ADSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING FREE AND IMMOBILIZED ALGAE CELLS

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ABSTRACT

This study was aimed to investigate the potential adsorptive behavior of mixed algae for decolorization of methylene blue dye from aqueous solution in the form of free and immobilized. Effects of initial pH value (3-9), biosorbent dosage (0.02-0.5)g/L, and initial concentration (10-50) mg/L for different contact time (0-180) min at 200 rpm shaking speed were investigated. In addition, experimental data were analyzed using adsorption (Langmuir and Freundlich) isotherms as well as kinetic models. The results demonstrated that the maximum decolorization percentage was 93% and 91% by free and immobilized algae, respectively for pH 6, 10 initial concentration, 0.3g/100mL algae dosage, and 90 min contact time. The results revealed that the Langmuir isotherm model was adequate for describing the dye removal process (R^2= 0.99) for both forms. Results of pseudo-second order kinetic model revealed best fitting with the sorption data indicating that chemisorption process is the dominant mechanism controlling the dye removal. Furthermore, the characterization study performed using FT-IR and scanning electron micrograph techniques, revealed that the used algal biomass has good biosorption capabilities associated to active groups and surface structure and confirming that the immobilization was successful.

Keyword: methylene blue; mixed algae; adsorption; isotherm; kinetic; algae characteristics

امتزاز صبغة المثيلين الزرقاء من المحاليل المائية باستخدام الطحالب الحرة والمقيدة

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المستخلص

تهدف هذه الدراسة إلى معرفة السلوك الامتزازي المحتمل للطحالب المختلطة لإزالة صبغة الميثيلين الزرقاء من المحلول المائي في بشكليها الحروالمقيد. تم دراسة تأثير قيمة الرقم الهيدروجيني (3–9)، جرعة الامتصاص الحيوي (0.02–0.5) غم / لتر والتركيز الأولي (10–50) ملغم / لتر ووقت تلامس مختلف (0–180) دقيقة عند سرعة اهتزاز 200 دورة في الدقيقة. بالإضافة إلى ذلك ، تم تحليل البيانات التجريبية باستخدام متساوي حرارة الامتزاز (Langmuir و Freundlich) وكذلك النماذج الحركية. أظهرت النتائج أن أقصى نسبة ازالة الصبغة كانت 93٪ و 91٪ بواسطة الطحالب الحرة والمثبتة على التوالي عند الظروف التالية : الرقم هيدروجيني 6 و التركيز الأولي10 ملغم/لتر و 0.3 غم / 100 مللتر من الطحالب وعند وقت تلامس 90 دقيقة وعند تحليل النتائج باستخدام موديلات الاتزان تبين أن نموذج متساوي الحرارة Langmuir كان مناسبًا لوصف عملية إزالة الصبغة (R^2 = 0.99) لكلا الشكلين كما بين تحليل الحركي للامتزاز ان عملية الامتزاز كيمياوية. علاوة على ذلك، كشفت دراسة التوصيف التي تم إجراؤها باستخدام تقنيات FTIR والمسح الضوئي للصور المجهرية الإلكترونية، أن الكتلة الحيوية الطحلبية المستخدمة لديها قدرة امتصاص حيوي جيدة مرتبطة بالمجموعات النشطة وبنية السطح كما اكدت نجاح عملية التقييد.

الكلمات المفتاحية: صبغة المثيل الزرقاء ، طحالب، امتزاز ، موديل متساوي الحرارة والحركي، توصيف الطحالب

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INTRODUCTION

Dyes or pigments used to color the end products in the textile, paper, plastics, leather, food, and other sectors are present in their effluents, and light penetration and photosynthesis are reduced when these contaminants are present in water. Additionally, some dyes are toxic, mutagenic, or carcinogenic. Different methods have been used for the removal of dyes from wastewater including sorption (8), coagulation and flocculation (25), advanced oxidations (31), biological treatment and nanofltration (33). Among them adsorption is a simple, versatile and feasible process (34;16). The commonly used adsorbent is the activated carbon. However, the price of activated carbon is relatively expansive. In recent years, many studies have carried out to use low-cost adsorbent, through using industrial and agricultural solid wastes (4;10). The use of biological materials, natural substance or biomass as a sorbent in the pollutant removal called biosorption .Biomass has been utilized to adsorb pollution from a variety of sources, including bacteria, yeast, algae, fungi, and plants. Algal biomass (both living and nonviable) is one of the most promising biosorbent under investigation (18).It has been found in many kinds of research that algal biomass is rich in functional groups, such as carboxyl, hydroxyl, phosphate, amine groups, and so on (1). Immobilization is an attractive technique to fix and retain biomass on suitable natural or synthetic support materials. The key advantages of immobilization include biomass retention within the working environment, easy separation of products from cells and relatively, high local cell density (2).Wastewater treatment by immobilized algae has been shown to offer numerous advantages over algal free cells. For example, it takes up less space and overcomes issues during the cell harvesting procedure. Immobilized algae are also more stable and resistant to severe conditions with high salinity, toxicity, and pH value, and recovering the concentrated algal cells for subsequent processes in a less harmful manner can improve cost-effectiveness by reusing the regenerated process (20). Several synthetic (acrylamide, polyurethane, polyvinyl, resins) and natural polymer derivatives of algal polysaccharides (alginate, arrageenan, agar, agarose), and chitosan, an amino polysaccharide derived from chitin, has been experimentally used. Regardless of the polymers used, the material must be hydrophilic, allowing wastewater to diffuse into the bead. The most commonly used Polymers are the natural polymers alginate and carrageenan (11). A number of microalgal species such as Caulerpa lentillifera (24), Chlorella sp. (20), Chlorella pyrenoidosa(28;23) and Ulva lactuca(27) has been used during biosorption studies on dyes and showed varying removal efficiencies. The effects of different parameters, such as initial pH, algae dosage and initial methylene blue (MB) dye concentration on the sorption capacity were investigated. Equilibrium modeling will be carried out using the Langmuir and Freundlich isotherm equations. In addition, the kinetics of the MB dye adsorption were analyzed by using Lagergren's pseudo-first-order and pseudo second-order kinetics.

