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# Removal of methylene blue dye by immobilized mixture of brown alga *Dictyota cervicornis* and activated carbon

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**ABSTRACT**

Dyes are one of the most dangerous chemical compounds which are present in several industrial effluents. In this study, the ability of the combination of brown alga *Dictyota cervicornis* and activated carbon, which were immobilized on calcium alginate, for removal of methylene blue (MB) dye from aqueous solutions was investigated. The effects of contact time, initial dye concentration, and initial pH were studied. Kinetics and isotherm data were modeled and the mechanism of the process was verified. The algal biomass was characterized through potentiometric titration and Fourier transform infrared (FTIR) analyses. Potentiometric titration predicted the quantity of the total acidity on the algal surface equal to 2.4 meq $g^{-1}$ dry biomass. FTIR spectrum indicated the presence of functional groups such as carboxylic, sulfonic, hydroxyl and amines on the biomass surface. The highest removal efficiency was achieved for the mixture of 75% activated carbon and 25% alga. Langmuir model predicted the maximum adsorption capacity equal to 582 mg $g^{-1}$ which is a relatively high value. Pseudo-second-order model described kinetics data appropriately. Ion exchange was a mechanism for MB removal.

*Keywords:* Activated carbon; Adsorption; Alga; Immobilization; Methylene blue

## 1. Introduction

One of the most important pollutants is colors which are mainly originated from the presence of dyes in wastewaters [1]. The wastewaters which contain dyes are toxic and considered as a threat for the environment and aquatic life. Methylene blue (MB) with the chemical formula of $C_{16}H_{18}N_3SCl$ is a heterocyclic aromatic dye which is widely used in biological applications as well as for dyeing silk, wool, cotton, and paper. It influences human health such that after ingestion, nausea, vomiting, and diarrhoea may occur [2]. Therefore, it is essential to remove MB from wastewaters.

Several methods such as electrocoagulation, froth flotation, reverse osmosis, ion exchange, membrane filtration and flocculation are used for treatment of effluents containing dyes [3]. The use of these techniques has been limited due to their low efficiencies, high expenses, and production of a large volume of sludge.

Activated carbon (AC) is a common adsorbent for dye removal because of its large surface area and high adsorption capacity to organics [4]. However, treating large amounts of wastewaters with low concentrations in the range of 1–100 mg $L^{-1}$ by activated carbon is considerably expensive [5]. There are several papers which studied MB removal from aqueous solutions using activated carbon as the adsorbent. For instance, Hajati et al. [6] made use of ruthenium nanoparticle loaded activated carbon as the adsorbent for MB removal. Gong et al. [7] studied MB removal from contaminated water using activated carbon derived from finger citron residue and Hajati et al. [8] optimized MB removal from aqueous solutions by walnut carbon through response surface methodology.

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Recently, adsorbents with biological origins such as agricultural wastes, and the biomass of fungi, bacteria, and algae have been widely used for treating diluted dye solutions [9]. For instance, Shih [10] used rice husk and acid modified rice husk for MB removal in the range of 10–100 mg $L^{-1}$ and El Sikaily et al. [11] investigated MB removal by marine green alga *Ulva lactuca* in the range of 5–25 mg $L^{-1}$.

In order to prepare adsorbents with a right size and high mechanical strength and rigidity, immobilization in solid structures is performed. Immobilization can also produce beads and granules that can be regenerated and reused such as ion exchange resins [12].

This paper was aimed to make use of a new adsorbent for MB dye removal from aqueous solutions in a wide range of dye concentrations. As mentioned before, activated carbon is not efficient for treating diluted streams while adsorbents with biological origins are generally applied to wastewaters with low concentrations (below 100 mg $L^{-1}$) of dyes. Therefore, to provide an adsorbent which can be used in a wide range of dye concentration, different compositions of both activated carbon and an algal biomass were prepared and immobilized on calcium alginate to improve the properties of the adsorbents. For this purpose, the brown marine macroalga of *D. cervicornis* was used. Generally, algae are among interesting biosorbents because of their high biosorption capacity and availability almost in all parts of the world [13]. The alga *D. cervicornis* is also highly available in Oman Sea costal water in Iran. Therefore, it can be provided for the experiments with no cost. Furthermore, it is insoluble in water which makes it appropriate for adsorption purposes [10]. To the best of our knowledge, there is no study on adsorption of MB dye by the alga *D. cervicornis* and especially its immobilized mixture with activated carbon. Fourier transform infrared (FTIR) analysis and potentiometric titration were performed to characterize the algal biomass. The optimum combination of algal biomass and AC in the produced granules was obtained. Afterwards, effects of initial solution pH, contact time, and initial dye concentration on MB removal by the immobilized adsorbent were studied. Kinetics and isotherm data were modeled and ion exchange was verified as a probable mechanism of adsorption.

