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The Effectiveness of *Scolymus Maculatus* in the Removal of Basic Blue Dye 41 in Aqueous Solutions: Kinetics and Thermodynamics

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Abstract: The presence of cationic dyes; especially the basic ones in an aqueous solution causes several problems. Therefore, it is necessary to reduce itfrom industrial effluents before being discharged into the environment. This study aimed to investigate the removal of Basic Blue 41 (BB41) dye from an aqueous solution using agricultural waste as an adsorbent. This study was conducted in a batch experimental system. The effect of various parameters such as initial dye concentration, pH, pH_{zpc} and adsorbent dosage was studied. The data were examined by Freundlich, Temkin, Debinin-Radushkevich, pseudo first order and pseudo second order kinetic, and thermodynamic parameters. The characterization of the adsorbent was determined by the Scanning Electron Microscopy (SEM), Fourier transform infrared (FTIR) and X-Ray Diffraction (DRX). The results of this work showed that the *Scolymus Maculatus* adsorbent was proven most effective in removing Basic Blue 41 from an aqueous solution at pH=7,09 with 85,14%. The results showed also that the adsorption process follows the Freundlich isotherm as well as pseudo-second-order kinetic. The results of the thermodynamic process showed that the adsorption is spontaneous and endothermic in nature.

Keywords: Scolymus Maculatus, BB41, Adsorption, Kinetic, Thermodynamic

1. Introduction

A lot of people throughout the world especially in the developing countries like parts of Asia and Africa are very much struggling to get pollution free hygienic water both for drinking as well as for household use [1]. Water pollution is one of the most undesirable environmental problems in the world. Textile industries produce a lot of wastewater; about 700.000 tons of organic dyes every year, 200,000 tons of these dyes are discharged in wastewater during the production of textile without any treatment [2]. Wastewater containing dyes is one of the most serious water pollutions caused by textile, paper, plastic, leather and other industries [3]. Generally; they are very stable compounds and thus are very much difficult to get them removed from the environment.

Many of these dyes do not only destroy aquatic organisms but also harm human beings because of their carcinogenic, mutagenic and teratogenic properties; as well as respiratory toxicity [4-6]. In addition to that; the presence of dyes in the effluents reduces the photosynthetic activity in aquatic plants and thus disturbs the equilibrium of nature [7]. Moreover, dyes give a significantlybad taste and odor to water bodies [8, 9].

Given the unhealthy consequences of the water pollution resulting from dyes; removal of these toxic organic dyes from wastewater is a major problem faced by textile industries, therefore; it is necessary to find effective ways to remove them.

There are several available processes for color removal from wastewater; such as ultrafiltration [10], electrodialysis

[11], electrochemical oxidation [12] and advanced oxidation processes [13]. Some of these treatment methods have shown to be effective, however, they have some limitations; such as the excess amount of chemical usage and lack of effective color reduction. The adsorption technique is a promising way to remove dyes and organic compounds from aqueous effluent [14]. Different types of adsorbents that are used for the treatment of wastewater contaminated by textile effluents.; the ones that come in their natural form such as Xanthium Strumarium L. Seed hull [15] and coconut mesocarp [16], and others that come in their activated forms such as oxalic acid treated Artocarpus odoratissimus peel [17], surfactant treated saponite [18], Modéfication clay mineral boron enrichment, zeolitic tuff [19], and Prolin polymer [20].

There are few studies related to the use of a type of *Scolymus* as an adsorbent to the removal of dyes and metals [21, 22]. *Scolymus Maculatusis* is a cost effective plant, abundant and easily available in the Mediterranean countries, it is known to be non-toxic as it is used in food [23] and some medical treatments [24, 25].

The objective of this work is to study for the first time, the adsorption capacity of *Scolymus Maculatus* from Algeria; in the removal of the cationic Basic Blue 41 (BB41).

2. Material and Methods

2.1. Adsorbate

De-ionized water was used throughout the experiments for solution preparations. The Basic Blue 41 (BB41) was supplied by FITAL Company, Algeria and was used as received. The structure of BB41 is shown in Figure 1. A stock solution of 200 mg/L was prepared by dissolving an accurate quantity of the dye in distilled water and diluting it to obtain the experimental solution to the designed initial dye concentration.

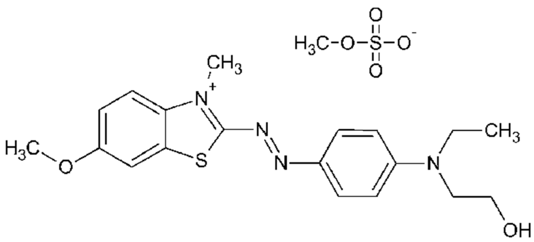


Figure 1. *Chemical structure of basic blue 41.*

2.2. Preparation and Characterization of Adsorbent

The *Scolymus Maculatus* plant was naturally harvested in July in Ain Defla, Algeria. The sample was washed several times with distilled water to remove the soluble impurities, dried at 353 K for 24h [21]. Then the dried plant was cut into small pieces and powdered using a mixer. The structure, surface morphology, texture and porosity of the adsorbent were observed using scanning electron microscopy (SEM, JEOL JSM 6830), X- ray Diffraction and FT-IR spectra.

Figure 2. *(a) Image of Scolymus Maculatus (b) Scolymus Maculatus powder.*

2.3. Batch Adsorption Studies

Batch experiments were conducted to investigate the parametric effects of contact time, initial dye concentration, the dose of adsorbent, pH of solution and temperature. We have followed the same experimental protocolfor all the factors studied; where samples were prepared from a stock solution and diluted to the required initial concentration (5-25mg/L). Samples were withdrawn at the suitable interval and were separated from the sorbent by centrifugation for 10 minutes; and their residual dyes concentration was determined by spectrophotometer UV visible OPTIZEN 3220at λ=610nm.

