 10, 20, and 50 mg L<sup>-1</sup>), pH levels (2, 4, 7, and 11), and contact time (0, 0.08, 0.5, 1, 2, 4, 6, and 24 h) on MB removal. Furthermore, powdered *Padina* sp. was analyzed before and after MB adsorption using Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy. The results showed optimal removal efficiency under neutral and alkaline conditions, as opposed to acidic environments. The Freundlich model accurately represents experimental adsorption data ( $R^2=0.9902$ ). Kinetic analysis revealed that MB adsorption onto *Padina* sp. primarily followed a pseudo-second order mechanism ( $R^2=0.9982$ ). The characterization and experimental findings suggest that the proposed mechanisms for MB adsorption by *Padina* sp. involve electrostatic interactions, pore filling, and hydrogen bonding. The experimental results suggest that powdered *Padina* sp. is a promising adsorbent for removing MB from water.

**Keywords:** Water pollution, adsorption, dye removal, bio-adsorbent, *Padina* sp.

**Öz:** Deniz ekosistemlerinde yaygın olarak bulunan makroalgler, yüksek yüzey alanları, zengin fonksiyonel grupları ve doğal adsorpsiyon kabiliyetleri nedeniyle su arıtımı için umut vadeden doğal adsorbanlardır. Bu çalışmada, kurutulmuş toz formunda kahverengi bir makroalg olan *Padina* sp.'nin sudan toksik metilen mavisi (MB) boyasının uzaklaştırılması için adsorpsiyon kapasitesi değerlendirilmiştir. Başlangıç MB konsantrasyonları (2, 5, 10, 20 ve 50 mg L<sup>-1</sup>), pH seviyeleri (2, 4, 7 ve 11) ve temas süresi (0, 0.08, 0.5, 1, 2, 4, 6, ve 24 saat) dahil olmak üzere çeşitli operasyonel faktörlerin MB eliminasyonu üzerindeki etkilerini incelemek için bir dizi adsorpsiyon testi yürütülmüştür. Ayrıca, toz haline getirilmiş *Padina* sp., MB adsorpsiyonundan önce ve sonra Fourier dönüşümlü kızılötesi spektroskopisi ve taramalı elektron mikroskobu kullanılarak analiz edilmiştir. Sonuçlar, asidik ortamların aksine, nötr ve alkali koşullar altında optimum bir giderme verimliliği olduğunu göstermiştir. Freundlich modeli, deneysel adsorpsiyon verilerini doğru bir şekilde temsil etmektedir ( $R^2 = 0.9902$ ). Kinetik analiz, MB adsorpsiyonunun *Padina* sp. üzerine öncelikle psödo-ikinci dereceden bir mekanizmayı izlediğini ortaya koymuştur ( $R^2 = 0.9982$ ). Karakterizasyon ve deneysel bulgulara dayanarak, *Padina* sp.'nin önerilen MB adsorpsiyon mekanizmaları arasında hidrojen bağı, elektrostatik etkileşimler ve gözenek doldurma yer almaktadır. Deneysel sonuçlar, toz halindeki *Padina* sp.'nin sudan MB'yi uzaklaştırmak için umut verici bir adsorban olduğunu göstermektedir.

**Anahtar kelimeler:** Su kirliliği, adsorpsiyon, boya giderimi, biyo-adsorban, *Padina* sp.

## INTRODUCTION

Even at low levels, synthetic organic dyes are important industrial contaminants that seriously endanger human health, aquatic ecosystems, and environment (Benhouria et al., 2023; Saheed et al., 2021). Methylene blue (MB; 3,7-bis(dimethylamino) phenothiazine chloride tetra methylthionine chloride) is used for fabric dyeing in the textile industry and is also preferred for dyeing paper and leathers (Oladoye et al., 2022; Khodaie et al., 2013). MB is a cationic synthetic dye known for its toxic effects, including teratogenicity, mental confusion, nausea, hypertension, mutagenicity, neurotoxicity, and damage to nucleic acid (Martínez Cadena et al., 2025; Ucuncu et al., 2022; Ghosh et al., 2021). Due to the monoamine oxidase inhibitor properties of MB dye, doses exceeding 5 mg kg<sup>-1</sup> can pose a threat to the fauna in aquatic ecosystems and may also cause fatal serotonin toxicity in humans (Oladoye et al., 2022). To prevent the harmful effects

of this toxic feature of dyes on humans and all living organisms, wastewater must be properly treated.

Several methods for dye removal have been employed, including coagulation (Mcyotto et al., 2021), flocculation (Ihaddaden et al., 2022), oxidation (Bravo-Yumi et al., 2022), photodegradation (Gomes et al., 2023), ion exchange (Joseph et al., 2020), and membrane separation (Zhou et al., 2023). Nevertheless, these methods are difficult to carry out, and highly expensive (Benhouria et al., 2023). Adsorption with inexpensive biological materials is widely considered to be a successful method for treating water that contains dyes (Şenol et al., 2024; Şen and Şenol, 2023; Aragaw and Bogale, 2021). Biologically derived adsorbents, such as bacterial, fungal, and agricultural wastes, have been utilized extensively to treat diluted dye solutions (Tsoutsas et al., 2024; Hamad and Idrus,

2022; Eyupoglu et al., 2025). Among these, algae have emerged as particularly promising biosorbents, attributed to their rich functional groups, high binding capacity, and porous cell walls that allow for effective pollutant uptake (Sheng et al., 2004; Srinivasan and Viraraghavan, 2010). Additionally, algae are widely available and exhibit straightforward growth requirements, making them an attractive and sustainable option for water treatment applications (Aragaw and Bogale, 2021).

Macroalgae species (e.g., *Fucus spiralis*, *Ulva intestinalis*, *Corallina officinalis*, *Codium* sp., *Padina sanctae-crucis*) are non-toxic, easily available, and provide effective results in the treatment of dye-contaminated waters (Boukarma et al., 2024; Şahin et al., 2024; Boukarma et al., 2023; Mahini et al., 2018). Algae of the class Phaeophyceae contain extracellular biopolymers, mainly alginic acid or alginate, which include small amounts of fucoidan that facilitate the transition of small ions (Vieira and Volesky, 2000). *Padina* sp., a macroalgae species from the Phaeophyceae class, is commonly found in intertidal to subtidal zones and is often referred to as sea fan ribbon weed (Ansari et al., 2019).

