Alqalam Journal of Medical and Applied Sciences. 2025;8(1):428-434
https://doi.org/10.54361/ajmas.258161

Original article

Removal of the Medical Dye Safranin from Aqueous Solutions by Sea Grasses Activated Carbon: A Kinetic Study

Hamad Hasan*[1], Abdelgader Imragaa[2], Hanan Emrayed[1], Karema Abdel-Gany[1]

[1]*Department of Chemistry, Faculty of Science, Omar Al-Mukhtar University, Al Bayda, Libya*
[2]*Department of Chemistry, Faculty of Science, Benghazi University, Benghazi, Libya*
Corresponding Email. *hamad.dr@ommu.edu.ly*

Abstract
Safranine is one of the most common indicators used in different applications, especially for chemicals. It is a dye that mainly causes many problems in the environment, such as aqueous solutions. The adsorbents of activated carbon used in this study were prepared from seagrasses. The kinetic behaviour of the process was investigated. To study the adsorption efficiency, several parameters, such as contact time and adsorbent ratio, were used. Langmuir and Frundlish adsorption isotherm models were tested for the adsorption process. The linear regression coefficient R^2 was used to elucidate the best-fitting isotherm models. Adsorption kinetics fitted well with the first-order kinetic model. The inobtained results indicated successful adsorption of the studied dye using sea grasses-activated carbon.
Keywords. Removal, Safranin, Aquouse Solution.

Introduction

The application of dyes in many chemical industries has undoubtedly influenced the environment, especially on water sources. However, dyes are classified as crucial in chemical industries such as coloring, printing, pharmaceutical, ink, cosmetics, and food industries that production cannot be complete [1]. This is because they are mainly used to color their products to make them attractive. Consequently, they become a common source of industrial pollutants during their synthesis and later during their applications in these industries, especially in some medical uses [2]. 20% of dyes produced annually are discharged as effluents from manufacturing operations, whilst approximately 40-65% are discharged from industries [3]. However, indiscriminate discharge of wastewater into water bodies without proper treatment from these industries as byproducts has been reported to negatively impact the normal function of aquatic life and changes in the food web [4].
Dyes are classified as anionic, cationic, and nonionic depending on the ionic charge of the dye molecules. Investigations have shown that cationic dyes are more toxic than anionic dyes [5]. Safranin was used as a case study in the present study. It is a cationic dye primarily used in the pharmaceutical industries. Literature reveals that exposure to these effluents may irritate respiratory systems, skin, and digestive tract infections when ingested [6], therefore, it is imperative to decolorize wastewater to the lowest permissible concentration to safeguard the water bodies as stated by environmental regulations.
The conventional wastewater treatment methods include oxidation or ozonation, membrane separation, precipitation, coagulation flocculation, ion exchange, and reverse osmosis [6]. However, many findings have indicated that it is challenging to use conventional methods to effectively remove dyes from wastewater because of their synthetic origin and the complex nature of structures, mainly aromatic structures, which are biologically non-degradable and may be toxic to health [6-8]. To remove dye from industrial effluents, several processes are used. Among several chemical and physical methods available, the adsorption process has been reported as one of the most effective techniques successfully employed for color removal from wastewater [9]. However, commercial activated carbon is one of the most widely used agents or decontaminating or decolorizing waste water due to its high adsorption capacity, surface area, degree of surface reactivity, and micro-porous structures [10]. Also, its effectiveness in yielding good results after treatment has been proven [11]. However, economically, the cost of using commercial activated carbon is very high; as such, researchers developed an alternative low-cost adsorbent that can compete favorably with commercial activated carbons, among which are agricultural wastes which have been proven to be an effective, green and more economical method that can alternate the more expensive commercially available activated carbons [11,12]. Furthermore, studies have shown that the consumption of fruits such as cocoa nuts, bananas, and oranges is increasing daily, which is attributed to the fact that they have high nutritional and medicinal values. Consequently, they also generate waste in the environment. Therefore, they are converted into adsorbents such as activated carbon. The chemical structure of safranin is presented in Figure 1.