## 2. Materials and methods

### 2.1. Materials

MB (C.I. 52015, ACROS Organics, USA) with the chemical formula $C_{16}H_{18}N_3SCl$ was used without further purification. Charcoal activated carbon with the CAS No. 7440-44-0 was obtained from Merck Chemicals (Germany). Chemicals such as sodium hydroxide (≥97.0%), nitric acid (65.0%), hydrochloric acid (37%), and calcium chloride were of analytical grade and obtained from Merck Chemicals (Germany). Calcium alginate was prepared from Sigma-Aldrich (USA).

### 2.2. Preparation of the algal biomass

The biomass of *D. cervicornis* was available at coastline of Oman Sea in Chabahar, Iran. In order to remove debris and salt, the biomass was washed with distilled water several times and then dried at 70°C for 24 h. Afterwards, it was ground and sieved to get particles with sizes between 106–250 μm.

### 2.3. FTIR analysis of the algal biomass

In order to determine the functional groups on the algal biomass, FTIR analysis was performed by a FTIR spectrometer (Perkin Elmer 65, USA) in the range of 3,800–600 $cm^{-1}$ with a resolution of 1 $cm^{-1}$.

### 2.4. Determination of acidic sites on the algal biomass

The quantity of acidic sites on the algal biomass was also determined through potentiometric titration. An amount of 0.25 g of the algal biomass was added to 50 ml of 0.1 M HCl solution. After agitating for 2 h, the suspension was titrated by 0.1 M NaOH solution. In each stage, an amount of 0.25 ml of sodium hydroxide solution was added to the suspension and the equilibrium pH was measured. Similarly, another titration on a control solution (without biomass) was also performed. The plot of pH as a function of alkali volume was used to determine the quantity of acidic sites on the biomass surface [14].

### 2.5. Adsorbent immobilization

In order to find the optimum composition of the immobilized adsorbent, five samples with the total mass (activated carbon and *D. cervicornis* biomass) of 0.06 g containing 0%, 25%, 50%, 75%, and 100% of alga were prepared. An amount of 15 ml of calcium alginate solution (2% w/v) was added to the samples and the suspension was injected to solutions of calcium chloride (15 ml, 4% w/v) to form granules. Afterwards, the granules were separated through filtration and dried at room temperature.

### 2.6. Characterization of the adsorbent granules

In order to study the morphology of the adsorbent granules (75% activated carbon and 25% algal biomass), scanning electron microscopy (SEM) was used. The adsorbent was coated with gold and subjected to SEM (XL30, Philips, Netherlands). The images were provided by a secondary electron detector in high vacuum mode at 15–20 kV. Furthermore, the specific surface area ($S_{BET}$) for the mentioned granules and activated carbon was measured by $N_2$ adsorption analyzer (NanoSORD, SensIran Co., Iran).

### 2.7. Adsorption experiments

A stock solution of MB dye (1000 mg $L^{-1}$) was prepared and used for preparation of other solutions with lower concentrations. An amount of 50 ml of dye solution with a specific concentration was added to a 250 ml flask and the solution pH was adjusted using solutions of NaOH and $HNO_3$ (0.1 M). An amount of 0.03 g of the produced granules was added to the solutions and the flasks were agitated in a shaker-incubator (150 rpm) at 24°C±1°C.

The optimum composition of the immobilized adsorbent was obtained by using the five immobilized samples in adsorption experiments ($m$ = 0.03 g, pH = 4, $C_0$ = 200 mg $L^{-1}$)

to reach equilibrium. The equilibrium concentrations for the samples were measured and the sample with the highest adsorption capacity was used in the remaining experiments.