The dye removal percentage can be calculated by the following equation:

$$R(\%) = \frac{(C_0 - C_f)}{C_0} * 100 \tag{1}$$

$$q_e = \frac{C_0 - C_f}{m} * V \tag{2}$$

Where: C_0 and C_f are the initial and final concentration respectively, V is the volume of the solution (L) and m is the adsorbent weight (g).

3. Results and Discussion

3.1. Characterizations of the Adsorbents

The SEM micrograph of the *Scolymus Maculatusis* illustrated in Figure 2. It is clear that the adsorbent (*Scolymus Maculatus*) has a considerable number of heterogeneous pores, which indicates that the adsorbent has a porous structure [26], where there is a good possibility for the dye to be trapped and adsorbed [27]. In addition; EDX analysis showed the surfaces of the adsorbent. The presence of carbon and oxygen was detected. There are also impurities such as Mg, Ca, Al, Si, Fe, Cu, Cl, S and P.

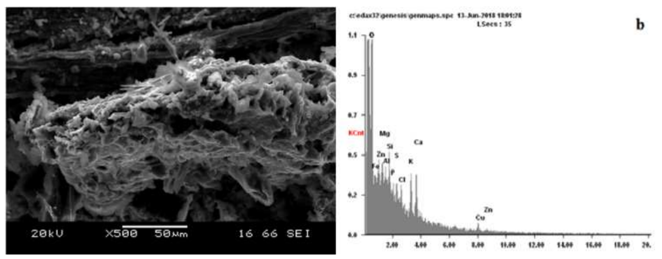


Figure 3. *(a) SEM image and (b) EDX of the Scolymus Maculatus adsorbent.*

X- ray Diffraction was used to identify the phases present in the sample. The measurements were performed using an x-ray Diffractometer X'Pert-Pro MPD Panalytical with Cu $K\alpha_1$ radiation scan, and were conducted from (2Θ=5-70°). The *Scolymus Maculatus* showed in the Figure 3, a typical spectrum having two main peaks and secondary ones. The main peaks are taken as indicative of the presence of highly organized crystalline while, the secondary peaks indicate that there is an amorphous structure.

The FT-IR specter of *Scolymus Maculatus* biomass in the range of 400-4000 cm^{-1} was taken to obtain information on the nature of the functional groups at the surface of the adsorbent. The specter presented in Figure 4 showed broad and superposed bands around 3500 - 3200 cm^{-1} which could be due to the over lapping of O-H and N-H stretching vibration. The specter displays absorption peaks at 2921.45 - 2923.50 cm^{-1} and 2851.99 – 2862.78 cm^{-1} which correspond to C-H stretching vibration for CH2 and CH3 respectively. The adsorption peaks around 1598.86 and 1608.06 cm^{-1} are indicative of C=C stretching vibrations. The band at 1319.73 cm^{-1} was assigned to C-N for the aromatic amine group. The biomass surface was slightly shifted to 1319.17 cm^{-1}. The band at 1235.30 cm^{-1} and 1238.49 cm^{-1} are indicated of C-O of acid groups stretching vibrations.