Previous studies have investigated both micro- and macroalgae as biosorbents for dye removal from aqueous solutions (Kousha et al., 2012; Omar et al., 2018; da Fontoura et al., 2017; Ucuncu et al., 2022). However, the direct application of *Padina* sp. as a biosorbent for MB dye remains relatively underexplored. While some studies have utilized *Padina* sp. in the removal of MB via the green synthesis of zinc oxide nanoparticles (Alprol et al., 2024; Pandimurugan and Thambidurai, 2016), its direct biosorption potential has not been comprehensively examined.

The primary aim of this work was to evaluate the ability of *Padina* sp., biomass to adsorb MB dye from aqueous solution. Dye removal capacity of *Padina* sp. was assessed under varying conditions, including different dye concentrations (2, 5, 10, 20, and 50 mg L<sup>-1</sup>), pH values (2, 4, 7, and 11), and contact time (0, 0.08, 0.5, 1, 2, 4, 6, and 24 h). The intrinsic mechanisms involved in the adsorption were explained by means of Fourier Transform Infrared Spectroscopy (FT-IR), equilibrium isotherm models, Scanning Electron Microscopy (SEM), and kinetic models.

## MATERIAL AND METHODS

### Macroalgae

*Padina* sp. (family Dictyotaceae, class Phaeophyceae) was collected from Black Sea coast, (Ordu Province, Türkiye) (41°07'34.5"N 37°41'32.7"E). The collected *Padina* sp. has a light brown thallus with a slightly calcareous structure, shaped like a semicircle or circle.

After being taken from their natural habitat, the samples were cleaned in the laboratory using distilled water to get rid of any sand or other organisms. Following this, the samples were dried in an oven at 60 °C until their weight stayed constant (Ucuncu et al., 2022). Following grinding and sieving utilizing a

941 µm mesh sieve, dried macroalgae samples were used in tests.

### Experimental design

MB, a cationic dye obtained from Pancreac®, was used in this study. Initial pH values of trials were adjusted to 2, 4, 7, and 11 utilizing 0.1 M NaOH and HCl. Using a stock dye solution, various dye concentrations (2, 5, 10, 20, and 50 mg L<sup>-1</sup>) were prepared. Adsorbent dosage was adjusted at 0.1 g L<sup>-1</sup> for all experimental groups. Erlenmeyer flasks containing 100 ml of dye solution were used for the experiments. The samples were shaken continuously at 80 rpm and 30 °C using a shaking culture incubator for different time (0, 0.08, 0.5, 1, 2, 4, 6, and 24 h). UV-vis spectroscopy was utilized to evaluate absorbance value of MB at 664 nm (Ucuncu et al., 2022; Türe, 2023). All the experiments were conducted in fresh distilled water to evaluate the adsorption performance of *Padina* sp.

### Isotherm models

The adsorption capacity of *Padina* sp. was assessed utilizing the following equation (Ucuncu et al., 2022; Türe, 2023).

$$q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

While  $C_o$  and  $C_e$  (mg L<sup>-1</sup>) denote the initial and equilibrium concentrations of MB, respectively,  $q_e$  (mg g<sup>-1</sup>) stands for the equilibrium adsorption capacity in this context. The dry weight of the adsorbent is indicated by  $m$  (g), and the volume of the test solution is  $V$  (L).

The Langmuir and Freundlich models were employed for identifying mechanisms involved in adsorption. Langmuir adsorption isotherm model was assessed using the following equation: (Ucuncu et al., 2022; Türe, 2023)

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{1}{q_{max}} \quad (2)$$

Here,  $q_e$  (mg g<sup>-1</sup>) denotes the concentration of MB at equilibrium on the adsorbent,  $C_e$  (mg L<sup>-1</sup>) represents the equilibrium dye concentration in the solution,  $b$  is the Langmuir constant, and  $q_{max}$  indicates the monolayer adsorption capacity (mg g<sup>-1</sup>).

The following equation shows the Freundlich model, which may be applied to heterogeneous surfaces (Ucuncu et al., 2022; Türe, 2023):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

In this context,  $n$  and  $K_f$  (L mg<sup>-1</sup>) are constants, which represent intensity and adsorption capacity, respectively.

### Adsorption kinetics

Kinetics of adsorption were evaluated using 0.1 g algal powder with an initial MB concentration of 10 mg L<sup>-1</sup>, contact time of 0 to 24 h, and pH of 8.0. Intra-particle diffusion and

pseudo-first and pseudo-second order models were used to fit experimental data for explaining adsorption kinetics of MB on biomass (Sahu et al., 2021; Türe, 2023).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Here,  $k_1$  represents the equilibrium rate constant of the pseudo-first order model ( $\text{min}^{-1}$ ), while  $q_e$  and  $q_t$  indicate the amounts of MB adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.

The linear equation for the pseudo-second order kinetic model is shown in the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  is the equilibrium rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ) for the pseudo-second order model.

The following is an expression for intra-particle diffusion:

$$q_t = k_{dif} t^{1/2} \quad (6)$$

where  $k_{dif}$  is intra particle constant.

#### Characterization of the adsorbent

Using an FT-IR spectrometer (Bruker Tensor 27), the functional groups found on the surface of *Padina* sp. were investigated. Additionally, the surface morphology was investigated with a SEM (Hitachi SU 1510).

#### Statistical analysis

The analyses were performed twice. Following data analysis using ANOVA, Tukey's test was utilized to determine group average differences at a significance level of 0.05. OriginPro2024-Learning Version (Software, USA) was used for graphing and analysis.

### RESULTS

#### Adsorption experiments results

##### Effect of pH

Figure 1 illustrates the effect of pH on MB uptake by *Padina* sp. at 30 °C. The most efficient removal was observed in neutral and basic media, in contrast to acidic pH. Furthermore, no significant differences were observed between pH values of 7 and 11, with a calculated  $q_e$  of approximately 9.88.

##### Effect of MB initial concentration

To investigate the effect of dye concentration, 0.1 g of *Padina* sp. underwent exposure to 0.1 L solutions of MB dye at concentrations of 2, 5, 10, 20, and 50  $\text{mg L}^{-1}$ . The treatment was conducted at 30 °C and pH of 8 for 4 h (Figure 2). According to the findings, *Padina* sp. was able to remove more dye when the concentration of dye increased. Figures 3a and 3b show the linear fitting of the Langmuir and Freundlich models, respectively, to the equilibrium data. Table 1 lists the experimental constants for both models. The Freundlich model,

as indicated by its high correlation coefficient ( $R^2=0.9902$ ), offers a more accurate representation of the isotherm data when *Padina* sp. was utilized as an adsorbent (Figure 3b). Additionally, the values of  $K_F$  and  $n$  were greater than 1, which supports the suitability of the model for adsorption applications (Table 1) (Batool et al., 2018). The Langmuir constant  $q_{max}$  represents the maximum adsorption capacity and indicates that *Padina* sp. can adsorb up to 107.5 mg of MB per gram of adsorbent. The Langmuir constant,  $b$ , is related to the affinity of the adsorbent for the adsorbate, indicating good adsorption interactions (Table 1) (Ucuncu et al., 2022).