The effects of contact time ($t$ = 30–2850 min) on adsorption efficiency was studied at pH = 4 for the initial dye concentration of 200 mg $L^{-1}$. Furthermore, the effects of initial dye concentrations ($C_0$ = 50, 100, 150, 200, and 250 mg $L^{-1}$) and initial pH (pH = 3.0–7.0) on adsorption capacity were investigated respectively at pH = 4 and for $C_0$ = 200 mg $L^{-1}$. Similarly, control flasks (containing no biomass) were also prepared simultaneously. At the desired time, a sample was taken, filtered, and the concentration of MB in the supernatant was measured by a UV spectrophotometer (RAYLEIGH/UV-T70, Japan) at 665 nm. Adsorption capacity, which is the mass of MB removed by the unit mass of the adsorbent, was calculated using Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where $C_0$ and $C_e$ (mg $L^{-1}$) are the initial and final concentrations of MB, respectively. $V$ is the volume of the solution (50 ml) and $m$ is the mass of the granules added to the solution (0.03 g). All experiments were performed twice and the average value was considered.

### 2.8. Determination of pH of zero charge for the adsorbent

The pH of zero charge ($pH_{ZPC}$), at which the electrical charge density on a surface is zero, was determined for the adsorbent granules (75% AC, 25% alga). For this purpose, the method of Mall et al. [15] was used. Different flasks containing 50 mL of 0.1 M $KNO_3$ solutions with different pH values in the range of 1–8 were prepared. One gram of the adsorbent was added to each flask, the suspension was agitated for 24 h, and the final pH was measured. The initial pH for which initial and final pH values are the same was considered as $pH_{ZPC}$.

### 2.9. Ion Exchange mechanism

In order to investigate if ion exchange is a mechanism of adsorption, 50 ml of MB solution (200 mg $L^{-1}$) at pH 4 and 50 ml of deionized water at the same pH were prepared. An amount of 0.03 g of granules (75% AC, 25% alga) was added to the flasks. After reaching equilibrium, the concentrations of Ca, K, Mg, and Na ions in both MB solution and deionized water were measured using an ICP–OES analyzer (Optima 7300DV, Perkin Elmer, USA). The differences between these concentrations were considered as the amount of ions which was released by the adsorbent because of MB removal.

## 3. Results and discussion

### 3.1. Characterization of the algal biomass (FTIR analysis and potentiometric titration)

In order to characterize the algal biomass, FTIR analysis and potentiometric titration were performed. The results of FTIR analysis is presented in Fig. 1. Accordingly, the band at 3,622 and 3,288 $cm^{-1}$ may be for N–H and O–H stretching vibrations. The band at 2,938 $cm^{-1}$ is due to –CH stretching vibration of C–$CH_3$. The band at 1,658 $cm^{-1}$ is for C=O stretching mode of amide I band or carboxylic acids. The band at 1,454 $cm^{-1}$ is for the stretching of C=O bond from carboxylic acids. The band at wavelengths of 1,088 and 1,026 $cm^{-1}$ are for C–OH stretching vibrations of carboxylic acids [16] or P–O–C bond of phosphate groups [17]. Furthermore, the band at 880 $cm^{-1}$ is because of the presence of phosphate groups [18] or S O and C–S–O bands from ester sulfonate groups [19]. Therefore, amine, hydroxyl, amide I, carboxylic acids, phosphate groups, and sulfonate groups are the functional groups present on the biomass. In general, the constituents of the cell wall of a brown alga are cellulose (the structural support), alginic acid or alginate (the salts of sodium, potassium, magnesium, and calcium), and sulphated polysaccharides (fucoidan matrix) [5]. Alginate polymer, which constitutes up to 40% of the biomass dry weight, contains acidic functional groups. In brown algae, carboxylic groups constitute the most abundant acidic functional group and sulfonic acid of fucoidan is the second most abundant one. Hydroxyl groups which are less abundant, also present considerably since it exists in cellulose as a constituent of the cell wall [19].