Received*: 16-01-2025 -* ***Accepted****: 02-03-2025 -* ***Published****: 11-03-2025*

https://doi.org/10.54361/ajmas.258161

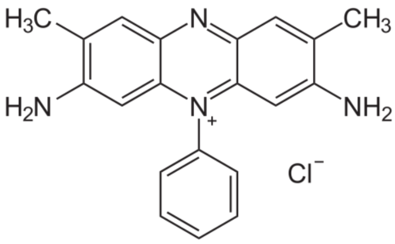

Figure 1. Chemical structure of safranin

The activated carbon of sea is an low-cost material for removing, indicators were the removal of some dyes, including two types of indicator some dyes including two indicators types w The aims of this study can be summarized in the following points: Using the residual sea grasses some industrial organic dyes, such as chemical indicators, including Safranin, from aqueous solutions and studying the impact of some factors, including different dosages different concentrations, and the effect of time on adsorbed materials, using in some mathematical relationships by calculating the Langmuir, Freundlich isotherms and adsorption kinetics.

Materials and Methods

Materials

All chemicals used in this study are grade: The Safranin from BDH company, Equipment's: Whatman filter paper, shaker. Spectrophotometer (Type DU 800- Beckman Coulter). Oven 30–1000 °C. Digital pH meter. Digital Balance, Digital Heater with thermostat system.

Preparation of activated carbon from residual sea grasses

Sea grasses were collected from the coast of Al-Hamama town, Libya. The seagrasses were washed several times with distilled water. They were dried overnight for several days, ground into a powder, and burned in the oven at 600°C for about three hours.

Preparation of safranin solutions

Stock solutions of the studied dye of 100 ppm were prepared by dissolving the appropriate amount of dye in water and making up to the 100 ml mark with deionized water. Different concentrations of 10-50 mg L^{-1} of the dye were prepared from the stock solution. Deionized water was used to prepare all of the solutions and the reagents. A calibration curve of absorbance versus concentration was constructed using a UV-VIS spectrophotometer (Type D-U 800) at a maximum wavelength of 519 nm (Figures 2 & 3).

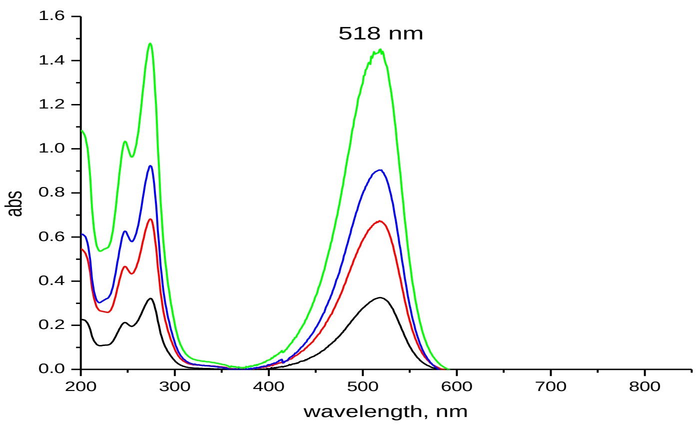

Figure 2. λ $_{max}$ of Safranin

***Received**: 16-01-2025 - **Accepted**: 02-03-2025 - **Published**: 11-03-2025*

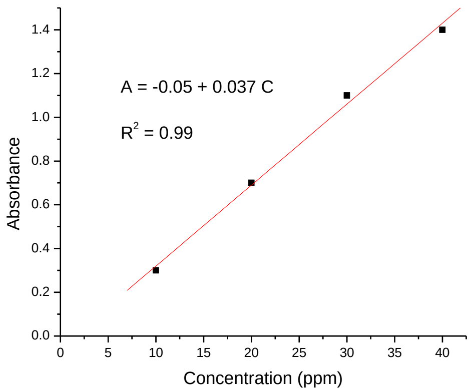

Figure 3. Standard Curve of Safranin.

Adsorption factors
Effect of Dosage
Adsorbent dosage was optimized by performing the experiments at varying adsorbent dosages of (0.01, 0.02, 0.03, 0.04, and 0.05 g), with 10 ml of dye solution concentration of 100 mg/L concentration for Safranin; the bottles were shacked for 20 min at room temperature and then filtered. The absorbance of the dye solution was recorded by UV-VIS spectrometer. The adsorption process was carried out according to some previous studies [13-17].