MATERIALS AND METHODS

Chemicals: Methylene blue dye was used in this study as the target pollutants in aqueous solutions and their properties are (Color index C.I (52015), Molecular weight, MW, 3373.9g.mol^{-1}, and chemical formula $C_{16}H_{18}ClN_3S.3H_2O$. The cationic thiazine dye was used without any further purification. Stock solution of MB dye was prepared by dissolving 1.0 g of MB dye in 1L of distilled water to obtain1000 mg/L. Further, from the stock solution, dye solutions were prepared, by dilution. Moreover, the HCl and NaOH solutions of 0.1M enabled the adjustment and control of the pH of the prepared solutions throughout the experimental work. However, for beads preparation sodium alginate of the chemical structure ($NaC_6H_7O_6$) and main source algal polysaccharides derivatives (marine-seaweed algae) was manufactured in China and supplied from amazon and $CaCl_2$ were used.

Algae collection and preparation

A mixture of three classes of algae (abbreviated as MA), was chosen as a model of biosorbent in its nonliving form, and was gathered from the canal near College of

Engineering at University of Baghdad where the algae floated at the canal water. The major proportions of the classes of MA samples under analysis are Chlorophyceae (37.77٪), Cyanophyceae (32.88٪), and Bacillariophyceae (29.34%). Thereafter MA was cleaned many times with distilled water to get rid of impurities, dirt, and other undesired elements such as (non-vertebrate animals, small worms, crustaceans, bird feathers), then sun drying for three days, crashed and sieved at mesh no. 63 µm, Fig 1a.

Mixed algae immobilized

Immobilized algal cells were prepared by entrapping a selected amount of dried MA biomass in 2% alginate solution. The mixture was filled into a syringe and injected into 5% $CaC1_2$ solution to form the immobilized granular cells with 4±0.1 mm diameter. Ca-alginate gel immobilized MA beads were stored in calcium chloride solution at 4 ˚C for 4 h to complete gelation before used, Fig 1b. For blank alginate beads, similar procedures were followed, but without MA.

a- free MA

b- immobilized MA

Fig. 1.Free and immobilized MA

Experimental work

Batch sorption experiments were carried out in 250 mL conical-flasks, each flask was filled with 100 mL of MB dye solution of the desired concentration and sorbent amount. Experiments carried out with; initial pH (3–9), biosorbent dosage of (0.02–0.7) g/100 mL, contact time (0–180) min, initial concentration of MB (10–50) mg/L at 200 rpm agitation speed and room temperature. The sorption mechanisms were specified through the identification of the active functional groups responsible for MB binding on the immobilized MA by application of Fourier transform infrared (FT-IR) analysis, and Scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Agitation of flasks in the form of shaking performed for a definite time using orbital shaker (Edmund Buhler SM25, German). Volume of 10 mL of the contaminated solution was withdrawn from each flask, (filtered for free MA), then the concentration of MB was determined by using UV-visible spectrophotometer (Cary-100 conc., Varian, USA) at a wavelength corresponding to the maximum absorbance of the dye solution (λmax= 665nm).Further, the results obtained from the effects of the biosorbent content and contact time were subsequently applied, for the isotherm and kinetic studies, respectively. During the biosorbent phase, the percentage removal of MB dye, in addition to, the biosorption capacity (q_t, mg/g) at any time of experiment (min), can be calculated using Eqs.(1) and (2), respectively.

$$\text{Removal percentage} = \frac{C_i - C_t}{C_i} \times 100 \quad \ldots(1)$$

$$q_t = \frac{(C_i - C_t)V}{m} \quad \ldots..(2)$$

Where: C_i and C_t refer to initial and equilibrium dye concentration (mg/L), respectively; q_t ; represent the contaminant uptake, (mg/g), m is the biosorbent mass (g) and V is the contaminant solution volume (L).The experiments were done with duplicate for more accurate result, thereby determining the average results.

RESULTS AND DISCUSSION

Parameters for sorption process

Ph: The pH of industrial effluent is a determining element, and its variation can have a direct impact on dye uptake and

adsorption. The mechanism of the process alters when the pH of the reaction media changes on a regular or irregular basis. The textile industry wastewater discharge criteria are expected to be in the pH ranges of 6 to 9 (23). The solution pH is a significant issue impacting the subtraction of contaminant from aqueous solutions, affect the functional groups on the adsorbent surface, and determine the solubility of contaminant in the aqueous medium (13). Different pH value (3, 5, 6, 9) were studied while keeping other parameters constant (MB dye of 30mg/L , 0.1g of MA dosage free or immobilized for every 100 mL of dye solution and for contact time not exceeded 120 min). And there results were plotted in Fig.2. It was observed that, when the pH increased from 3 to 6, an increase in the dye removal efficiency from 75 to 89% by free MA and from 70 to 88% by immobilized MA. Further increase in the pH value to 9 decreases the removal percentage to 77 and 72 by free and immobilized MA, respectively. The mechanism of the process alters when the pH of the reaction media changes on a regular or irregular basis. The textile industry wastewater discharge criteria are expected to be in the pH ranges of 6 to 9.

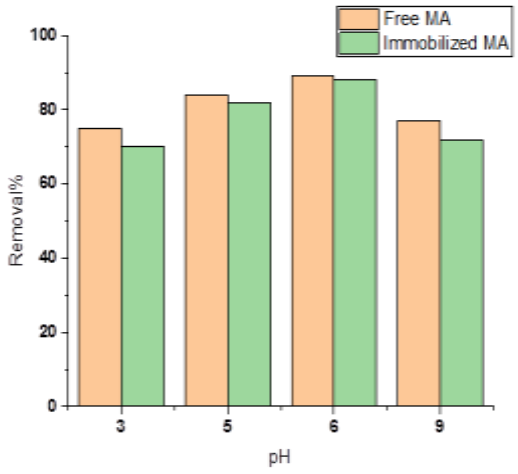


Fig.2.The removal efficiency of MB dye as a function of pH

Biomass dosage

The biomass dosage is a significant parameter used to determine the capacity of biosorbent for specific initial concentration, it is one of the most essential factors that effected the biosorption process (5). The effect of different dosage including (0.02, 0.1, 0.3, 0.5, 0.7) g/100 mL were studied while keeping other parameters constant (pH 6, 30 mg/ L initial MB concentration and for 120 min contact time) and their results were plotted in Fig.3. It can be observed from this figure that removal efficiency of MB improved with increasing biosorbent dosage. By increasing the amount of algal biomass, the pollutants may be fully adsorb or reach an equilibrium state when reaching a plateau at a fixed concentration of each pollutant (3). The maximum removal efficiency was 93 and 91 for free and immobilized MA, respectively.