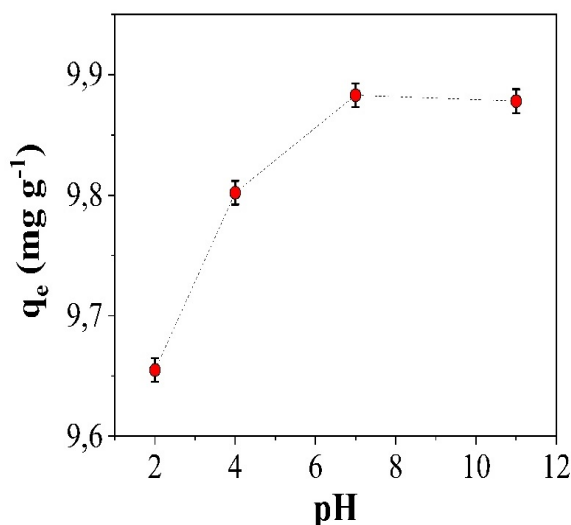


Figure 1. Effect of pH on MB adsorption capacity ( $q_e$ ) of *Padina* sp. (Weight = 0.1 g, Volume = 0.10 L, initial MB dye level = 10  $\text{mg L}^{-1}$ , temperature = 30 °C, and stirring rate = 80 rpm, contact time= 4 h)

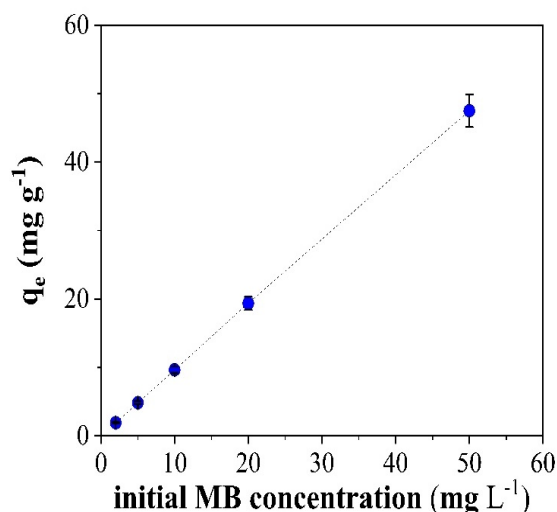


Figure 2. Effect of MB dye concentrations on adsorption capacity ( $q_e$ ) of *Padina* sp. (Weight = 0.1 g, Volume = 0.10 L, temperature = 30 °C, and stirring rate = 80 rpm, contact time= 4 h, pH=8)

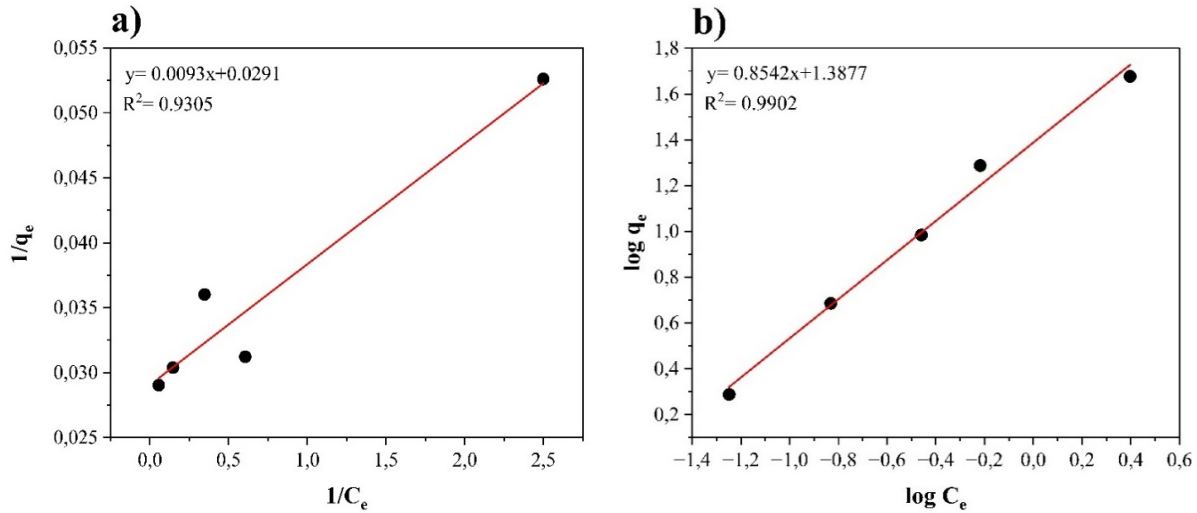


Figure 3. Linear fitting graphs of (a) Langmuir and (b) Freundlich, isotherm models

Table 1. Values of isotherm for MB adsorption on *Padina* sp.

Models	Parameters	Values
Langmuir	$q_{\max}$ (mg g <sup>-1</sup> )	107.5
	$b$ (L mg <sup>-1</sup> )	0.32
Freundlich	$K_F$	24.42
	$n$	1.17

#### Effect of contact time

The effect of various contact times (0, 0.08, 0.5, 1, 2, 4, 6, and 24 h) on MB sorption yield was investigated at a MB concentration of 10 mg L<sup>-1</sup>, pH 8, and 0.1 g L<sup>-1</sup> of *Padina* sp. The findings, which are displayed in Figure 4, reveal that the removal efficiency increases with contact time up to 6 hours, at which point the sorption of MB onto *Padina* sp. has almost achieved equilibrium.