Effect of Time
To establish the effect of time on the absorption, the equilibrium investigations were carried out at the initial concentration of each reagent of 100 mg/L after selecting the best weight of adsorbent, which gave the high percentage of removal (0.01 – 0.05 g) for the dye. The adsorbent dose was added at different times of (5, 10, 15 and 20 min). The data obtained were used to plot the isotherm values.

Effect of concentrations
The effect of the initial concentration on the removal of dye by adsorbents at a higher dose of each adsorbent was obtained. Experiments were carried out with a constant dose of the adsorbents, which showed high removal percentages.

Effect the temperature
The Effect of temperature on the removal of selected dyes was studied at each concentration, where different temperature values ranged between (20 and 30 ^{0}C) of at fixed values of adsorbent dose and time.

Adsorption Studies
The concentration of absorbed dye was obtained by comparing the recorded absorbance from a standard curve of the dye.

Calculations of the capacity of adsorption
The amount of dye adsorbed per gm (qe) was calculated based on the following equation:

$$(q_e) = \frac{(c_\circ - c_e)}{m} \times v$$

$C_\circ$ and C_e are the initial and equilibrium concentration of adsorbate (here, Safranin T dye), respectively; V is the volume of dye solution (in liter); m is the weight of adsorbent.
The removal percentage of dye was calculated based on the following equation:

$$Removal\ \% = \frac{c_\circ - c_e}{c_\circ} \times 100$$

Adsorption Isotherms
Adsorption isotherms can be generated based on theoretical principles. Two isotherm equations have been tested in the present research, namely, Langmuir and Freundlich, to describe the equilibrium characteristics of adsorption.

Langmuir adsorption isother
The Langmuir equation is the most widely used isotherm equation for modeling the equilibrium. The Langmuir linear equation is commonly expressed as follows:

***Received**: 16-01-2025 - **Accepted**: 02-03-2025 - **Published**: 11-03-2025*

https://doi.org/10.54361/ajmas.258161

$$\frac{Ce}{qe} = \frac{1}{kl} + (\frac{al}{kl})Ce$$

A plot of Ce versus Ce/qe was linear showing the applicability of Langmuir adsorption isotherm for Alizarin red and Ruthenium red adsorption. K_L and a_L are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively, which are calculated from the slope and intercept of the plot Ce versus Ce/qe. The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter 'RL', which is defined by,

$$R = \frac{1}{1 + al\,.Ci}$$

Ci = initial concentration of the dye and al = Langmuir constant. RL >1 Unfavorable, RL=1 Linear, 0 < RL <1 Favorable, RL=0 Irreversible.

Freundlich adsorption isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. It also assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir, which is given by the following nonlinear equation below:

$$q=KC$$

KF is a system constant related to the bonding energy. KF can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the adsorbent for unit equilibrium concentration. 1/n indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value of 1/n below 1 indicates a normal Freundlich isotherm, while 1/n above 1 indicates cooperative adsorption. The above equation can be linearized in the logarithmic form of the following equation, and the Freundlich constants can be determined:

$$\log qe = \log K_F + \frac{1}{n}\log Ce$$

A plot of log Ce versus log qe was linear, where kF is a measure of adsorption capacity (mg/g), and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1). The values of 1/n and kF can be calculated from the slope and intercept, respectively.

Results

Effect of dosage on the adsorption of Safranin

According to the results of removal percentage (%) of the effect of doses on the adsorption of safranin, showed that the dose of 0.01 g of sea grasses carbon gave the highest removal percentage value of (98.26%) followed by the dose of 0.02 g (98.13 %). On the other side, the lowest removal percentage values of (97. 21%) were recorded for a dose of (0.05), respectively, as shown in Table 1.

Table 1. Effect of adsorbent doses on the adsorption of safranin at room temperature.