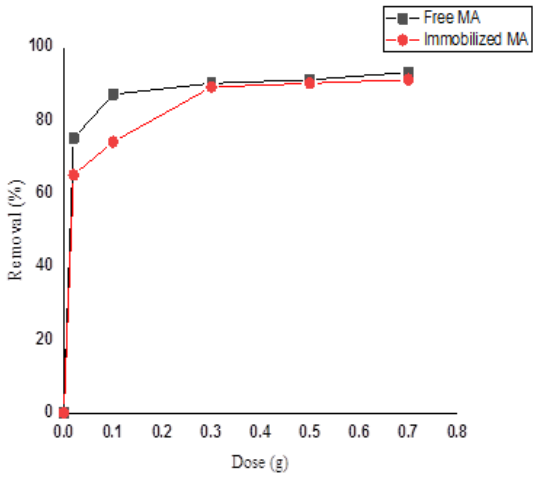
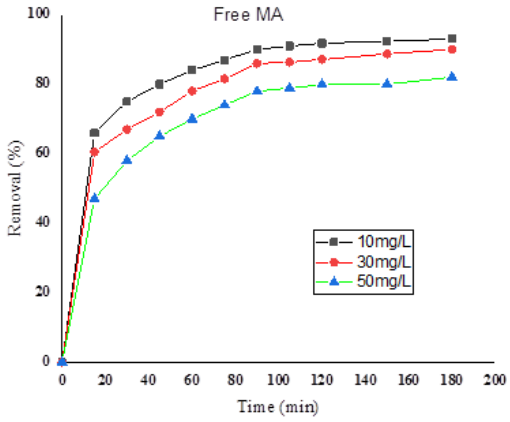


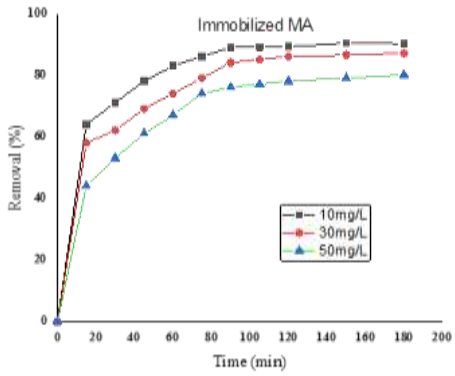
Fig. 3. The removal efficiency of MB dye as a function of adsorbent dose

Initial concentration and sorption time

Fig. 4 shows the profiles of MB dye removal at various initial concentrations of 10, 30, and 50 mg/l, as well as contact time (0-180min). The analysis indicates that as the initial concentration of the MB dye was increased, the percentage elimination reduced. The decline in dye removal percentage can be attributed to the absence of binding groups on the surface of algal biomass at greater concentrations or to the cell offering an infinite number of surface binding sites, resulting in saturation at higher species concentrations (6). This figure also shows that as contact time increase, the percentage of MA removed rose until it reached 90 minutes, at which point equilibrium was reached for both free and immobilized MA. Adsorption by the outer surface of the sorbent-free and immobilized MA could explain the fast rate of sorption during the first 90 minutes of contact time.



(a) free MA



(b) immobilized MA

Fig.4. The removal efficiency of MB dye as a function of initial concentration

Equilibrium and kinetic studies

Equilibrium isotherms: The adsorption isotherms are required for the design of adsorption systems (15). At a given temperature, equilibrium isotherm is the equilibrium relationship between the adsorbate concentration in the adsorbent particles and the adsorbate concentration in the fluid phase. The widely used isotherm models Langmuir (Eq.3), and Freundlich (Eq.4), were used in this study for modeled the obtained data from the experiments of MB dye biosorption by free and immobilized MA. The following publications could be reviewed for more information on the physical background of the application of these two formalisms in pollutant sorption research (30).

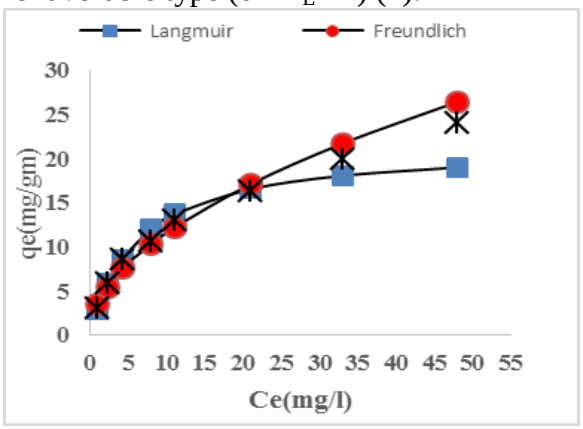
$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad \ldots(3)$$