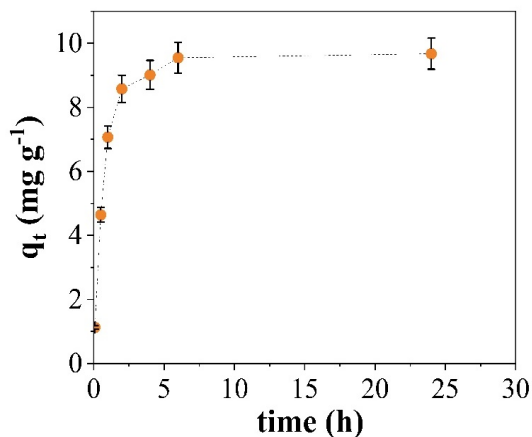


Figure 4. Effect of time on the biosorption of MB dye by *Padina* sp. (Weight = 0.1 g, Volume = 0.10 L, initial MB dye level = 10 mg L<sup>-1</sup>, temperature = 30 °C, stirring rate = 80 rpm, pH=8)

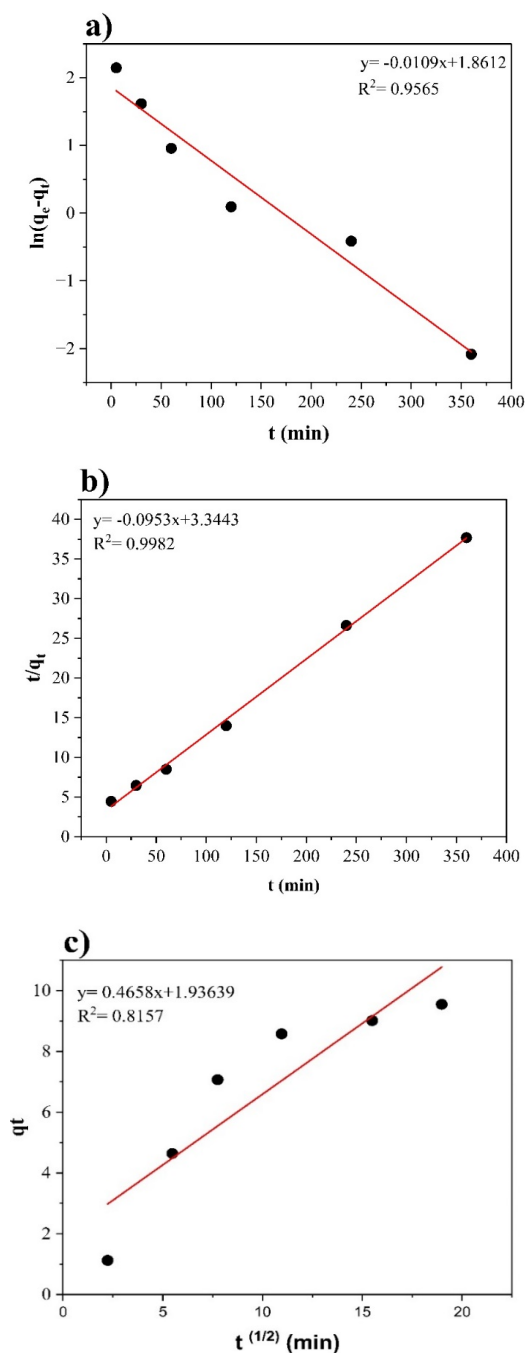
Additionally, the adsorption kinetics were examined to obtain a deeper understanding of the kinematics of MB adsorption on *Padina* sp. The kinetic data was calculated using pseudo-first order (PFO) and pseudo-second order (PSO) models, which were derived from Eqns. (4) and (5). Using the linear plots in Figures 5a and 5b, the adsorption kinetic parameters for the PFO and PSO models were determined, and results are listed in Table 2. The PSO kinetics were found to offer the best correct explanation for the kinetic data, with an  $R^2$  value of 0.9982. Furthermore, the measured adsorption capacity of 9.65 mg g<sup>-1</sup> (Figure 4) and predicted  $q_e$  (10.5) obtained by plotting time vs.  $t/q_t$  on the PSO graph are quite comparable. Additionally, process design requires an understanding of an adsorption system's dynamic behavior. Removal of MB dye by adsorption on biomass was initially rapid but subsequently decelerated as the contact time increased.

Table 2. Values for kinetic model of MB adsorption on *Padina* sp.

Models	Parameters	Values
Pseudo-first order kinetic	$q_{e, \text{calc}}$ (mg g <sup>-1</sup> )	6.43
	$k_1$ (min <sup>-1</sup> )	$9.2 \times 10^{-5}$
Pseudo-second order kinetic	$q_{e, \text{calc}}$ (mg g <sup>-1</sup> )	10.5
	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$1.2 \times 10^{-3}$

Based on intra-particle diffusion (IPD) process, which explains the sorption of MB from its aqueous phase, dye molecules move from the bulk solution to the surface of the sorbent, traversing the boundary layer to reach the surface where adsorption and IPD take place (Long et al., 2024). The intercept was C (1.94), and the slope directly predicted the rate constant  $K_{\text{diff}}$  (0.46), as shown in Figure 5c.



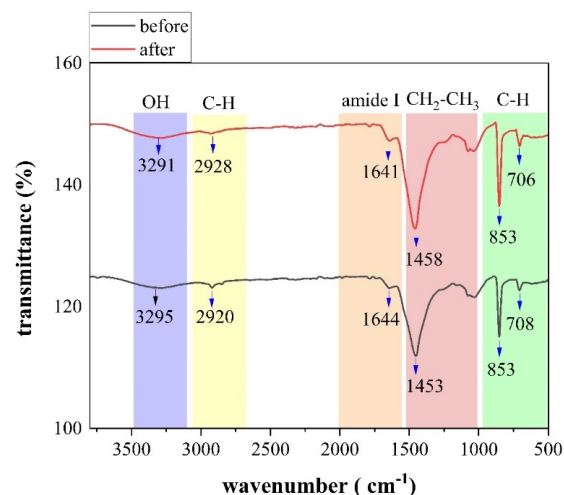


**Figure 5.** Adsorption kinetics of MB dye on *Padina* sp. (a) Pseudo-first order kinetic; (b) Pseudo-second order kinetic and (c) intra-particle diffusion models.

#### FT-IR analysis

The FT-IR spectra of *Padina* sp. biomass before and after MB removal are displayed in Figure 6. Broad peaks at 3291 and 3295  $\text{cm}^{-1}$  show the existence of -OH groups, whereas C-H bond stretching is indicated by the peaks at 2920 and 2928  $\text{cm}^{-1}$ . The Amide I band was attributed to the region between 1600 and 1690  $\text{cm}^{-1}$ . The peaks at 1453 and 1458  $\text{cm}^{-1}$  are associated with the symmetrical stretching of the C=O group

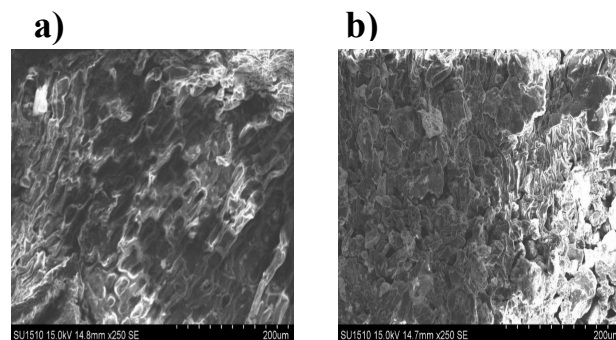
and the bending vibration of the  $\text{CH}_2$  and  $\text{CH}_3$  groups in the production of carboxyl (-COOH). The peaks that show C-H stretching are at around 850 and 700  $\text{cm}^{-1}$  (Seoane et al., 2022; Samar et al., 2022; Abdel-Raouf et al., 2019). Figure 6 shows that the biomass's FT-IR spectra either showed minor changes in the peaks corresponding to certain functional groups or were comparable before and after adsorption. This finding implies that the compound's main biosorption mechanism could be electrostatic attraction.