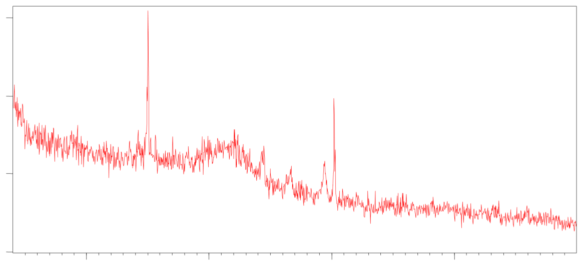


Figure 4. *X-ray diffraction for ScolymusMaculatus before adsorption.*

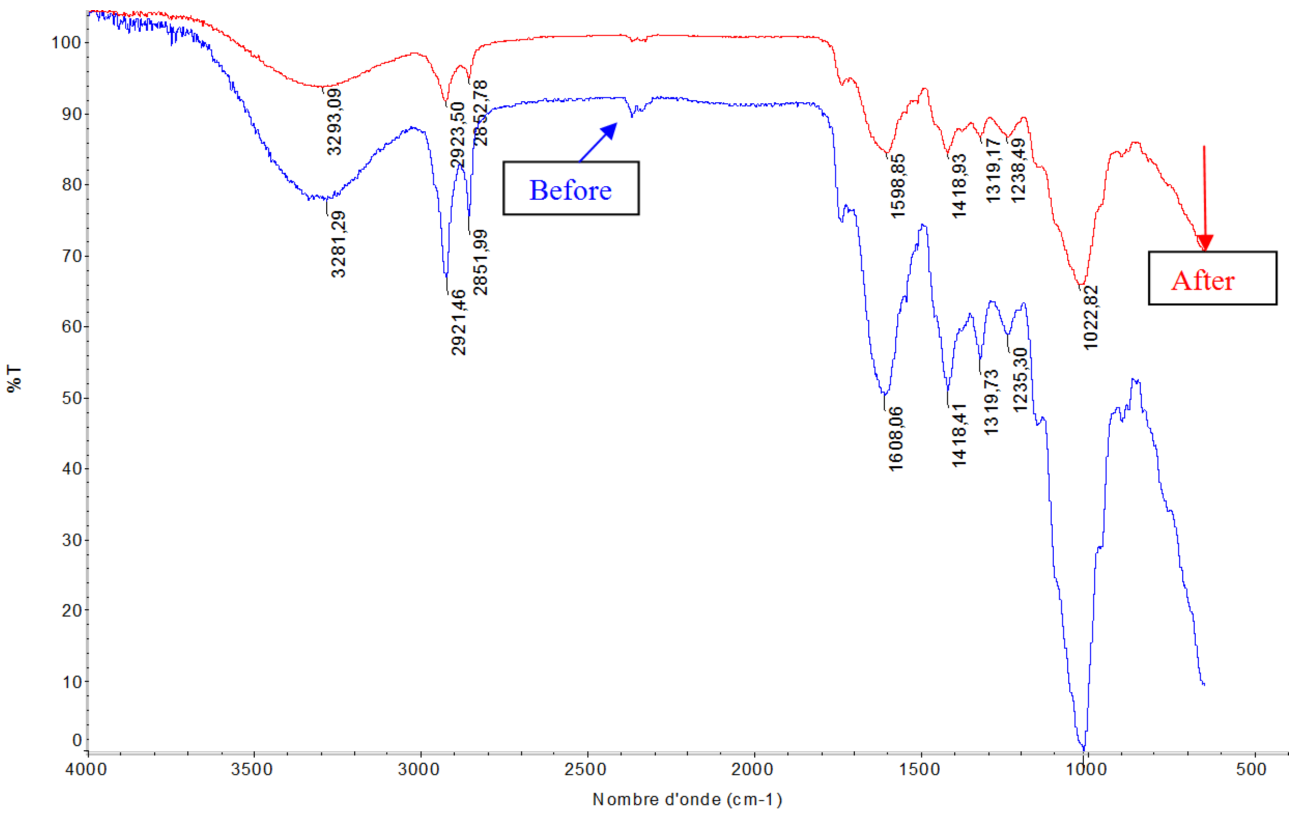


Figure 5. *FT-IR spectra of Scolymus Maculatus before and after adsorption respectively.*

3.2. Effect of Contact Time and Initial Dye Concentration

The contact time is an important parameter for economical wastewater treatment. The effect of contact time on removal is shown in Figure 5. This figure shows that the adsorption is very fast in the first 20 minutes of contact. This may be due to the availability of active sites on the adsorbent at the beginning of adsorption. Equilibrium adsorption was established within 75 minutes in the range from 5 to 25mg/L of BB41.

The yield of removal of the adsorption of BB41 onto *Scolymus Maculatus* increased significantly from 75.71 to 86.14% when concentration increased from 5 to 25mg/L as shown in Figure 5, dye adsorption in primary stages of treatment was fast and after that became slow near the equilibrium point which was due to many empty surface sites available for adsorption in primary stages. As time passes; occupation of empty maintained surface sites becomes difficult due to repulsive force between molecules of dye adsorbed on the solid phase and dye molecules present in the solution phase.

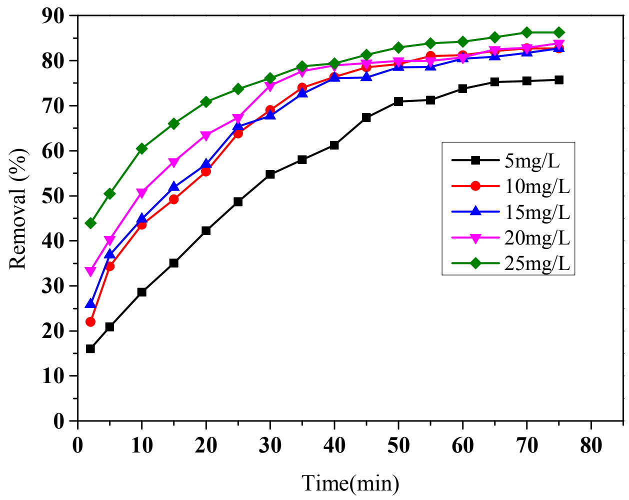


Figure 6. *The effect of contact time and initial dye concentration on the removal of BB41 onto Scolymus Maculatus.*

3.3. Effect of the Dose of Adsorbent

The effect of the biomass amount on the adsorption of basic blue 41 (BB41) was examined by varying the amount from 0.5 to 6g/L. the initial concentration was fixed at 10mg/L, the pH remained without any adjustment at room temperature and a time of 75min. Data obtained from experiments are presented in Figure 5 which shows that the increasing adsorbent dosage resulted in a sharp increase in the adsorption yield. The adsorption yield increased from 63.68 to 85.14% when the adsorbent dosage increased from 0.5 to 4g/L. This result could be due to an increase in the number of the possible binding site and surface area of the adsorbent [21]. A further increase in biomass concentration over 4g/L to 6g/L causes a decrease in adsorption yield, and that could be explained as a consequence of a partial aggregation of biomass.

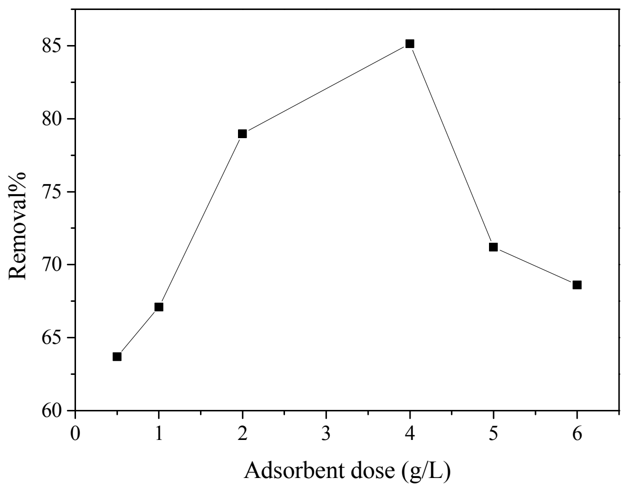
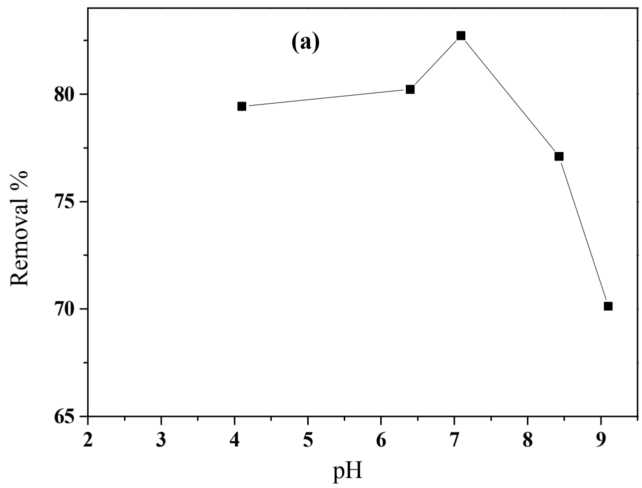