$$q_e = K_F C_e^{\,1/n} \quad .. (4)$$

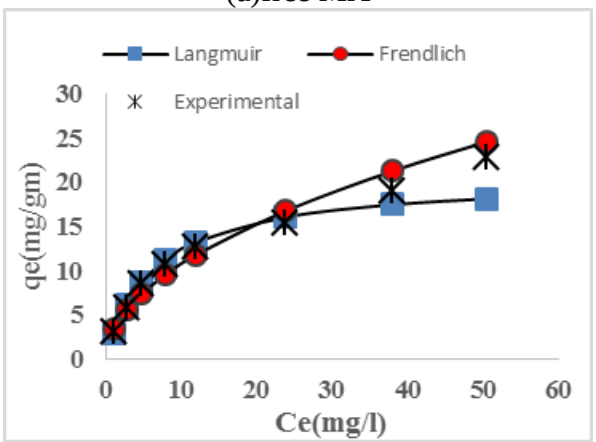
Where: q_e(mg/g) is the dye sorbed, q_m(mg/g) represents the maximum biosorption capacity of the used biosorbent for target pollutant (uptake); K_L (L/mg) is a Langmuir model constant; n(g/L) and K_F(mg/g) are the two Freundlich equation constants denoting the biosorption process intensity and biosorbent capacity toward the pollutant's molecules, respectively. The equilibrium parameter, R_L, is used to predict if an adsorption system is ''favorable" or ''unfavorable". It is obtained by the following relationship:

$$R_L = \frac{1}{1+K_L C_o} \quad \ldots(5)$$

The value of R_L indicates whether the form of the isotherm to be either is unfavorable (R_L > 1), linear (R_L = 1), favorable (0 < R_L < 1) or irreversible (R_L = 0). The non-linear isotherm model was used to examine the experimental data. Origin software was used to estimate the nonlinear isotherm model parameters. These models are plotted in Fig.5 and their parameters with correlation coefficients are presented in Table 2. Based on the value of the coefficient of determination (R^2), the obtained data were found to fit well with the Langmuir model for MB dye, indicating that the process was controlled by chemisorption. Furthermore, the equilibrium isotherm for MB dye was of the favorable type (0 <R_L< 1) (7).



(a)free MA



(b) immobilized MA

Fig. 5. Equilibrium of MB dye adsorption onto MA

Table 1. Equilibrium adsorption isotherm and kinetics parameters for MB dye onto free and immobilized MA

Isotherm models					
	q_m	Langmuir		Freundlich	
Free MA	21.6	K_L	0.16	K_F	3.5
		R_L	0.17	n	1.9
		R^2	0.992	R^2	0.98
Immobilized MA	20.5	K_L	0.152	K_F	3.5
		R_L	0.18	n	1.95
		R^2	0.995	R^2	0.95
		Kinetic models			
		Pseudo- first - order		Pseudo- second- order	
Free MA		q_e	6.9	q_e	9.05
		K_1	4E-04	K_2	0.02
		R^2	0.91	R^2	0.997
Immobilized MA		q_e	7.7	q_e	9.11
		K_1	5E-04	K_2	0.01
		R^2	0.89	R^2	0.99

Kinetic parameters

Biosorption kinetic modeling describes the response of a biosorption system caused by variations in experimental conditions, by the properties of biosorbents. The parametric sensitivity of the model to process parameters is also assessed by biosorption kinetic modeling (14). In this study, the sorption kinetic was modelled using the pseudo first-order model (Eq.6) and pseudo second-order kinetic model (Eq.7), and their results were plotted in Fig.6 and their parameters were tabulated in Table 1, the results present that the two models are capable of explaining the links between the experimental and predicted values; however, the pseudo-second order model for sorption provided a better fit based on R^2 values. This suggests that the sorption process was chemisorption (17).

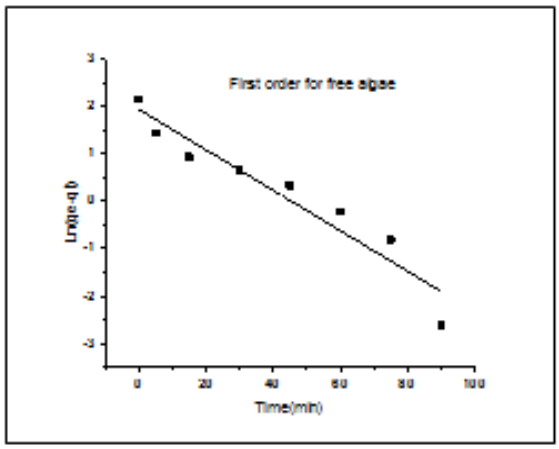
$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad \text{....(6)}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \text{....(7)}$$

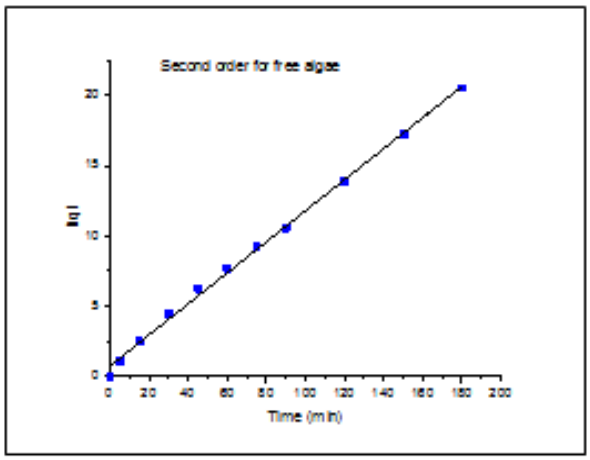
Where :q_e (mg/g) represents equilibrium amount of MB dye onto CA; q_t(mg/g) sorbed amount from the metal at time t; and k_1 and k_2 represent pseudo first order equilibrium rate sorption constant (1/min) and rate constant of the pseudo-second order sorption. (g/mg min), respectively.