**Figure 6.** FT-IR spectra of *Padina* sp. before and after the removal process of MB (Weight = 0.1 g, Volume = 0.10 L, initial MB dye concentration = 10  $\text{mg L}^{-1}$ , temperature = 30  $^{\circ}\text{C}$ , stirring rate = 80 rpm, contact time = 4 h, pH=8)

#### Surface morphology

Images of *Padina* sp. taken with SEM before and after dye absorption are depicted in Figure 7. As can be seen in Figure 7a, adsorbent's porosity structure is consistent. The adsorbent surface's pores may aid in the efficient absorption of MB dye. Following MB adsorption, the surface morphology underwent notable changes, and discrete aggregates formed on their surfaces (Figure 7b). Furthermore, the porous texture filled and disappeared when coming into contact with MB dye.



**Figure 7.** SEM image of *Padina* sp. (a) before and (b) after adsorption of MB dye. (Weight = 0.1 g, Volume = 0.10 L, initial MB dye concentration = 10  $\text{mg L}^{-1}$ , temperature = 30  $^{\circ}\text{C}$ , stirring rate = 80 rpm, contact time = 4 h, pH=8)

## DISCUSSION

### Effect of pH

Because pH influences adsorbate's surface characteristics and degree of ionization, it is a crucial component in determining a material's adsorption capability (Benhouria et al., 2023). Both the functional groups of the dye and the macroalgal surface may be influenced by the pH of the dye solution (Chin et al., 2020). Due to the increased negative surface charge of biomass at higher pH value, which electrostatically attracts cationic dyes, efficient MB adsorption occurs on the surface of the adsorbent (Ali, 2010). Furthermore, the adsorption of MB may be explained by the strong interactions between adsorbate molecules (MB) and the several functional groups found in the phenols and flavonoids within the non-cellulosic cells of *Padina* sp. (Mansour et al., 2022). Similar patterns on how pH affects MB remediation in the aqueous phase have been documented in earlier research (Chin et al., 2020; Mansour et al., 2022).

### Isotherm and kinetic models

The Langmuir and Freundlich models, two of the most widely used adsorption models, were chosen to fit the experimental findings (Zhu et al., 2018). The Langmuir isotherm model depicts an adsorbate-adsorbent system where the adsorption process is not distributed, the surface is homogenous, and each adsorbate molecule occupies a single site (Al-Trawneh et al., 2021). The Freundlich model, which validates solid phase's heterogeneity and rough surface properties, was also used to assess the experimental MB adsorption values. This isotherm highlights how surface-bonded and unbound molecules interact in the liquid state to produce sorbate molecules in many layers (Alobaidi and Alwared, 2023). The isotherm analysis indicated that the removal of MB by *Padina* sp. showed a stronger correlation with the Freundlich model. This illustrates how MB was adsorbed onto *Padina* sp. via a multilayer process on a surface that was heterogeneous. The MB biosorption value of  $n = 1.17$  ( $>1$ ) shows strong MB/biosorbent interactions (Alobaidi and Alwared, 2023). This finding supports the conclusion that the Freundlich model more effectively describes the use of marine algae adsorbents for MB removal. However, the Langmuir model's constant  $q_{max}$  can be used to compare the adsorption capacity of *Padina* sp. with other adsorbents because its  $R^2$  (0.9305) value is comparable. The data shown in Table 3 indicate that the  $q_{max}$  values of MB dyes on *Padina* sp. are comparable to or higher than those of the other adsorbents.

Figure 4 demonstrates that the adsorbent's MB adsorption rate is quick in the first phase of the experiment. This result can be attributed to the active sites on its surface and a greater concentration of MB molecules in the solution that can easily reach the adsorbent's surface. Over time, however, the rate of MB biosorption slowed because there were fewer active sites available on the *Padina* sp. surface. This typical tendency of decreasing biosorption effectiveness as the adsorbent and

adsorbate's contact duration increases has been revealed by numerous studies (Long et al., 2024; Sahu et al., 2021).

The removal rate at the solid-liquid interface that establishes the adsorbate's retention time is known as adsorption kinetics (Pandey et al., 2010). The structure of Figure 5c, which illustrates that straight lines do not pass through origin, indicates that IPD is not the only rate-controlling step; other processes, such as boundary layer mass transfer and contact, also influence the adsorption process (Long et al., 2024).

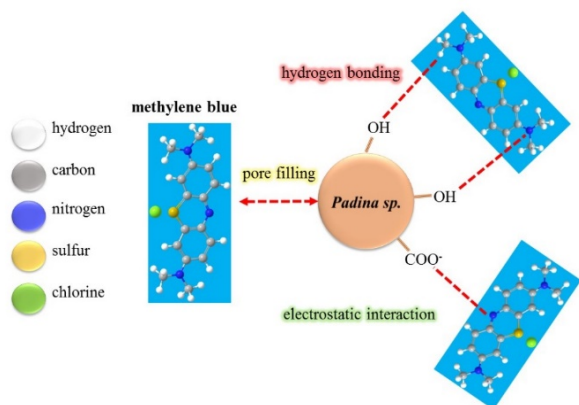
**Table 3.** Comparison of various adsorbents utilized for the removal of MB

Adsorbent	$q_{max}$ (mg g <sup>-1</sup> )	Reference
<i>Chlorella vulgaris</i>	10.142	Chin et al. (2020)
<i>Chlamydomonas moewusii</i>	212.41	Seoane et al. (2022)
<i>Treptacantha barbata</i>	73.53	Ucuncu et al. (2022)
<i>Sargassum latifolium</i>	0.819	Mansour et al. (2022)
<i>Sargassum ilicifolium</i>	99.7	Tabaraki and Sadeghinejad (2017)
<i>Ulva lactuca</i>	10.99	El Sikaily et al. (2006)
Rice husk	8.07	Shih (2012)
Glass fibres	2.24	Chakrabarti and Dutta (2005)
<i>Padina</i> sp.	107.5	This study