Figure 7. *The effect of dose of adsorbent on the removal of BB41 onto Scolymus Maculatus.*

3.4. pH Effect

The pH is one of the most important factors affecting the adsorption process. In order to study the influence of pH on the BB41 removal on *Scolymus Maculatus*, experiments were carried out over a pH range of 4-9. The Figure 8 indicates that in the acidic range (<7.09) the pH has a strong effect on the adsorption process; reaching an optimal value of pH =7.09. However, for a pH between (7.09 and 9.01) the removals decrease. The isoelectric point of *Scolymus Maculatus* was found to be at a pH of 6.56 (Figure 7), this result demonstrates that the *Scolymus Maculatus* surface has a positive charge when pH values less than the point of zero charges is (pH_z=6.93), and thus should be able to absorb anions.

Figure 7 shows an increase in the rate of removal of BB41 in a pH range between 4.1 and 7.09, the maximum value is 82.72% for a pH equal to 7.09, and beyond this value, we can observe a free fall in basic Environment. We can conclude that the molecular form has better retention than the cationic form. Similar studies [28, 29] indicated that when the values of pH increased; the basic blue 41 removals in *Scolymus Maculatus* adsorbent decreased.



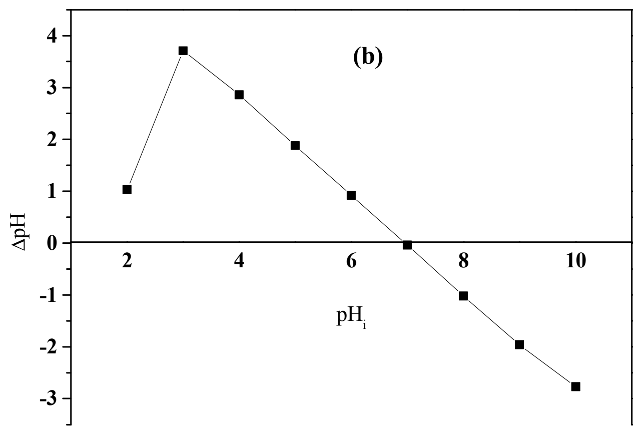


Figure 8. *Effect of pH solution on adsorption of BB41 on Scolymus Maculatus (a) and (b) at the point of zero charge.*

3.5. Adsorption Isotherms

The analysis of the isotherm data is fundamentally important to determine the adsorption capacity of the adsorbent. The adsorption equilibrium is reached when the concentration of adsorbate in bulk solution is in dynamic balance with the one in the liquid-adsorbent interface.

Several isotherms of adsorption equilibrium were applied for the analysis of this equilibrium data. In this work, models such as Freundlich (Freundlich, 1906), Temkin, and Dubinin-Radushkevich were used to describe the data derived from the adsorption of basic blue 41 onto *Scolymus Maculatus*.

The empirical equations of the Freundlich model [30] are based on sorption on a heterogeneous surface, and suggested that the model be adsorbed in monolayer or multilayer. The linear Freundlich equation is given by the following equation:

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

Where q_e: is equilibrium dye concentration on adsorbent (mg/g), C_e is the equilibrium dye concentration in solution (mg/L), K_F (mg/g) $(L/g^{1/n})$ is the Freundlich constant related to adsorption capacity, and n is the heterogeneity factor.

The Freundlich isotherm constants K_F and n were calculated from the slope and the intercept of the plot between Ln q_e and Ln C_e.

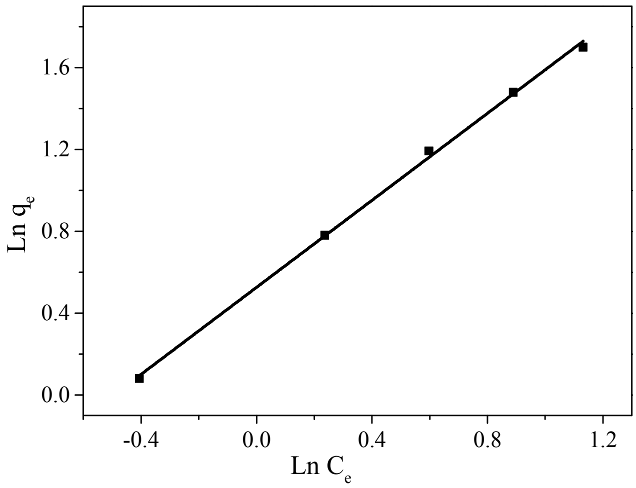


Figure 9. *Freundlich plot for the adsorption of basic blue 41on Scolymus Maculatus.*