The quantities of acidities on a heterogeneous surface such as the algal surface are determined through potentiometric titration. Strong acidities ($A_S$) is originated from the presence of high affinity acidic groups such as sulfonate and carboxylic linked to aromatic at pH < 4. At 4 < pH < 7, ionization of carboxylic groups results in weak acidities ($A_W$). At pH > 7, the presence of phenolic and amine groups, including the ionization of amino groups of proteins results in very weak acidities ($A_{VW}$). Naja et al. [17] used NaOH into HCl titration curve for quantifying three types of acidities. Fig. 2 shows the titration curve for the algal biomass. The quantities of strong, weak, and very weak acidities which were calculated by the Gran's method were respectively 1.23, 0.88, and 0.29 meq $g^{-1}$ dry biomass ($A_{TO}$ = 2.4 meq $g^{-1}$). The value of $A_{TO}$ indicates the available sites on the surface for removal of the adsorbate and shows the upper limit of adsorption. The calculated value of $A_{TO}$ for *D. cervicornis* biomass (2.4 meq $g^{-1}$) is relatively high in comparison with other algal biomasses such as *Ulva lactuca* (1.81 meq $g^{-1}$ [20]), *Ulva* spp. (1.94 meq $g^{-1}$ [20]), and *Chlorella vulgaris* (0.22 meq $g^{-1}$ [21]) which indicates its higher adsorption ability.

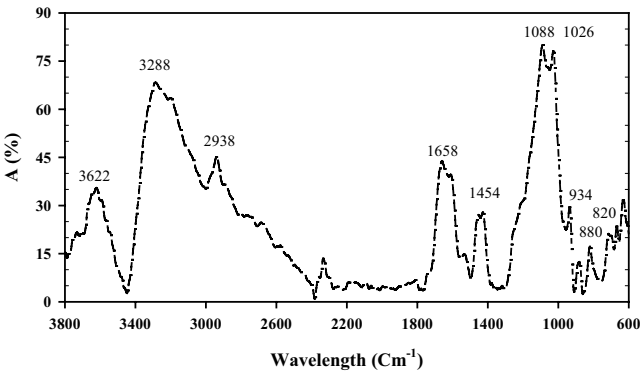


Fig. 1. FTIR spectrum of *D. cervicornis* biomass.

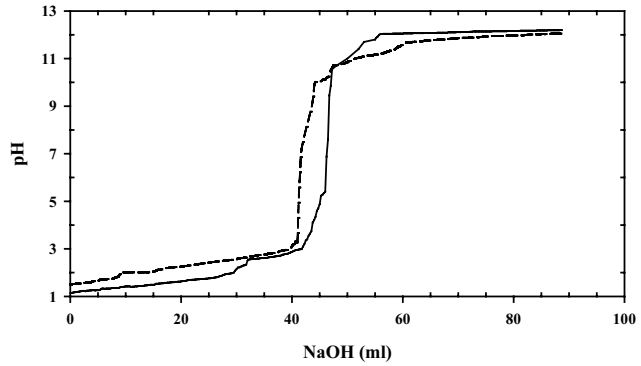


Fig. 2. Potentiometric titration curve for control (---) and *D. cervicornis* sample (−).

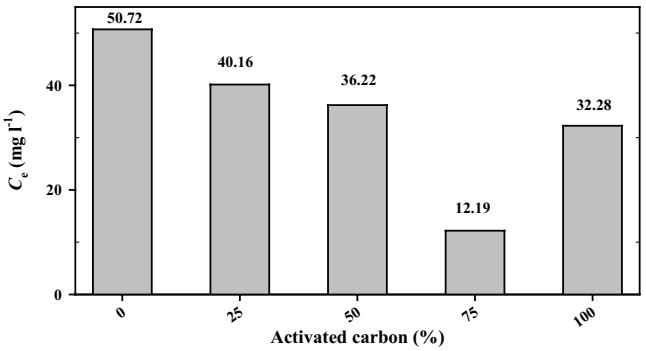


Fig. 3. Equilibrium concentrations of MB obtained by granules with various ratios of AC to the alga.

### 3.2. Determination of the optimum composition of granules

The optimum ratio of the alga to activated carbon in the immobilized adsorbent was determined using five samples containing 0%, 25%, 50%, 75%, and 100% of activated carbon which were immobilized and used in adsorption experiments to reach equilibrium. The equilibrium concentrations were measured and are presented in Fig. 3. Accordingly, the granules containing 75% activated carbon and 25% algal biomass indicated the most appropriate performance for MB dye removal from aqueous solutions. Therefore, granules with this composition were used for the remaining experiments.