Algae characteristics

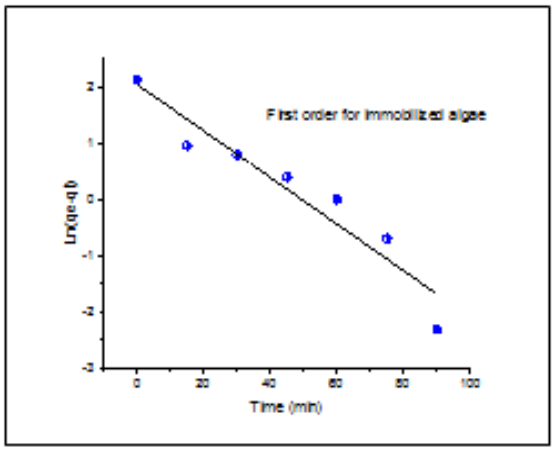
(sem)/ (eds): SEM images combined with EDS are of importance to detect the changes in the surface of the MA as powder and beads form before and after loaded with MB dye. The SEM/EDS analysis was carried out in Tehran University using SEM/EDS device (ARYA Electron Optic, FE-SEM). The representative images are shown in Fig.7. It can be present from this figure that there are a number of cavities and pores found on the surface of algae cell, whereas immobilized cells after treatment of these pores were filled with unknown molecules of colored compounds and calcium present in the aqueous solution which indicated ,that the surface morphology of algae was heterogeneous. The EDS analysis for free and immobilized algae shows C, O, Mg, Al, Ca, and Si elements are present, which alkali and alkaline earth metals that are usually available in algal biomass (12). Increasing the peaks of Ca, C and O after immobilization can be explained by the chemical composition of the algal beads. Alginate, i.e. alginic acid, is a heteropolysaccharide consisting of 1→ 4 linked b-D-mannuronic acid and its C-5 epimer a-L-guluronic acid (26). While increasing Ca^{2+} ions was from the $CaCl_2$ used during the preparation procedure of the biosorbent as the hardening agent of the alginate beads. After adsorption of MB dye, it can be noticed from EDS analysis that the percentage of the C increased after adsorption of MB, while the percentage of Al and Mg decreases slightly.



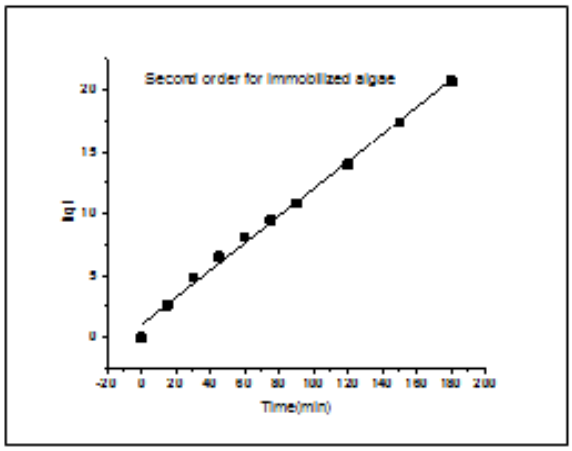
(a) first order- free MA



(b) second order- free MA

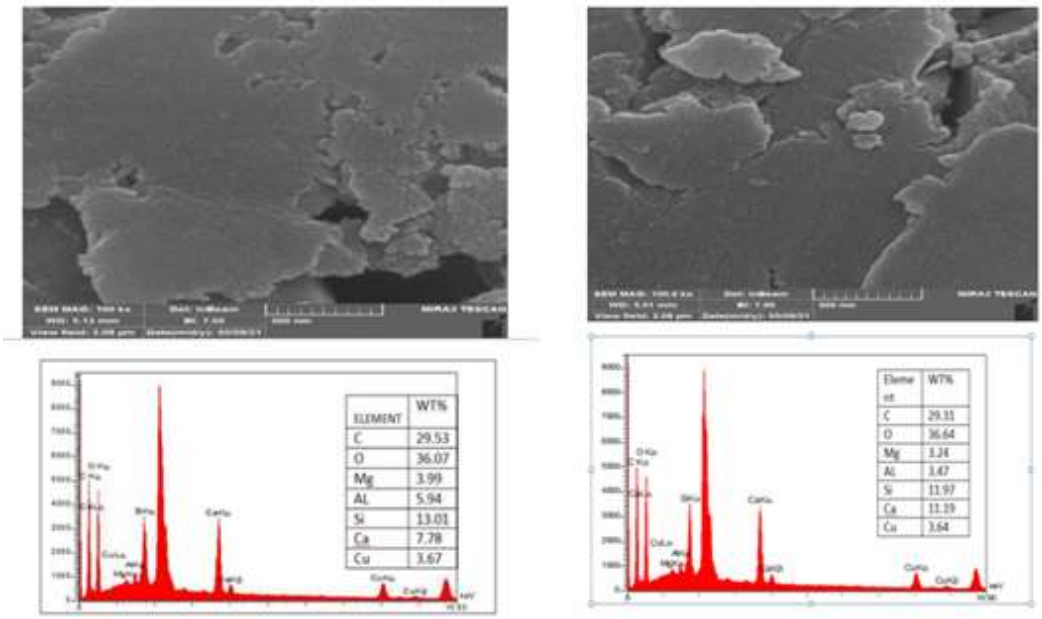


(c) first order- immobilized MA



(d) second order- immobilized MA

Fig. 6. Kinetic models for sorption of MB dye into free and immobilized MA (a) free MA before adsorption (b)free MA after adsorption (c) immobilized MA before adsorption (d) immobilized MA after adsorption