### Mechanism of MB on *Padina* sp.

The way that a pollutant is adsorbed onto a particular material depends on nature of adsorbate, properties of adsorbent, and possible interactions between them (Türe, 2023). Figure 8 shows a model of MB adsorption. According to pseudo-second order kinetic model, adsorption between *Padina* sp. and MB was hypothesized to be chemical. However, the absence of significant differences observed in the FT-IR analysis between *Padina* sp. before and after dye adsorption suggests that classical chemical bonds (such as covalent or ionic bonds) may not be present. In this case, adsorption may occur through weak chemical interactions or strong physical interactions. Several possibilities may explain this phenomenon: MB is a positively charged dye, and its binding is facilitated by negative charges, which are provided by a variety of components primarily found on the cell surface of macroalgal biomass (Pandey et al., 2010). This characteristic may be one of the factors contributing to the suitability of macroalgal biomass for biosorption of cationic sorbates. These electrostatic attractions can conform to pseudo-second order kinetics but might not demonstrate distinct chemical changes in FT-IR. Groups such as -OH in *Padina* sp. can form weak hydrogen bonds with the functional groups in MB. These hydrogen bonds are considered to be more physical interactions than strong chemical bonds. Such interactions may not be detectable by FT-IR or produce very weak signals. Additionally, a comparison of the SEM images taken before and after adsorption showed that the adsorbed *Padina* sp. had a rougher surface, which could be a sign that

MB molecules had partially filled the pores. When the algal cell surface interacted with MB, its porous texture changed to an uneven shape. Mansour et al. (2022) also noted similar results when *Sargassum latifolium* was utilized as an adsorbent to remove MB from water.



**Figure 8.** The suggested MB adsorption process on *Padina* sp.

## CONCLUSION

In this work, MB was removed from aqueous solutions using the macroalgae *Padina* sp. as an adsorbent. The results demonstrate that *Padina* sp. is effective as a natural sorbent for eliminating cationic dyes. The isotherm analysis revealed that MB removal by *Padina* sp. aligned more closely with Freundlich model, suggesting multilayer adsorption during experiments. The pseudo-second order model provided the best explanation for the kinetic data for MB adsorption. Additionally, an investigation of adsorption mechanism identified hydrogen bonding, electrostatic interactions, and pore filling as the primary factors contributing to the

significantly enhanced adsorption capacity. These findings indicate that the dried powder of this macroalga serves as an efficient biosorbent, making it highly suitable for elimination of MB dye from water. This study demonstrates the potential of natural adsorbents to address water contamination issues and contribute to the development of green technologies for environmental remediation. The regeneration and reusability of *Padina* sp. as an adsorbent can be further studied to increase its applicability in large-scale wastewater treatment applications.

## ACKNOWLEDGMENTS AND FUNDING

No grant, money, or other assistance from a governmental, private, or nonprofit organization was obtained for this study.

## AUTORSHIP CONTRIBUTIONS

Hasan Türe contributed through conceptualization, drafting, writing, reviewing, editing, and analyzing data and supervision. Pınar Akdoğan Şirin was responsible for the collecting of the samples and conducting laboratory experiments. The final version of the work has been reviewed and approved by all authors.

## CONFLICT OF INTEREST

The authors claim that there are no conflicts of interest.

## ETHICS APPROVAL

For this investigation, no ethical approval was needed.

## DATA AVAILABILITY

The relevant author should be contacted with any queries about the datasets.

## REFERENCES

- Abdel-Raouf, N., Al-Enazi, N.M., Ibraheem, I.B.M., Alharbi, R.M., & Alkhulaifi, M.M. (2019). Biosynthesis of silver nanoparticles by using of the marine brown alga *Padina pavonia* and their characterization. *Saudi Journal of Biological Sciences*, 26(6), 1207-1215. <https://doi.org/10.1016/j.sjbs.2018.01.007>
- Ali, H. (2010). Biodegradation of synthetic dyes—a review. *Water, Air, & Soil Pollution*, 213, 251-273. <https://doi.org/10.1007/s11270-010-0382-4>
- Alobaidi, D. S., & Alwared, A. I. (2023). Role of immobilised Chlorophyta algae in form of calcium alginate beads for the removal of phenol: isotherm, kinetic and thermodynamic study. *Heliyon*, 9(4). <https://doi.org/10.1016/j.heliyon.2023.e14851>
- Alprol, A.E., Eleryan, A., Abouelwafa, A., Gad, A.M., & Hamad, T.M. (2024). Green synthesis of zinc oxide nanoparticles using *Padina pavonica* extract for efficient photocatalytic removal of methylene blue. *Scientific Reports*, 14(1), 32160. <https://doi.org/10.1038/s41598-024-80757-9>
- Al-Trawneh, S.A., Jiries, A.G., Alshahateet, S.F., & Sagadevan, S. (2021). Phenol removal from aqueous solution using synthetic V-shaped organic adsorbent: kinetics, isotherm, and thermodynamics studies. *Chemical Physics Letters*, 781, 138959. <https://doi.org/10.1016/j.cpl.2021.138959>
- Ansari, A.A., Ghanem, S.M., & Naeem, M. (2019). Brown alga *Padina*: a review. *International Journal of Botany Studies*, 4(1), 01-03.
- Aragaw, T.A., & Bogale, F.M. (2021). Biomass-based adsorbents for removal of dyes from wastewater: a review. *Frontiers in Environmental Science*, 9, 764958. <https://doi.org/10.3389/fenvs.2021.764958>
- Batool, F., Akbar, J., Iqbal, S., Noreen, S., & Bukhari, S. N.A. (2018). Study of isothermal, kinetic, and thermodynamic parameters for adsorption of cadmium: an overview of linear and nonlinear approach and error analysis. *Bioinorganic Chemistry and Applications*, 2018, 1, 1-11, 3463724. <https://doi.org/10.1155/2018/3463724>
- Benhouria, A., Zaghouane-Boudiaf, H., Bourzami, R., Djerboua, F., Hameed, B., & Boutahala, M. (2023). Cross-linked chitosan-epichlorohydrin/bentonite composite for reactive orange 16 dye removal: Experimental study and molecular dynamic simulation. *International Journal of Biological Macromolecules*, 242, 124786. <https://doi.org/10.1016/j.ijbiomac.2023.124786>
- Boukarma, L., Aboussabek, A., El Aroussi, F., Zerbé, M., Sinan, F., & Chiban, M. (2023). Insight into mechanism, Box-Behnken design, and artificial neural network of cationic dye biosorption by marine macroalgae *Fucus spiralis*. *Algal Research*, 76, 103324. <https://doi.org/10.1016/j.algal.2023.103324>
- Boukarma, L., Aziam, R., Aboussabek, A., El Qdhy, S., Zerbé, M., Sinan, F., & Chiban, M. (2024). Novel insights into crystal violet dye adsorption onto various macroalgae: Comparative study, recyclability and overview of chromium (VI) removal. *Bioresource Technology*, 394, 130197. <https://doi.org/10.1016/j.biortech.2023.130197>