### 3.3. Characterization of the adsorbent granules

SEM has been extensively used for adsorbent characterization. The surface morphology of the adsorbent at different magnifications is represented in Fig. 4. It is observed that the adsorbent surface is rough and flaky. Besides, the presence of pores, which are irregularly distributed at the surface of the adsorbent in the μm range, provides active sites for dye to be adsorbed on the adsorbent surface. This makes the adsorption capacity of granules high for MB removal. Specific surface area ($S_{BET}$) for the immobilized adsorbent was obtained equal to 2.839 $m^2$ $g^{-1}$. The corresponding value for the activated carbon was 1784.349 $m^2$ $g^{-1}$. The lower value of $S_{BET}$ for granules in comparison with individual activated carbon is because of the presence of algal biomass and calcium alginate in the structure of adsorbent granules.

### 3.4. pH of zero charge and effect of pH on adsorption

The pH of zero point charge ($pH_{ZPC}$) is an advantageous parameter for evaluation of the effect of pH on the adsorption process. For the adsorbent granules, which were used

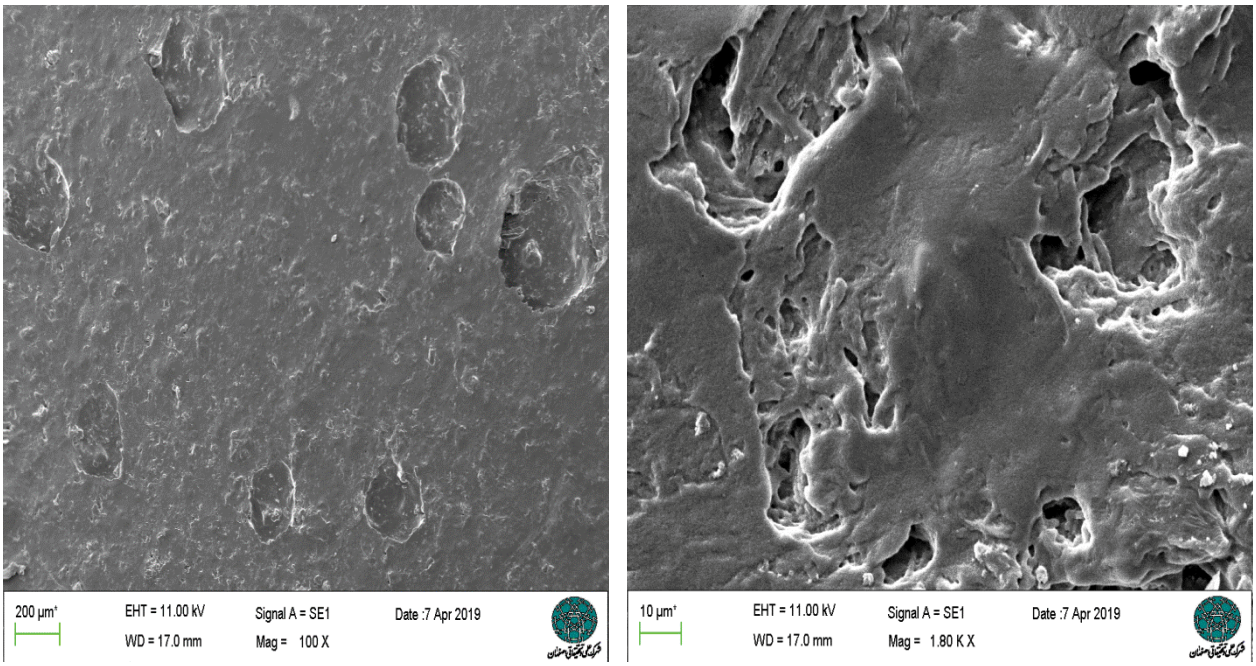


Fig. 4. SEM images of granules at different magnifications.

in the removal experiments; it was determined and obtained equal to 3.3. It is resulted that at this pH value, the charge of the negative surface sites is equal to the charge of the positive surface sites. In another word, the electrical charge density on the surface is zero at this pH. When pH is lower than the pH of zero charge, the electrical charge density on the surface is positive, therefore, the surface can interact with negative species. On the other hand, at pH values higher than $pH_{ZPC}$, the sorbent's surface is negatively charged and could interact with positive species.