(a) free MA before adsorption (b)free MA after

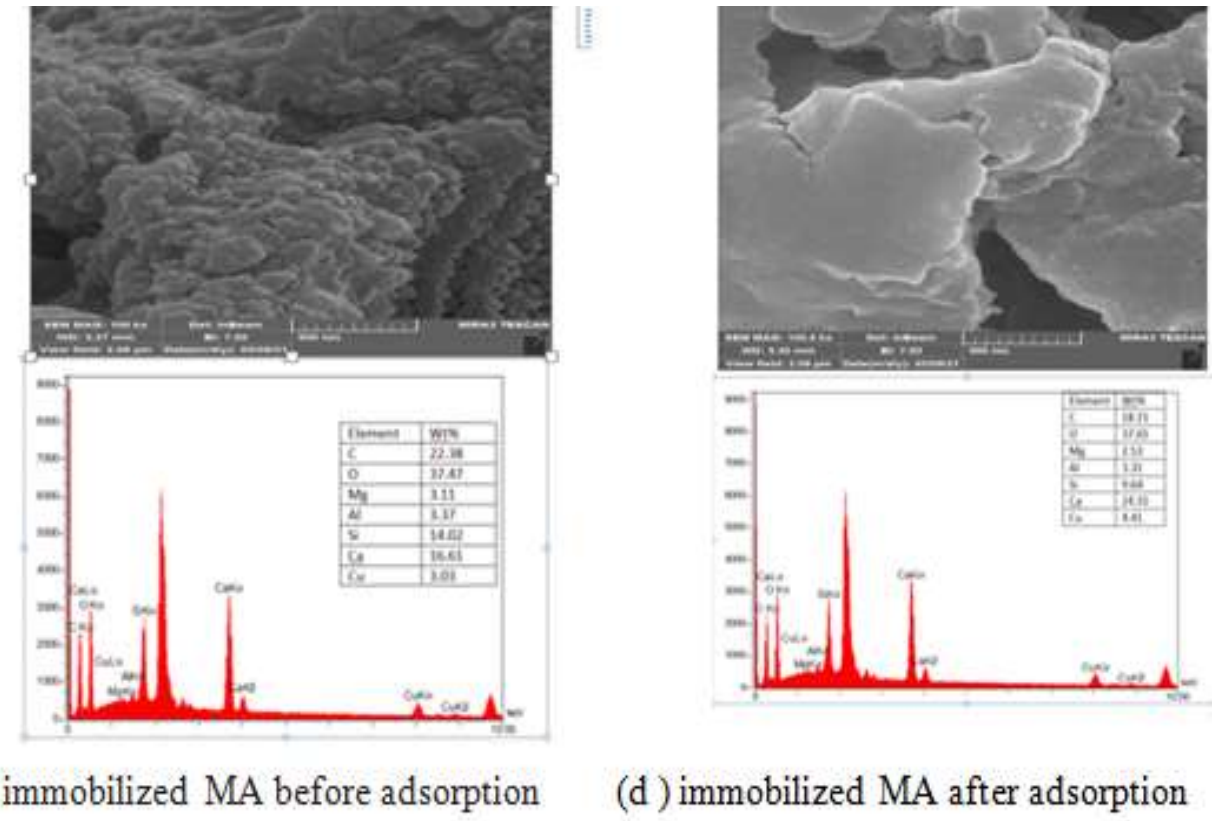
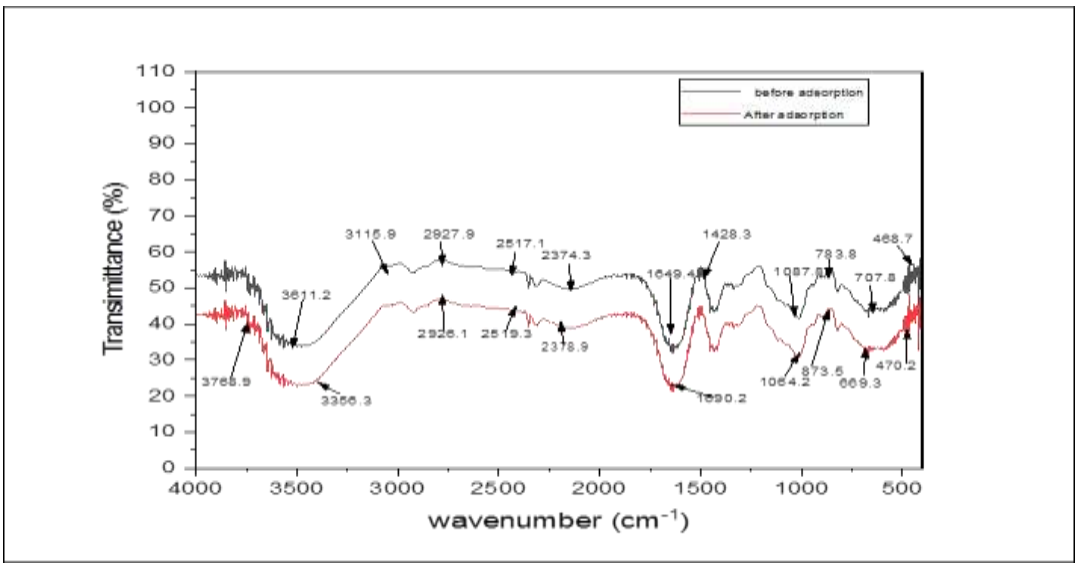


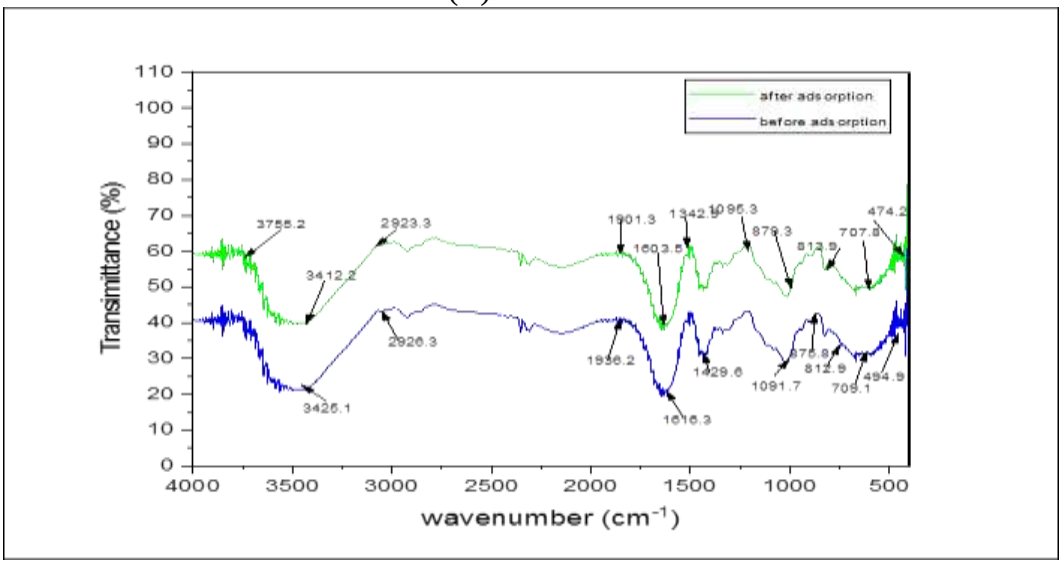
Fig. 7. SEM-EDS of free and immobilized MA before and after MB dye adsorption