- Bravo-Yumi, N., Pacheco-Álvarez, M., Bandala, E.R., Brillas, E., & Peralta-Hernández, J.M. (2022). Studying the influence of different parameters on the electrochemical oxidation of tannery dyes using a  $\text{Ti}/\text{IrO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  anode. *Chemical Engineering and Processing-Process Intensification*, 181, 109173. <https://doi.org/10.1016/j.cep.2022.109173>
- Chakrabarti, S., & Dutta, B.K. (2005). On the adsorption and diffusion of methylene blue in glass fibers. *Journal of Colloid and Interface Science*, 286(2), 807-811. <https://doi.org/10.1016/j.jcis.2005.01.035>
- Chin, J.Y., Chng, L.M., Leong, S.S., Yeap, S.P., Yasin, N.H.M., & Toh, P.Y. (2020). Removal of synthetic dye by *Chlorella vulgaris* microalgae as natural adsorbent. *Arabian Journal for Science and Engineering*, 45, 7385-7395. <https://doi.org/10.1007/s13369-020-04557-9>
- da Fontoura, J.T., Rolim, G.S., Mella, B., Farenzena, M., & Gutierrez, M. (2017). Defatted microalgal biomass as biosorbent for the removal of Acid Blue 161 dye from tannery effluent. *Journal of Environmental Chemical Engineering*, 5(5), 5076-5084. <http://dx.doi.org/10.1016/j.jece.2017.09.051>
- El Sikaily, A., Khaled, A., Nemr, A.E., & Abdelwahab, O. (2006). Removal of methylene blue from aqueous solution by marine green alga *Ulva lactuca*. *Chemistry and Ecology*, 22(2), 149-157. <https://doi.org/10.1080/02757540600579607>
- Eyupoglu, V., Akin, M.B., Kaya, S., Çaylak, O., Berisha, A., & Çetinkaya, S. (2025). Effective removal of methylene blue dye from aqueous solution using *Macrolepiota procera* mushroom: Experimental and theoretical studies. *Journal of Molecular Liquids*, 418, 126714. <https://doi.org/10.1016/j.molliq.2024.126714>
- Ghosh, I., Kar, S., Chatterjee, T., Bar, N., & Das, S.K. (2021). Removal of methylene blue from aqueous solution using *Lathyrus sativus* husk: adsorption study, MPR and ANN modelling. *Process Safety and Environmental Protection*, 149, 345-361. <https://doi.org/10.1016/j.psep.2020.11.003>
- Gomes, G.H., Olusegun, S.J., Gabriel, J.B., Costa, R.C., & Mohalle, N.D. (2023). The role of crystalline  $\text{Nb}_2\text{O}_5$  nanoparticles for enhanced dye adsorption and photodegradation. *Ceramics International*, 49(4), 6164-6176. <https://doi.org/10.1016/j.ceramint.2022.10.126>
- Hamad, H.N., & Idrus, S. (2022). Recent developments in the application of bio-waste-derived adsorbents for the removal of methylene blue from wastewater: a review. *Polymers*, 14(4), 783. <https://doi.org/10.3390/polym14040783>
- Ihaddaden, S., Aberkane, D., Boukerroui, A., & Robert, D. (2022). Removal of methylene blue (basic dye) by coagulation-flocculation with biomaterials (bentonite and *Opuntia ficus indica*). *Journal of Water Process Engineering*, 49, 102952. <https://doi.org/10.1016/j.wpe.2022.102952>
- Joseph, J., Radhakrishnan, R.C., Johnson, J.K., Joy, S.P., & Thomas, J. (2020). Ion-exchange mediated removal of cationic dye-stuffs from water using ammonium phosphomolybdate. *Materials Chemistry and Physics*, 242, 122488. <https://doi.org/10.1016/j.matchemphys.2019.122488>
- Khodaie, M., Ghasemi, N., Moradi, B., & Rahimi, M. (2013). Removal of methylene blue from wastewater by adsorption onto  $\text{ZnCl}_2$  activated corn husk carbon equilibrium studies. *Journal of Chemistry*, 2013(1), 383985. <https://doi.org/10.1155/2013/383985>
- Kousha, M., Daneshvar, E., Sohrabi, M., Koutahzadeh, N., & Khataee, A. (2012). Optimization of CI Acid black 1 biosorption by *Cystoseira indica* and *Gracilaria persica* biomasses from aqueous solutions. *International Biodeterioration & Biodegradation*, 67, 56-63. <https://doi.org/10.1016/j.ibiod.2011.10.007>
- Long, Z., Wang, Z., Huang, Q., Jia, Y., Jiao, Z., Wang, Y., & Du, Y. (2024). High-performance adsorption of methylene blue using novel bio-adsorbent based on *Sargassum fusiforme*. *Heliyon*, 10(18). <https://doi.org/10.1016/j.heliyon.2024.e37949>
- Mahini, R., Esmaeili, H., & Foroutan, R. (2018). Adsorption of methyl violet from aqueous solution using brown algae *Padina sanctae-crucis*. *Turkish Journal of Biochemistry*, 43(6), 623-631. <https://doi.org/10.1515/tjb-2017-0333>
- Mansour, A.T., Alprol, A.E., Abualnaja, K.M., El-Beltagi, H.S., Ramadan, K.M., & Ashour, M. (2022). Dried brown seaweed's phytoremediation potential for methylene blue dye removal from aquatic environments. *Polymers*, 14(7), 1375. <https://doi.org/10.3390/polym14071375>
- Martínez Cadena, G., Vargas Hernández, D., Villegas Coronado, D.L., Tánori Córdova, J.C., & Maldonado Arce, A.D. (2025). Synthesis, characterization, and application of carbon black nanoparticles in the removal of methylene blue dye. *Adsorption*, 31(1), 8. <https://doi.org/10.1007/s10450-024-00566-4>
- Mcyotto, F., Wei, Q., Macharia, D.K., Huang, M., Shen, C., & Chow, C.W. (2021). Effect of dye structure on color removal efficiency by coagulation. *Chemical Engineering Journal*, 405, 126674. <https://doi.org/10.1016/j.cej.2020.126674>
- Oladoye, P.O., Ajiboye, T.O., Omotola, E.O., & Oyewola, O.J. (2022). Methylene blue dye: Toxicity and potential elimination technology from wastewater. *Results in Engineering*, 16, 100678. <https://doi.org/10.1016/j.rineng.2022.100678>
- Omar, H., El-Gendy, A., & Al-Ahmary, K. (2018). Bioremoval of toxic dye by using different marine macroalgae. *Turkish Journal of Botany*, 42(1), 15-27. <https://doi.org/10.3906/bot-1703-4>
- Pandey, P., Sharma, S., & Sami, S. (2010). Kinetics and equilibrium study of chromium adsorption on zeolite Nax. *International Journal of Environmental Science and Technology*, 7, 395-404. <https://doi.org/10.1007/bf03326149>
- Pandimurugan, R., & Thambidurai, S. (2016). Synthesis of seaweed-ZnO-PANI hybrid composite for adsorption of methylene blue dye. *Journal of Environmental Chemical Engineering*, 4(1), 1332-1347. <https://doi.org/10.1016/j.jece.2016.01.030>
- Saheed, I.O., Oh, W.-D., & Suah, F.B.M. (2021). Enhanced adsorption of acid Blue-25 dye onto chitosan/porous carbon composite modified in 1-allyl-3-methyl imidazolium bromide ionic liquid. *International Journal of Biological Macromolecules*, 183, 1026-1033. <https://doi.org/10.1016/j.ijbiomac.2021.05.042>
- Sahu, J., Karri, R.R., & Jayakumar, N. (2021). Improvement in phenol adsorption capacity on eco-friendly biosorbent derived from waste Palm-oil shells using optimized parametric modelling of isotherms and kinetics by differential evolution. *Industrial Crops and Products*, 164, 113333. <https://doi.org/10.1016/j.indcrop.2021.113333>
- Samar, J., Butt, G.Y., Shah, A.A., Shah, A.N., Ali, S., Jan, B.L., Abdelsalam, R.N., & Hussaan, M. (2022). Phytochemical and biological activities from different extracts of *Padina antillarum* (Kütz.) Piccone. *Frontiers in Plant Science*, 13, 929368. <https://doi.org/10.3389/fpls.2022.929368>
- Seoane, R., Santaefemia, S., Abalde, J., & Torres, E. (2022). Efficient removal of methylene blue using living biomass of the microalga *Chlamydomonas moewusii*: Kinetics and equilibrium studies. *International Journal of Environmental Research and Public Health*, 19(5), 2653. <https://doi.org/10.3390/ijerph19052653>
- Sheng, P.X., Ting, Y.-P., Chen, J.P., & Hong, L. (2004). Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *Journal of Colloid and Interface Science*, 275(1), 131-141. <https://doi.org/10.1016/j.jcis.2004.01.036>
- Shih, M.C. (2012). Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: effect of acid-modified process and dye concentration. *Desalination and Water Treatment*, 37(1-3), 200-214. <https://doi.org/10.5004/dwt.2012.1133>
- Srinivasan, A., & Viraraghavan, T. (2010). Decolorization of dye wastewaters by biosorbents: a review. *Journal of Environmental Management*, 91(10), 1915-1929. <https://doi.org/10.1016/j.jenvman.2010.05.003>
- Şahin, M., Arslan, Y., Tomul, F., Akgül, F., & Akgül, R. (2024). Green synthesis of metal nanoparticles from *Codium* macroalgae for wastewater pollutants removal by adsorption. *CLEAN-Soil, Air, Water*, 52(5), 2300187. <https://doi.org/10.1002/clen.202300187>
- Şen, N.E., & Şenol, Z.M. (2023). Effective removal of Allura red food dye from water using cross-linked chitosan-diatomite composite beads. *International Journal of Biological Macromolecules*, 253, 126632. <https://doi.org/10.1016/j.ijbiomac.2023.126632>
- Şenol, Z.M., El Messaoudi, N., Çiğeroğlu, Z., Miyah, Y., Arslanoğlu, H., Bağlam, N., Kazan-Kaya, E.S., Kaur, P., & Georgin, J. (2024). Removal of food dyes using biological materials via adsorption: A