Dose(g)	Final concentration (C_e)ppm	Removal %
0.01	1.10	98.90
0.02	1.71	98.29
0.03	1.75	98.25
0.04	1.10	98.90
0.05	1.78	98.22

Table 2. Effect of adsorbent doses on the adsorption of Safranin at 30 ^{0}C temperature.

Dose(g)	Final concentration (C_e)ppm	Removal %
0.01	1.10	99.10
0.02	1.71	98.80
0.03	1.75	98.30
0.04	1.10	99.10
0.05	1.78	98.15

This indicates that at the low contents of adsorbent, the adsorption of Safranin (Removal percent) gave a high rate compared with the other high doses(g). This is important for the used activated carbon obtained from sea grasses because small quantities from low-cost materials gave a high percent of removal of the Safranin.

***Received**: 16-01-2025 - **Accepted**: 02-03-2025 - **Published**: 11-03-2025*

Effect the time on the adsorption of dyes
From the results shown in Table 3, there are variations of the applied time (min) on the removal percentage of the Safranin, where the high removal percentage was obtained at 20 min. The results also indicated that the percentage of removal of the dye was increased with increasing the applied time.

Table 3. Effect of time on the adsorption of Safranin

Time (min)	q_e (mg/g)
0	0
5	1.90
10	1.92
15	1.84
20	1.94

Adsorption Isotherms (Langmuir and Frindulich)
Langmuir isotherms
The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation. The Langmuir linear equation is commonly expressed as follows:

$$\frac{Ce}{qe} = \frac{1}{kl} + (\frac{al}{kl})Ce$$

A plot of Ce versus Ce/qe was linear, showing the applicability of Langmuir adsorption isotherm for bromo cresol purple and cresol red adsorption. K_L and a_L are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively, which are calculated from the slope and intercept of the plot Ce versus Ce/qe. The effect of different adsorbent times on the adsorption of the studied dyes was monitored. A linearized Ce versus Ce/qe was obtained, as shown in Table 4.

Table 4. The Langmuir isotherms values of safranin

Time(min)	Final Concentration C_e(ppm)	q_e (mg/g)	C_e / q_e
0	0	0	0
5	1.90	9.843	0.193
10	1.92	9.830	0.195
15	1.84	9.822	0.199
20	1.94	9.821	0.215

The fits are guide for the sorbent to suggest applying the Langmuir model for the investigated system. The values of the Langmuir parameter with correlation were computed from the fitted Langmuir equation's intercept and slope. The Langmuir parameters for the adsorption of Safranin using sea grasses. Were as follows: 0.1005, 0.0016 and 0.99 for the Langmuir values of Al, Kl and R^2, respectively. Both values of r2 of the studied dyes high enough to assign the successful application to adsorbent the dyes on the sea grasses. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL as follows.

$$RL = \frac{1}{1 + al\,.Ci}$$

Where Ci = initial concentration of the dye and al=Langmuir constant.

The equilibrium isotherms types are related to the RL values for RL > 1 Unfavorable, RL =1 Linear, 0< RL < 1 Favorable, RL=0 Irreversible. In the present study, the values of RL were found to be less than (1) and slightly higher than (0) value, indicating the favorable adsorption of the selected dyes on the seagrasses. The RL values of adsorption of safranin were 0.497.

Freundlich adsorption isotherm
The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. It also assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir equation. It is given by the following nonlinear equation below:

$$\mathbf{q=KC}$$

KF is a constant for the system and is related to the bonding energy. KF can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the adsorbent for unit equilibrium concentration. 1/n indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below 1 indicates a normal Freundlich isotherm, while 1/n above 1 indicates cooperative adsorption. The above

***Received**: 16-01-2025 - **Accepted**: 02-03-2025 - **Published**: 11-03-2025*

equation can be linearized in the logarithmic form of the following equation, and the Freundlich constants can be determined:

$$\log qe = \log K_F + \frac{1}{n} \log Ce$$

A plot of log Ce versus log qe was linear, where K_F is a measure of adsorption capacity and (n) is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1). The values of 1/n and kF can be calculated from the slope and intercept, respectively. The Freundlich isotherms for the adsorption of Safranin were as follows: 0.007, 3.54, and 0.99 for 1/N, KF and R^2, respectively. The results of Freundlich's present study are illustrated in Table 5.