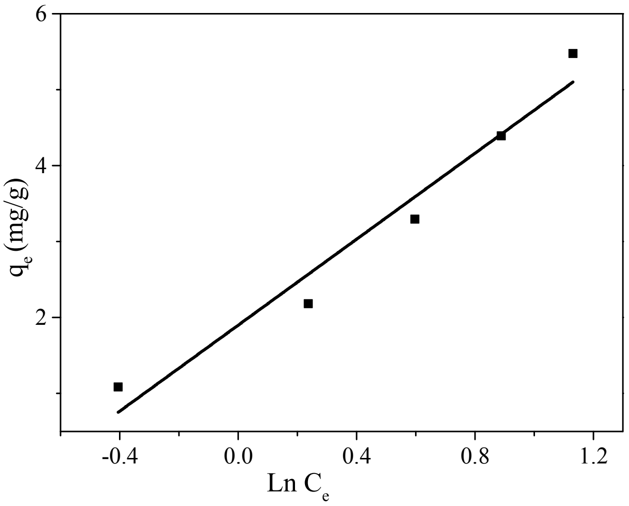


Figure 10. *The linearized Temkinisothermfor the adsorption of basic blue 41on ScolymusMaculatus.*

The Temkin isotherm suggests that the adsorption heat of molecules decreases for the first adsorbed layers of the dye and then increases.

The Temkin equation is given by:

$$q_e = \frac{RT}{b_T} * LnA_T * C_e \quad (4)$$

Where b_T(J/mol) is a constant related to the adsorption heat and A_T (L/mg) is the isotherm constant. The Temkin isotherm constants b_T and A_T were determined from the slope and the intercept of the plot between q_e and Ln C_e.

The Dubinin-Radushkevich (D-R) isotherm model [31] focuses on the heterogeneity of the surface energies and has the following expression:

$$Lnq_e = Lnq_m - \beta * \varepsilon^2 \quad (5)$$

$$\varepsilon = RT * Ln(1 - \frac{1}{C_e}) \quad (6)$$

Where q_m is the maximum adsorption capacity (mg/g), β is a coefficient related to the mean free energy of adsorption (mol^2/J^2), ε is the polarity potential (J/mol), R is the gas constant (8.314J/mol.K), T is the temperature (K), and C_e is the equilibrium concentration (mg/L).

The D-R constants can be determined from the intercept and the slope of the plot between Ln q_e and ε^2 (Figure 9). For β value obtained; the adsorption energy can be calculated using the following relationship.

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

It is important to present the D-R isotherm in this study because it can be used to estimate the type of adsorption. If the E is between (8 and 16 KJ/mol) range, the adsorption process can be explained to be chemisorption, while for values of E < 8KJ/mol, the adsorption process is physical in nature.

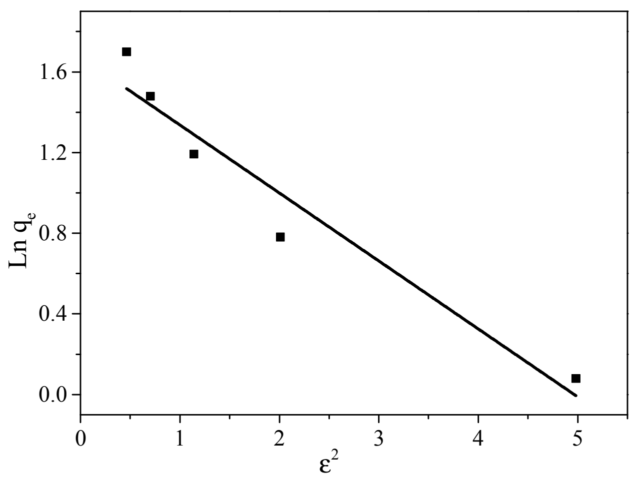


Figure 11. *The linearized D-R isotherm for the adsorption of basic blue 41on Scolymus Maculatus.*

The parameters of the different isotherms are shown in the table below.

The Freundlich isotherm showed a good fit to the experimental data with a high correlation coefficient (0.998). Values of n between 1 and 10 (1/n less than 1) represent favorable adsorption.

The correlation coefficient for the Temkin isotherm model (0.946) indicates that the adsorption process was characterized by the uniform distribution of bending energy, and to distinguish between chemical and physical adsorption on the heterogeneous surface; the equilibrium data were tested with the D-R isotherm model. The estimated values of energy E were found less than 8 KJ/mol which means that adsorption of basic blue 41 on *Scolymus Maculatus*is physical in nature.

Table 1. *Isotherm Parameters for the adsorption of basic blue 41 dye on Scolymus Maculatus.*

Freundlich			Temkin			D-R			
r^2	1/n	K_F (mg/g) (L/g$^{1/n}$)	r^2	b_T (J/mol)	A_T (L/mg)	r^2	q_s (mg/g)	β	E (Kj/mol)
0.998	0.94	1.0691	0.946	861.5	1.957	0.92	5.332	0.337	1.218

3.6. Adsorption Kinetic

Legergren's pseudo order equation is widely used to investigate the kinetics of the adsorption process from aqueous solution. In this work, pseudo-first-order and pseudo-second-order processes was used to describe the adsorption process of Basic blue 41 onto *Scolymus Maculatus*, using the following equations:

Pseudo first order [32], Pseudo second order [33].

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 * t}{2.303} \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{\left(K_2 * q_e^2\right)} + \frac{t}{q_e} \quad (9)$$

Where; q_t and q_e are the amounts of BB41 adsorbed (mg/g) at time t (min) and equilibrium, respectively. The K_1 (min^{-1}) and K_2 (mg/g.min) are the rate constants of the pseudo-first-order and pseudo-second-order adsorptionmodels, which are determined from the slope of the linear plot of log (q_e-q_t) versus t and the intercepts of the lines t /q_t versus t respectively for the five concentrations used.