Ft-ir analysis of algae biomass

Adsorption capacity of solid adsorbents not only depends on surface area but also on chemical surface functional groups. The purpose behind the FT-IR analysis is to identify the different functional groups found in algae biomass that is responsible for the adsorption process (19). The FT-IR analysis was carried out at Tehran University using a Jasco 4100 device in the spectral range 400–5000 cm^{-1} and their results were plotted in Fig. (8), it can be noticed from this figure that the peaks for unloaded MA free and immobilized form are as follows, respectively: the bands around (3412.08, 3751.55) $cm^{-1}$and (3425.58, 3755.4) cm^{-1} are the indication of the existence of the –OH groups. While the bands around 2927.94 cm^{-1} and 2926.01cm^{-1} confirm the existent of C-H aldehyde stretch. However, the band around 1649.14 and 1616.35 confirms that the presence of – C=O stretching, which could be attributed to amide I and II. The band around (1425.4, 1087.85) cm^{-1} and (1429.25, 1091.71 cm^{-1} signifies the presence of Amines (18). However, the band around (873.75, 707.88, 468.7) cm-^{1} and (875.68,709.80, 474.49) cm^{-1} indicates the presence of Aromatic and alkyl halides(C-Cl) and Alkyl halides. This suggested that the –OH, C-H, and – C=O groups were major contributors in the mechanism for the biosorption MB onto algae and alginate support matrix thus verifying that immobilization had successfully been performed (9). The free algae have more transmittance intensity than the immobilized algae, this indicated the higher removal efficiency by free MA. After MB biosorption, some peaks for free and immobilized MA disappeared, shifting or decreasing in their intensity, the peaks that disappeared after MB biosorption showing active involvement of these peaks in the biosorption (21).



(a) Free MA



(b) Immobilized MA

Fig. 8 FT-IR spectra of MB-loaded and unloaded free and immobilized MA

Brunauer emmett teller (bet)

The specific surface area (m^2/g), specific pore volume (cm^3/g), average pore diameter was measured by Brunauer Emmett Teller (BET) analysis at the University of Tehran, by using Barrett Joyner and Halden (BJH) method (32). The pore volume (V), the pore diameter (D), and the pore size distribution were determined by the graph drawn between quantity adsorbed (cm^3/g STP), and their results were tabulated in Table 2.

Table 2. Surface characteristics of the immobilized MA

Material	S_{BET} (m^2/g)	Total volume pore(cm^3 / g)	Average diameter of the pore (nm)
Free MA	**1.667**	**0.5641**	**45.723**
Immobilized MA	**0.799**	**0 .007715**	**38.623**

CONCLUSIONSS

The present study revealed the potential of using immobilized MA with alginate matrix for removing MB dye from synthetic wastewater. This was achieved through studying the effect of pH, initial concentration of MB dye, algae dosage and contact time on the removal efficiency and compared the results with the effect of using free algae. Both biosorbents have been found capable of adsorbing MB dye effectively, with a maximum removal efficiency of 93 and 91% by free and immobilized algae, respectively at pH 6, 0.3 g /100ml biomass dosage, 200 rpm shaking speed, 30 ppm initial dye concentration, and for 90 min. Experimental

isotherm data fit best with the Langmuir model in comparison to the Freundlich model with maximum adsorption capacity at 21.6 and 20.5 mg/g. by free and immobilized algae, respectively. Furthermore, based on R^2 values, the kinetic research demonstrated that the pseudo-second order model for sorption provided a better fit. SEM and FTIR techniques were employed to characterize the algal biomass, which revealed that it has good biosorption characteristics linked to surface shape and active groups.

REFERENCES

1. Abd, I. N. and M.J. Mohammed- Ridha 2021, Simultaneous adsorption of tetracycline and amoxicillin by cladophora and spirulina algae biomass, Iraqi Journal of Agricultural Sciences, 52(5):1290-1303. https://doi.org/10.36103/ijas.v52i5.1467

2. Abdulkareem, H. N. and A. I. Alwared 2019 Immobilization dried mix of algae for copper removal, Iraqi Journal of Agricultural Sciences ,50(3):800- 808. https://doi.org/10.36103/ijas.v50i3.697

3. Abdullah, S. A., A. H. J. Abdullah and M. A. Ankush 2019. Assessment of water quality in the Euphrates River, southern Iraq, Iraqi Journal of Agricultural Sciences, 50(1):312-319. https://doi.org/10.36103/ijas.v50i1.297

4. Ahluwalia, S. S. and D.Goyal 2007 Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol., 98(12): 2243-2257

5. Akbari, M., A. Hallajisani, A.R. Keshtkar, H. Shahbeig, and S.A. Ghorbanian 2015 Equilibrium and kinetic study and modeling of Cu (II) and Co (II) synergistic biosorption from Cu (II)-Co (II) single and binary mixtures on brown algae C. Indica. Journal of Environmental Chemical Engineering, 1: 140-149

6. Aksu, Z. 2002 Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto chlorella Vulgaris. Process Biochemistry, 38(1): 89-99

7. Al-Rub, F. A. A., El-Naas, M. H., Benyahia, F., I. Ashour 2004. Biosorption of nickel on blank alginate beads, free and immobilized algal cells. Process Biochem 39:1767–1773

8. Alwared, A. I., T. J. Al-musawi, L. F. Muhaisn, and A.A. Mohammed 2021 The biosorption of reactive Red dye onto orange peel waste: A Study on the isotherm and kinetic processes and sensitivity analysis using the artificial neural network approach, Environmental Science and pollution research, 28:2848–2859

9. Daemi, H. and M. Barikani, 2012, Synthesis and characterization of calcium alginate nanoparticles, sodium homopolymannuronate salt and its calcium nanoparticles. Scientia Iranica, 19(6): 2023–2028