Solution pH is an important parameter which affects biosorption process because it influences the biosorbent surface properties and the ionic forms of the adsorbate in the solution. The effect of initial solution pH on MB adsorption was investigated by preparing different solutions with different initial pH values. The variation of adsorption capacity with initial solution pH for pH values in the range of 3.0–7.0 is presented in Fig. 5. It is observed that with increasing the initial pH from 3 to 4, adsorption capacity increases, while for higher pH values, it does not change and is constant. The $pK_a$ of MB was reported to be 3.8 [22]. At high pH values (solution pH > $pH_{zpc}$), the number of hydroxyl groups and so the number of negatively charged sites on the adsorbent surface increases. Therefore, the adsorbent surface is negative. On the other hand, at high pH values (solution pH > $pK_a$, MB), MB dye is positively charged. As a result, there is an electrostatic attraction between the positively charged MB and the negatively charged surface of the adsorbent at high pH values [23]. Similar trends were also reported by other researchers on the pH dependency of MB dye removal by activated carbon prepared from cashew nut shell [24] and Mediterranean green alga *Enteromorpha* spp. [25].

### 3.5. Kinetics model

Fig. 6 shows the amount of adsorption capacity at different times. Accordingly, the adsorption is performed at a high rate at initial moments after adding the granules to the flasks and about 43% of the total removed MB is adsorbed within the first 30 min. Afterwards, the adsorption is performed at lower rates and the equilibrium is achieved after about 12 h. At initial moments of the process, there is a high MB concentration gradient between the biomass surface and the dye solution as well as a high number of sites on the adsorbent which are not occupied. As a result, the initial rate of adsorption is rapid. Gradual occupation of the sites as well as a decrease in MB concentration gradient decreased the adsorption rate [26].

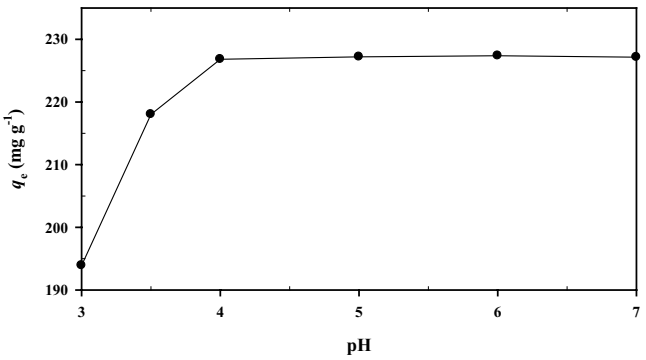


Fig. 5. Adsorption capacity of granules at different initial pH values.

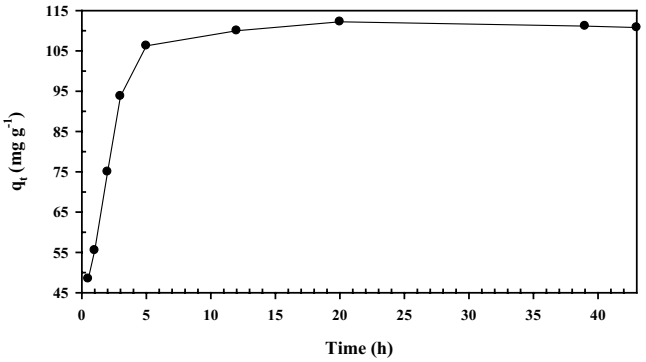


Fig. 6. Adsorption capacity of granules at different contact times.

In order to find a mathematical model for description of kinetics data, pseudo-first-order, pseudo-second-order [27], and Elovich [28] models were used and their relations are expressed in Eqs. (2)–(4).