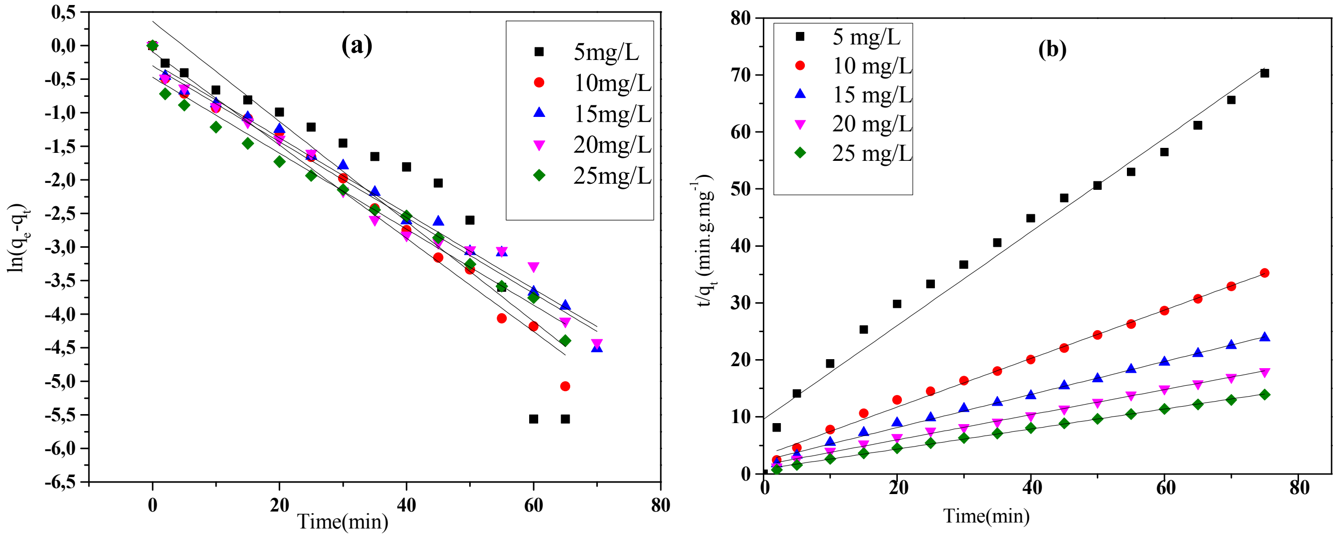


Figure 12. *Kinetic model for the BB41 adsorption on the ScolymusMaculatus.*

Table 2. *Kinetic parameters for the adsorption of BB41 onto Scolymus Maculatus adsorbent.*

Concentration	Pseudo premier order			Pseudo second order			
(mg/L)	K_1 (min^{-1})	q_e(mg g^{-1})	r^2	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h=K_2q_e	r^2
5	0,1704	1,4347	0,833	0.07	1.216	0.08512	0.972
10	0,1589	0,9125	0,979	0.05	2.329	0.11645	0.995
15	0,1296	0,7819	0,986	0.035	3.460	0.1211	0.995
20	0,1301	0,7408	0,972	0.03	4.537	0.13611	0.996

According to r^2 values (Table 2), the BB41 adsorption is well described by the pseudo second order kinetic model. The calculated adsorption capacities were acceptable compared to the experimental ones; the results suggest that the sorption process was controlled by chemical adsorption [33]. The rate constant generally decreased with the increase of the initial dye concentration. Similar fitting of pseudo-second-order has also been reported for the adsorption of AG25 polyaniline composite [34] and adsorption of MB using activated coconut shell [35].

3.7. Thermodynamic Parameters

Thermodynamic parameters such as enthalpyΔH°, entropy ΔS° and free energy of Gibbs ΔG° were determined using the following equations:

$$K_d = \frac{q_e}{C_e} \tag{10}$$

$$\Delta H° = -RT*LnK_d \tag{11}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

$$LnK_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{13}$$

Where: K_d is the thermodynamic equilibrium constant (L/g), R is the universal gas constant (8.314 J.mol/K) and T is the solution temperature in K.

The enthalpy (ΔH°) and entropy (ΔS°) were estimated from the slope and the intercept of the plot Ln K_d versus 1/T respectively (Figure 13).

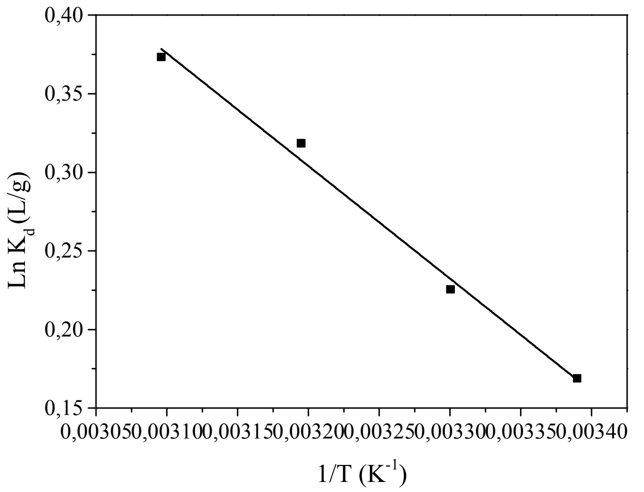


Figure 13. *The plot of ln K_D vs 1/T for Basic Blue 41 onto Scolymus Maculatus.*

Table 3. *Thermodynamic parameters for the adsorption of the BB41dye onto Scolymus Maculatus.*

parameters				
T(°C)	**ΔG°(kJ mol^{-1})**	**ΔH°(kJ mol^{-1})**	**ΔS°(KJ mol^{-1})**	**r^2**
22	-0,415	5.957	0.219	0.988
30	-0,5878			
40	-0,8038			
50	-1,020			

The negative values of ΔG° Table 3 indicate that the adsorption of BB41 onto *Scolymus Maculatusis* thermodynamically stable and spontaneous [36], it is also noticed that ΔG° values decreased from -0,415 to -1,0198 KJ/mol with increasing temperature which can be explained that the adsorption became lower at higher temperature as the overall reaction is endothermic.