10. Dahlan, I. and N. W. Ling 2021 Adsorption of acid violet 7 (AV7) dye using RHA-CFA adsorbent: modeling, process analysis, and optimization, Separation Science and Technology,56(1):54-67

11. De-Bashan, L. E. and Y. Bashan 2010 Immobilized microalgae for removing pollutants: review of practical aspects, Bioresource Technology, 101: 1611–1627

12. Du, Y., S. Zhang, R. Guo, and J. Chen, 2014, Understanding the algal contribution in combined UV-algae treatment to remove antibiotic cefradine RSC Advances, 274: 50-56

13. Gautam, R. K., A. Mudhoo, and M. C. Chattopadhyaya 2013 Kinetic, equilibrium, thermodynamic studies and spectroscopic analysis of alizarin red S removal by mustard husk, Journal of Environmental Chemical Engineering, 1(4):1283-1291

14. Giese, E. C., D.D. V. Silva, A. F. M. Costa, S. G.C. Almeida, and K. J. Dussán 2020 Immobilized microbial nanoparticles for biosorption, Critical Reviews in Biotechnology, 40(5):653-666

15. Hamdaoui, O. and E. Naffrechoux 2007 Modeling of adsorption isotherms of phenol and chlorophenols onto Two-parameter models and equations allowing determination of thermodynamic parameters, Journal of Hazardous Materials, 147(1–2): 401-411

16. Hasan Y. R. M A. A. Shaban and M A, Ibrahim 2023. Effect of calcination temperature on the adsorption performance of MG/AL layered double hydroxide nanoparticles, Iraqi Journal of Agricultural Sciences –2023:54(1):42-58. https://doi.org/10.36103/ijas.v54i1.1675

17. He, X., K. B. Male, P.N. Nesterenko, , D. Brabazon, B. Paull, and J. H. T. Luong 2013

Adsorption and desorption of methylene blue on porous carbon monoliths and nanocrystalline cellulose, ACS Applied Materials & Interfaces, 5 (17): 8796-8804

18. Kandah, M. I., F. A. Abu- Al-Rub, and N. Al-Dabaybeh 2003. The aqueous adsorption of copper and cadmium ions onto sheep manure, Adsorption Science and Technology 21(6):501-509

19. Kannan, S. 2014. FT-IR and EDS analysis of the seaweeds sargassum wightii (brown algae) and gracilaria corticata (red algae). International journal of current microbiological Applied Science, 3(4): 341-351

20. Kassim, M. A., N. F.Abdul Latif and N.F. Hashim 2018. Decolorization and total nitrogen removal from batik effluent using alginate immobilized freshwater microalgae chlorella sp. , Journal of Applied Biology & Biotechnology, 6(06): 26-34

21. Khan, M. A., M. Ngabura, T. S. Choong, H. Masood, and L. A. Chuah 2012 Biosorption and desorption of nickel on oil cake: batch and column studies. Bioresource technology, 103(1): 35-42

22. Khodadadi, M., T. J. AL-mosawi, M. Kamranifar, M. H. Saghi, and A. H.Panahi 2019. A comparative study of using barberry stem powder and ash as adsorbents for adsorption of humic Aacid. Environ Sci Pollut Res, 26: 26159

23. Majhi, P. K., R. Kothari, A. Pandey, and V. V. Tyagi 2020. Adsorptive behavior of free and immobilized chlorella pyrenoidosa for decolorization, Biomass Conversion biorefinery,11: 3023–3036

24. Marungruenga, K. and P. Pavasant 2006. Removal of basic dye (astrazon blue FGRL) using macroalga caulerpa lentillifera, Journal of Environmental Mmanagement,78: 268–274

25. Mohammed, S. J.and M. J. M-Ridha. 2021. Optimization of levofloxacin removal from aqueous solution using electrocoagulation process by response surface methodology. Iraqi Journal of Agricultural Sciences 52(1): 204–217. https://doi.org/10.36103/ijas.v52i1.1252

26. Petrovic, A. and M. Simonic. 2016. Removal of heavy metal ions from drinking water by alginate-immobilised Chlorella sorokiniana, International Journal of Environmental Science and Technology, 13:1761–1780

27. Pratiwi, D., D. J. Prasetyo, and C. D. Poeloengasih 2019. Adsorption of methylene blue dye using marine algae Ulva lactuca, 2nd International Conference on Natural Products and bioresource Sciences: Earth and Environmental Science 251 ,012012

28. Rosa, A. L. D., E. Carissimi, G. L. Dotto, H. Sander and I. A. Feris 2018.Biosorption of rhodamine B dye from dyeing stones effluents using the green microalgae chlorella pyrenoidosa, Journal of cleaner Production, 101 (2010): 1611–162

29. Sabah, I. and A. I. Alwared 2019.Adsorption of congo red dye from aqueous solution onto wheat husk in a fluidized bed reactor, Iraqi Journal of Chemical and Petroleum Engineering 20(4) :55 – 6

30. Samarghandi, M., T. AL-musawi, A. Mohseni-banpi, and M. Zarrabi 2015. Adsorption of cephalexin from aqueous solution using natural zeolite and zeolite coated with manganese oxide nanoparticles. Journal of Molecular Liquids, 211: 431-441

31. Shu, H., M. Chang, and W. Hsieh 2006.Remedy of dye manufacturing process effluent by UV/H_2O_2 process, Journal of hazardous materials B128:60–66

32. Sing, K. S.W. 1982. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (provisional). Pure and Applied Chemistry, 54(11) :2201-2218

33. Zahrim, A. Y. and N. Hilal 2013 Treatment of highly concentrated dye solution by coagulation/flocculation-sand filtration and nanofltration, Water Resources and Industry 3: 23–34

34. Zou, C.,W. Jiang, J. Liang, X. Sun, and Y. Guan 2019. Removal of Pb(II) from aqueous solutions by adsorption on magnetic bentonite. Environmental Science and Pollution Research, 26:1315–1322.