Table 5. The values of freundlich isotherm for Safranin.

Time (min)	Final Concentration C_e(ppm)	log C_e	q_e (mg/g)	Log q_e
0	0	0	0	0
5	1.90	0.278	9.843	0.9931
10	1.92	0.2833	9.830	0.9920
15	1.84	0.2648	9.822	0.9921
20	1.94	0.2878	9.821	0.9921

Kinetics of adsorption

According to the values obtained from the isotherms in this study, for cresol red and bromo cresol purple. The adsorption process follows the first-order reaction. The Kinetics of the adsorption was conducted by the values recorded according to the Effect of time on the adsorption of Safranin. The values are shown in Table 6. The adsorption rates are measured by determining the dye concentration as a function of time (C_t is the concentration of dyes at different times) versus time (min). The adsorption rates were calculated from the slopes (slope = -K/2.303). The adsorption rates of safranin on activated sea grasses was 0.0115.

Table 6. The relationship between time(min) and log C_e of Safranin.

Time (min)	Log Ce
0	0
5	0.278
10	0.2833
15	0.2648
20	0.2878

Discussion

In this study, the Safranin dye was selected. It was used in different medical laboratories, especially during histological investigations; most of the laboratories don't treat their wastes, which go directly into outlets. This study aimed to treat the residual dyes as Safranin by using activated carbon produced from low-cost material (seagrasses were used in this study). The treatment or removal efficacy showed a high percentage, an indication to succeed the adsorption presses. Our findings are in harmony with those studies [13-14], which stated that the removal of pollutants from aqueous solutions depended on the values of Langmuir and Fiendish isomers. The adsorption mechanism is attributed to the porosity size of the activated carbon [17], as well as the type of activation mainly affecting the removal of compounds by activated carbon, including temperature of activation, PH values of activated carbons, presence of surface minerals, and others [16]. The advantage of this study is that it used low-cost material (residual sea grasses) and did not add other materials during the activation.

Conclusion

This research aims to evaluate the efficiency of low-cost adsorbents of activated carbon obtained from seagrasses. The noteworthy observations and conclusions can be summarized as follows: The adsorption efficiency of dyes onto activated carbon increases in contact time till it reaches equilibrium. An increase in adsorbent dose led to % removal and a decrease in adsorption capacity. The adsorption isotherm studies showed that the best Langmuir isotherm was for the adsorption of Dye. However, the best Freundlich isotherm was recorded for the adsorption of Safranin. According to the results obtained in this study, the seagrasses can be converted into activated carbon and used as a low-cost and abundant material for removing some dyes. This is an indication to use it for the treatment of some samples as water in the field of economics and environment.

***Received**: 16-01-2025 - **Accepted**: 02-03-2025 - **Published**: 11-03-2025*

https://doi.org/10.54361/ajmas.258161

Acknowledgement
Special thanks to the central lab of the chemistry department, Faculty of Science, Omar Almukhtar University for their collaboration during the experimental part of this study.