The value of ΔH° was found to be 5.957 KJ/mol which demonstrates that the adsorption of BB41 onto *Scolymus Maculatusis* endothermic in nature and controlled by physisorption involving weak secondary forces of attraction [37-39]. The positive value of ΔS° (21.95 KJ/mol) reflects an increase in the degree of translational freedom at the solid-liquid interface.

4. Conclusion

Scolymus Maculatus, is a green, cost effective material and easily available, was found to be very effective adsorbent for the removal of Basic Blue 41 from aqueous solution. The equilibrium sorption of basic blue 41 by *Scolymus Maculatus* was explained using the Freundlish, Temkin and D-R isotherms. Freundlich isotherm was found to be the best fit (r^2=0.998) isotherm suggesting the multilayer coverage of BB41 by *Scolymus Maculatus*. The kinetic data show that the adsorption process follows a pseudo second order model. The thermodynamic study shows that the adsorption is spontaneous and endothermic, the small values of the heat of adsorption confirms well that the interactions between the dye molecules and the surface of *Scolymus Maculatus* are physical in nature. The same result was found by D-R isotherm model.

References

[1] Dutta, A. K., Ghorai, U. K., Chattopadhyay, K. K., & Banerjee, D. (2018). Removal of textile dyes by carbon nanotubes: A comparison between adsorption and UV assisted photocatalysis. Physical E: Low-dimensional Systems and Nanostructure, 99, 6-15.

[2] Kim, T. S. (2018). Fast adsorption kinetics of highly dispersed ultrafine nickel/carbon nanoparticles for organic dye removal. Applied Surface Science, 439, 364-370.

[3] Chen, Y. d., Yen-Chang, L., Shih-Hsin, H., Yan, Z., & Nan-qi R. (2018). Highly efficient adsorption of dyes by biochar derived from pigments extracted macro-algae pyrolyzed at different temperature. Bioresource Technology, 259, 104–110.

[4] Luan, J., Hou, P. X., Liu, C., Shi, C., Li, G. X., & Cheng, H. M. (2016). Efficient adsorption of organic dyes on a flexible single-wall carbon nanotube film. Journal of Material and Chemistry, 4, 1191–1194.

[5] Sharifpour, E., Khafri, H. Z., Ghaedi, M., Asfaram A., & Jannesar, R. (2018). Isotherms and kinetic study of ultrasound-assisted adsorption of malachite green and Pb2+ ions from aqueous samples by copper sulfide nanorods loaded on activated carbon: experimental design optimization. Ultrasonic Sonochemistry, 40, 373–382.

[6] Song, K., Xu, H., Xu, L., Xie K., & Yang, Y. (2017). Preparation of cellulose nanocrystalreinforced keratin bioadsorbent for highly effective and recyclable removal of dyes from aqueous solution. Bioresource Technology, 232, 254-262.

[7] Suyog Jain, N., & Parag Gogate R. R. (2018). Efficient removal of Acid Green 25 dye from wastewater using activated Prunus Dulcis as biosorbent: Batch and column studies. Journal of Environmental Management, 210, 226-238.

[8] Santos, R. M. M., Goncalves, R. G. L., Constantino, V. R. L., Santilli, C. V., Borges, P. D., Tronto, J., & Pinto, F. G. (2017). Adsorption of Acid Yellow 42 dye on calcined layered double hydroxide: effect of time, concentration, pH and temperature. Applied Clay Science, 140, 132-139.

[9] Subramaniam R., & Ponnusamy, S. K. (2015). Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: optimization by response surface methodology. Water Resources and Industry, 11, 64-70.

[10] Ng, H. K. M., Leo, C. P., & Abdullah, A. Z. (2017). Selective removal of dyes by molecular imprinted TiO_2 nanoparticles in polysulfone ultrafiltration membrane. Journal of Environmental and Chemical Engineering, 5, 3991-3998.

[11] Xue, C., Chen, Q., Liu, Y., Yang, Y., Xu, D., Xue, L., & Zhang, W. (2015). Acid blue 9 desalting using electrodialysis. Journal Membrane of Science, 493, 28-36.

[12] Singh S. A., & Shukla S. R. (2016). Adsorptive removal of cobalt ions on raw and alkalitreated lemon peels. International Journal and Environmental Science Technology, 13, 165-178.

[13] Huang, Y., Cui, C., Zhang, D., Li, L., & Pan, D. (2015). Heterogeneous catalytic ozonation of dibutyl phthalate in aqueous solution in the presence of iron-loaded activated carbon. Chemosphere, 119, 295-301.

[14] Fontoura, J. T. D., Rolim, G. S., Mella, B., Farenzena M., & Gutterres, M. (2017). Defatted microalgal biomass as biosorbent for the removal of Acid Blue 161 dye from tannery effluent. Journal of Environmental Chemical Engineering, 5, pp 5.

[15] Khamparia S., & Jaspal, D. K. (2017). Xanthium strumarium L. seed hull as a zero cost alternative for Rhodamine B dye removal. Journal of Environmental Manager, 197, 498-506.