Pseudo-first-order

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303}t \tag{2}$$

Pseudo-second-order

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

Elovich

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln\left(t + \frac{1}{ab}\right) \tag{4}$$

In these equations, $q_t$ and $q_e$ (mg g$^{-1}$) are the adsorption capacity at time $t$ (min) and at equilibrium, respectively. $K_1$ (min$^{-1}$), $K_2$ (g mg$^{-1}$ min$^{-1}$), $a$ (mg g$^{-1}$ min$^{-1}$), and $b$ (g mg$^{-1}$) are the parameters of the models. The obtained values of correlation factors for pseudo-first-order, pseudo-second-order, and Elovich models were 0.825, 0.999, and 0.830, respectively. Accordingly, pseudo-second-order model can be fitted to kinetics data well since its correlation factor is near to 1.00. Besides, it can predict the equilibrium adsorption capacity appropriately since the predicted value (112.8 mg g$^{-1}$) is close to the experimental one (110.8 mg g$^{-1}$). Therefore, MB removal by the granules was appropriately described by pseudo-second-order model. Pseudo-second-order model was also reported to describe kinetics data of MB removal from aqueous solutions by different adsorbents such as rice husk [10], activated carbon derived from finger citron residue [7], walnut carbon. [8] and the green alga *Ulothrix* sp. [29].

### 3.6. Isotherm model

Fig. 7 shows the equilibrium adsorption capacity versus equilibrium dye concentration for each initial MB

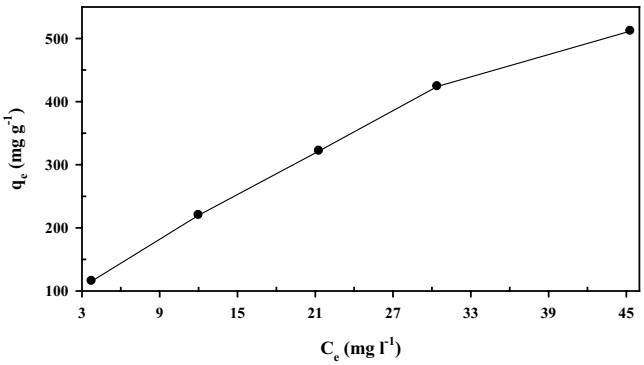


Fig. 7. Equilibrium adsorption of MB by granules at different initial dye concentrations.

concentration. It is observed that adsorption capacity increases with increasing the initial MB concentration. In order to express isotherm data mathematically and to understand how the adsorbate molecules distribute between liquid and solid phases at equilibrium, four models of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were used. The relations of these models are presented in Eqs. (5)–(8).

Langmuir

$$\frac{1}{q_e}=\frac{1}{q_{\max}}+\frac{1}{q_{\max}K_L C_e} \tag{5}$$

Freundlich

$$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e \tag{6}$$

Temkin

$$q_e=\frac{RT}{b_T}\left(\ln C_e+\ln A_T\right) \tag{7}$$

Dubinin–Radushkevich

$$q_e=q_m\times\exp\left(-\beta\varepsilon^2\right)\quad \varepsilon=RT\ln\left(1+\frac{1}{C_e}\right)\quad E=\frac{1}{\sqrt{2\beta}} \tag{8}$$

Langmuir model assumes that a monomolecular layer is formed and there is no interaction between the adsorbed molecules [30]. Freundlich model is a multi-site adsorption isotherm for heterogeneous surfaces [31]. Temkin isotherm assumes that the free energy of adsorption is related to the surface coverage. Dubinin–Radushkevich isotherm model is used to investigate if the mechanism of adsorption is physical or chemical [32]. If adsorption mean free energy ($E$) is in the range of 8–16 kJ mol$^{-1}$, a chemical mechanism is controlling, while for $E$ < 8 kJ mol$^{-1}$, a physical mechanism controls the adsorption.

The results of fitting models to isotherm data are presented in Table 1. Accordingly, Freundlich and Langmuir models are appropriately fitted to isotherm data since they have a high correlation coefficient. The Freundlich isotherm is an empirical model which is appropriate for solutions

Table 1
Parameters of isotherm models for MB removal by granules

| Model | | Parameter |
|---|---|---|
| Langmuir | $R^2$ | 0.9800 |
| | $q_{\max}$ (mg g$^{-1}$) | 582.30 |
| | $K_L$ (L mg$^{-1}$) | 0.0644 |
| Freundlich | $R^2$ | 0.9967 |
| | $n$ | 1.6404 |
| | $K_F$ (mg g$^{-1}$ (mg L$^{-1}$)$^{-1/n}$) | 50.5064 |
| Temkin | $R^2$ | 0.9414 |
| | $RT/b_T$ | 158.09 |
| | $A_T$ | 0.4476 |
| Dubinin–Radushkevich | $R^2$ | 0.7908 |
| | $q_m$ (mg g$^{-1}$) | 376.17 |
| | β | 3.6504 |
| | $E$ (kJ mol$^{-1}$) | 0.3701 |