References

1. Mohammed M, Ibrahim A, Shitu A. Batch removal of hazardous Safranin-O in wastewater using pineapple peels as an agricultural waste-based adsorbent. International Journal of Environmental Monitoring and Analysis.2014, 2(3): 128-133.
2. Malik R, Ramteke WD, Erl, SR. Adsorption of malachite green on groundnut shell waste-based powdered activated carbon. Waste Management.200, 27(9): 1129-1138.
3. Abdul Wahab O, El-Nemr A, El-Sikaily A, Khaled. Use of rice husk for adsorption of direct dyes from aqueous solution: A case study of direct f. scarlet. Egypt. Journal of Aquatic Research.2005, 3(1): 1110-1354.
4. Abdullah L, Salleh M, Mohd-Noor J, Osman M. Azo dye removal by adsorption using waste biomass: Sugarcane bagasse. Int. Journal of Engineering and Technology.2005, 2(1): 8-13.
5. Aci F, Nebioglu M, Arslan M, Imamoglu M, Zengin M, Kucukislamoglu M. Preparation of activated carbon from sugar beet molasses and adsorption of methylene blue. Environmental Bulletin.2008, 17(1): 997-1001.
6. Ansari R, Mosayebzadeh Z. Removal of basic dye methylene blue from aqueous solutions using sawdust and sawdust coated with polypyrrole. J. Iran. Chem. Soc.2010, 7 (2): 339-350.
7. Basar CA. Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared from waste apricot. J. Hazard Matter.2006, 135(1): 232- 241.
8. Bayazi S. Investigation of Safranin-Oadsorption on superparamagnetic iron oxide nanoparticles (SPION) and multi-wall carbon nanotube /SPION Composites," Desalin. Water Treat.2013, 1–10.
9. Babel S, Kurniawan TA. Cr(VI) Removal From Synthetic Wastewater using Coconut Shell Charcoal and Commercial Activated Carbon Modified with Oxidizing Agents and/or Chitosan. Chemosphere.2004, 54(1): 951–967.
10. Aksu Z. Equilibrium and kinetics modeling of cadmium (II) biosorption by C. Vulgaris in a batch system: Effect of temperatures. Sep. and Purif. Tech. 2001, 21(1): 285-294.
11. Arivoli S, Thenkuzhali M. Kinetic, mechanistic, thermodynamic and equilibrium studies on the adsorption of rhodamine B by acid activated low-cost carbon. E-jour. Chem.2008, 5(2):187-200.
12. Bansal M, Singh D, Garg VK, Rose P. Equilibrium and kinetic studies on the adsorption of methylene blue using orange peels activated carbon. Int. Journal of Environmental Sciences and Engineering.2009, 1(2): 108 – 114.
13. Mamdouh S M, El-Saraf W, Abdel-Halim A. Ali A, Essam A, Hasan H. Rice husk and activated carbon for waste water treatment of El-Mex Bay, Alexandria Coast, Egypt . Arabian Journal of Chemistry. Science direct .2016,1 (9):1590 -1596
14. Mohamed A, Elsayed A S, Batubara A, Hamad M, Mohammed A, Abel Moniem C, Mamdouh S. Masoud, Alaa-Eldin R. Mostafa E, Mohammed G. Usage of natural wastes from animal and plant origins as adsorbents for the removal of some toxic industrial dyes and heavy metals in aqueous media. Journal of Water Process Engineering. 2023,1, (55)
15. Alfutisi HM, Hamad M. Removing of Thymol Blue from aqueous solutions by Pomegranate peel. EPH - International Journal of Applied Science. 2019,1(1).: 111 -119.
16. Al Madani EA, Hasan HM, Safwan FK. Kinetic study of the adsorption of the removal of bromo cresol purple from aqueous solutions. International journal of research grathaalayah.2019, 7(12).
17. Haasn H. Studies on physicochemical parameters and water treatment for some localities along coast of Alexandria. unpublished thesis Ph D. Thesis. Alexandriea University.254 P.

المستخلص
يعد السافرانين أحد المؤشرات الأكثر شيوعًا المستخدمة في تطبيقات مختلفة، وخاصة في التطبيقات الكيميائية، وهو صبغة تسبب بشكل أساسي العديد من المشاكل البيئية من الوسائط البيئية مثل الماء والمحاليل المائية. تم تحضير المواد الماصة للكربون المنشط المستخدمة في هذه الدراسة من أعشاب البحر. تم التحقيق في السلوك الحركي للعملية. من أجل دراسة كفاءة الامتصاص، تم استخدام عدد من المعلمات، مثل وقت التلامس ونسبة المواد الماصة. تم اختبار نماذج معادلة الامتصاص Langmuir و Frundlish لعملية الامتصاص. تم استخدام معامل الانحدار الخطي R2 لتوضيح أفضل نماذج معادلة الامتصاص المناسبة. تتناسب حركية الامتصاص بشكل جيد مع نموذج الحركية من الدرجة الأولى. أشارت النتائج التي تم الحصول عليها إلى الامتصاص السلس للصبغة المدروسة باستخدام الكربون المنشط من أعشاب البحر.

Received*: 16-01-2025 -* ***Accepted****: 02-03-2025 -* ***Published****: 11-03-2025*