- review. *Food Chemistry*, 139398. <https://doi.org/10.1016/j.foodchem.2024.139398>
- Tabaraki, R., & Sadeghinejad, N. (2017). Biosorption of six basic and acidic dyes on brown alga *Sargassum ilicifolium*: Optimization, kinetic and isotherm studies. *Water Science and Technology*, 75(11), 2631-2638. <https://doi.org/10.2166/wst.2017.136>
- Tsoutsas, E.K., Tolkou, A.K., Kyzas, G.Z., & Katsoyiannis, I.A. (2024). An update on agricultural wastes used as natural adsorbents or coagulants in single or combined systems for the removal of dyes from wastewater. *Water, Air, & Soil Pollution*, 235(3), 178. <https://doi.org/10.1007/s11270-024-06979-9>
- Türe, H. (2023). Adsorption of methylene blue dye onto alginate-bioglass membranes: response surface method, isotherm, and kinetic studies. *Gümüşhane Üniversitesi Fen Bilimleri Dergisi*, 13(3), 538-552. <https://doi.org/10.17714/gumusfenbil.1245309>
- Ucuncu, E., Şirin, P.A., & Hasan, T. (2022). Prediction models of dye adsorption by *Treptacantha barbata*. *Ege Journal of Fisheries and Aquatic Sciences*, 39(4), 300-310. <https://doi.org/10.12714/legejfas.39.4.05>
- Vieira, R.H., & Volesky, B. (2000). Biosorption: a solution to pollution? *International Microbiology*, 3(1), 17-24.
- Zhou, M., Chen, J., Yu, S., Chen, B., Chen, C., Shen, L., & Lin, H. (2023). The coupling of persulfate activation and membrane separation for the effective pollutant degradation and membrane fouling alleviation. *Chemical Engineering Journal*, 451, 139009. <https://doi.org/10.1016/j.cej.2022.139009>
- Zhu, H., Chen, T., Liu, J., & Li, D. (2018). Adsorption of tetracycline antibiotics from an aqueous solution onto graphene oxide/calcium alginate composite fibers. *RSC Advances*, 8(5), 2616-2621. <https://doi.org/10.1039/c7ra11964j>