with medium and high concentrations. This model expresses multilayer adsorption on an energetically heterogeneous surface [31, 33]. A larger $n$ value indicates the presence of more heterogeneous surface while a value closer to or even one indicates that the adsorbent has relatively more homogeneous binding sites [34]. The value of Freundlich exponent $n$ in the range of 1–10, indicates a favorable adsorption at the selected experimental conditions. Langmuir equation predicts the maximum adsorption capacity ($q_{\max}$), which is the amount of adsorbed material to saturate unit mass of the adsorbent, equal to 582.30 mg g$^{-1}$. This value is considerably high in comparison with that obtained for MB removal by other adsorbents such as activated carbon prepared from pea shell (246.91 mg g$^{-1}$) [35], marine green alga *Ulva lactuca* (40.20 mg g$^{-1}$) [11], activated carbon prepared from cashew nut shell (68.72 mg g$^{-1}$) [24], rice husk (8.07 mg g$^{-1}$) [10], and walnut carbon (4.73 mg g$^{-1}$) [8]. Besides, it is as high as those of some other adsorbents which have been reported in the literature such as finger citron residue (581.4 mg g$^{-1}$) [7] and activated carbon produced from New Zealand coal (588 mg g$^{-1}$) [36]. The high adsorption capacity indicates the strong electrostatic force of attraction [37]. Furthermore, the $E$ value obtained by Dubinin–Radushkevich model value is 0.37 kJ mol$^{-1}$ which indicates that MB removal by the granules is performed through a physical mechanism.

### 3.7. Ion exchange mechanism

In order to investigate if ion exchange is a mechanism of adsorption of MB on the granules, a dye solution and a control sample (without dye) were prepared, the granules were added and the concentrations of Ca, Na, K, and Mg ions in both flasks were measured at equilibrium. The results are presented in Table 2. The differences between the concentrations of the ions in the two flasks were considered as the amounts of released ions due to adsorption of MB. It is observed that $K^+$ and $Ca^{+2}$ are highly released; while $Mg^{+2}$ ions are released at a lower amount. This indicates that ion exchange is a mechanism for MB dye removal by

Table 2
Ions concentration (mg $L^{-1}$) in control and dye solutions after adsorption

| Ion | Ca | K | Mg | Na |
|---|---|---|---|---|
| Control | 23.2 | 2.3 | 0.76 | 23.1 |
| Dye solution | 30.5 | 9.6 | 0.83 | 24.1 |
| Difference | 7.3 | 7.3 | 0.07 | 1.0 |

immobilized mixture of activated carbon and *D. cervicornis* alga. It was mentioned that generally, the cell walls of brown algae contain alginic acid and the corresponding salts of sodium, potassium, magnesium, and calcium. Alginate has an important role in adsorption by brown algae through binding to pollutants ions. Generally, metal ions such as $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$, which are available on the algal biomass, are obtained from seawater which bound to the acid functional groups. [19]. Ion exchange was also reported as the biosorption mechanism for copper removal by alga *Spirulina* sp. for which biosorption was accompanied with the release of Ca, Mg, Na, K, Fe, and Zn ions [38].

## 4. Conclusions

The purpose of this study was to provide an adsorbent that can be used in a wide range of dye concentrations. Several adsorbents composed of alga *Dictyota cervicornis* and activated carbon were immobilized on calcium alginate and their ability for MB dye removal from aqueous solutions were investigated. The granules containing 75% activated carbon and 25% alga was the most efficient one. Pseudo-second-order model could appropriately describe kinetics of the process. Langmuir and Freundlich models were fitted to isothermal data well. Langmuir model predicted the maximum adsorption capacity equal to 582 mg $g^{-1}$. This value is relatively high in comparison with several adsorbents which makes the new adsorbent an interesting material for treatment purposes. MB removal was performed through a physical mechanism as indicated by D-R isotherm model. Ions of $K^+$, $Ca^{2+}$, $Na^+$, and $Mg^{2+}$ were released into the solution upon dye removal which confirms that ion exchange is a mechanism of adsorption.

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