[16] Monteiro, M. S., Farias, F. R. D., Chaves, J. A. P., Santana, S. A., Silva H. A. S., & Bezerra, C. W. B. (2017). Wood (BagassaguianensisAubl) and green coconut mesocarp (cocoa nucifera) residues as textile dye removers (Remazol Red and Remazol Brilliant Violet). Journal of Environmental Manager, 204, 23-30.

[17] Dahri, M. K., Lim, L. B. L., Kooh M. R. R., & Chan, C. M. (2017). Adsorption of brilliant green from aqueous solution by unmodified and chemically modified Tarap (Artocarpusodoratissimus) peel. International Journal of Environmental Science Technology, 14, 2683-2694.

[18] Tangaraj, V., Janot, J., Jaber, M., Bechelany, M., & Balme, S. (2017). Adsorption and photophysical properties of fluorescent dyes over montmorillonite and saponite modified by surfactant. Chemosphere, 184, 1355-1361.

[19] Humelnicu, I., Baiceanu, A., Ignat, M. I., & Dulman, V. (2017). The removal of basic blue 41 textile dye from aqueous solution by adsorption onto natural zeolitic tuff: Kinetics and thermodynamics. Process Safety and Environmental Protection, 105, 274-287.

[20] Raghunath, S., Anand, K., Gengan, R. M., Nuyunigari, M. K., & Maity, A. (2016). Sorption isotherms, Kinetics and optimization process of amino acid prolin based polymer nanocomposite for the removal of selected textile dyes from industrial wastewater. Journal of photochemistry and photobiology, B: Biology, 165, 189-201.

[21] Barka, N., Abdennour, M., & El-Makhfouk, M. (2011). Removal of methylene blue and eriochrome Black from aqueous solution by biosorption on scolymushispanicus L: Kinetics, Equilibriums and Thermodynamics. Journal of the Taiwan Institute of Chemical Engineers, 42, 320-326.

[22] Barka, N., Abdennour, M., Boussaoud, A., & El-Makhfouk (2009). Biosorption characteristics of cadmium (II) onto scolymushispanicus. L as low cost natural biosorbent. Desalination, 258, 66-71.

[23] Nebel, S., Pieroni A., & Heinrich, M. (2006). Ta cho`rta: Wild Edible Greens used in theGraecanic Area in Calabria, Southern Italy. Appetite, 47, 333-342.

[24] Gonzalez-Tejero, M. R., Casares-Porcel, M., Sanchez-Rojas, C. P., Ramiro-Gutierrez, J.., Molero-Mesa, J., Pieroni, A., et al. (2008). Medicinal Plants in the Mediterranean Area: Synthesis of the Results of the Project Rubia. Journal of Ethnopharmacol, 116, 341-357.

[25] Ugurlu, E., & Secmen, O. (2008). Medicinal Plants Popularly used in the Villages of Yunt Mountain (Manisa-Turkey). Fitoterapia, 79, 126-31.

[26] Royer, E. C., Vaghelti, B., Simon, J. C. P. C., Cunha, N. M., Pavan, B. M., Benvenutti, F. A., et al. (2008). Application of Brazilian pine. Fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution kinetics and equilibrium study. Journal of Hazardous Materials, 155, 536-550.

[27] Hameed B., & El-Khaiary, M. (2008). Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K_2CO_3 activation and subsequent gasification with CO_2. Journal of Hazardous Materials, 157, 344-351.

[28] Dawood S., & Sen, T. K. (2012). Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. Journal of Water Research, 46, 1933-1946.

[29] Nautiyal, P., Subramanian K. A., & Dastidar, M. G. (2016). Adsorptive removal of dye using biochar derived from residual algae after in-situ transesterification: alternate use of waste of biodiesel industry. Journal of Environmental Manager, 182, 187-197.

[30] Freundlich, H. M. F. J. (1906). Kinetics and Thermodynamics of adsorption Methylene blue onto tea waste/$CuFe_2O_4$ composite. Journal of Physical Chemistry, 57: 385-417.

[31] Dubinin, M. M., & Radushkevich, L. V. (1947). The equation of the characteristic curve of the activated charcoal. USSR Physical Chemistry Section A, 55, 331-337.

[32] Ho, Y. S., & Ma Kay, G. (1999). Sorption of copper and nickel ions from aqueous solution using peat. Journal of Adsorption, 5, 409-417.

[33] Lo, I. M. C., & Zhang. (2005). EDTA-enhanced washing for remediation of Pb- and/or Zn contaminated soils. Journal of Environmental Management, 132, 1282-1288.

[34] Ayad, M. M., & El-Nasr A. A. (2012). Anionic dye (acid green 25) adsorption from water by using polyaniline nanotubes salt/silica composite. Journal of Nanostructure in Chemistry, 3, 1-9.

[35] Islam, M. A., Ahmed, M. J., & Khanday. W. A. (2017). Mesoporous activated coconut shell-derived hydrochar prepared via hydrothermal carbonization-NaOH activation for methylene blue adsorption. Journal of Environmental Management, 203, 237-244.

[36] Singh, V. K., & Kumar, E. A. (2016) Measurement and analysis of adsorption isotherms of CO_2 on activated carbon. Applied Thermal Engineering, 97, 77-86.

[37] Paşka, O. M., Păcurariu, C., & Muntean, S. G. (2014). Kinetic and thermodynamic studies on methylene blue biosorption using corn-husk. RSC Advances, 4, 62621-62630.

[38] Papita, S., & Shamik, C. (2011). Insight into adsorption thermodynamics. Prof. Tadashi, M (Ed.), Thermodynamic. InTech Open Access Publisher, 349-364.

[39] Vimonses, V., Sei, S., & Jin, B. (2009). Kinetic study and equilibrium isotherm analysis of Congo red adsorption by clay materials. Chemical Engineering Journal, 148, 354-364.