Eco-Friendly *scolymus hispanicus* for the Removal of Basic Blue 41

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ABSTRACT: *This study presents the feasibility of used untreated Scolymus hispanicus as a low-cost adsorbent for the adsorptive removal of Basic Blue 41 (BB41), a common pollutant in textile wastewater. The Scolymus hispanicus adsorbent was characterized by Fourier Transform InfraRed (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) analysis, and pH zero of point charge (pHzpc) method. The ability of the Scolymus hispanicus in removing the dye color was dependent on contact time, adsorbent dose, initial dye concentration, and solution pH. The optimum adsorption was found at around pH 7; contact time 75 min; adsorbent dose 4 g/L. The maximum percentage dye removal value was 81, 92 % with an initial dye concentration at 5 mg/L. The adsorption kinetics was best described by pseudo-second-order model for different initial concentrations and the adsorption isotherm follows the Freundlich model. Thermodynamic parameters such as enthalpy change (ΔH^o), free energy change (ΔG^o), and entropy change (ΔS^o) were studied, and the adsorption process of Basic Blue 41 was found to be endothermic, spontaneous, and physical in nature. The study revealed that the Scolymus hispanicus is a potential adsorbent for effective removal of BB41 from an aqueous solution.*

KEYWORDS: *Adsorption; Basic Blue 41; Scolymus hispanicus; Kinetic; Thermodynamic.*

INTRODUCTION

Azo dyes like Basic Blue 41 are the largest group of dyes used in the textile industry [1]. However, their low degree of fixation on the fiber results in the release of substantial amounts of the dye in the wastewater. Moreover; they are biologically non-degradable because of their aromatic structure [2, 3]. Blue Basic 41 is widely used by the textile industry for dying acrylics and polyesters. Its tinctorial value is high, Small quantity of dye in water (1ppm) can be toxic and highly visible and the textile industry presents an important share in total water consumption, as during dyeing processes about 10–15% of these dyes remain in the effluents [4]. Consequently, the removal of dyes from effluents is required, since; the removal of color from waste effluents becomes environmentally important. Color removal of dye can be divided into three classes: Biological, Chemical, and Physical methods. Biological treatment is the most economical method when compared with physical and chemical processes, but this method is unsatisfactory in color elimination with current biodegradation processes [5]. Chemical and physical

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1021-9986/2021/2/511-523 13/$/6.03

methods include coagulation- flocculation, filtration, precipitation, floatation and electro floatation, and conventional oxidation methods. Though, the dyes are removed completely by this process, it is so expensive and also excessive chemical use generates secondary pollution problem. On the other hand, Physical methods used commonly are adsorption processes. Adsorption is one of the most efficient techniques to remove dyes [6-8] and other organic compounds [9-11]. Therefore, several low-cost adsorbents have been used for the removal of dyes from aqueous solution. Several adsorbents were employed for the removal of a Blue Basic 41, such as native[12] and modified [13] Eucalyptus *camaldulensis barks,* Treated filamentous algae [14] ,modified rice husk [15] and biomass Pleurotus mutilus [1]. Adsorption by agricultural by-products used recently as an economical and realistic method for removal of different pollutants, has proved to be an efficient at removing many types of dyes [16-18]. In this context, the purpose of the present work is to validate the valorization of *scolymus hispanicus* as adsorbent for the removal of Basic Blue 41 (BB41), cationic dye from an aqueous solution. In our laboratory, the work is in progress to look into the possibility of the use of this biomass for industrial pollution control. *Scolymus-hispanicus* is cost effective, abundant and easily available plant in the Mediterranean countries. It is known to be non toxic as is used in food [19] and some medical treatments [20]. The bio-macromolecules on the *scolymus hispanicus* surface have several functional groups such as amino, carboxyl, thiol, and sulfydryl groups and are responsible for binding dye molecules.

To the best of our knowledge, there is only one study, which is available in the literature for the adsorption potential of *scolymus hispanicus* for dye removal. This study is reported by Barkat et al., [21], their work is focused on the adsorption of Methylene Blue (MB) and Eriochrome Black T from aqueous solutions. These authors have found that the maximum adsorption occurred at the pH value of 6.8 for Methylene Blue and 3 for Eriochrome Black T and adsorption kinetic data was properly fitted with the pseudo-second-order kinetic model.

The present work suggested that the *scolymus hispanicus* in native form can be used beneficially in treating aqueous solution containing basic dye (BB41). Effects of initial pH, dye concentration, adsorbent amount, and contact time on the batch adsorption performance of *scolymus hispanicus* were tested.

EXPERIMENTAL SECTION

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 Fig. 1. The stock solution was prepared by dissolving accurately weighed samples of anhydrous BB41 in distilled water to give a concentration of 1000 mg/L and diluted with distilled water when necessary. The initial pH of the BB41 solution is adjusted by using NaOH and HCl solutions.

Preparation and characterization of adsorbent

The Scolymus *hipanicus* 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 353K for 24h [21]. Then the dried plant was cut into small pieces and powdered using a mixer (Fig 2). The structure, surface morphology, texture and porosity of adsorbent were observed using scanning electron microscopy (SEM, JEOL JSM 6830) and Fourier Transform Infrared (FTIR) spectroscopy.

Adsorption studies

Kinetic studies

Batch kinetic biosorption studies were performed in a temperature-controlled stirrer using 100 mL of adsorbate solution. The samples at different time intervals (5–75 min) were taken and at the end of each agitation period, the mixtures were centrifuged for 20 min at 5000 rpm and then, analyzed using a UV spectrophotometer at λ=610 nm wavelength. During the adsorption, the temperature is kept constant at 22°C. The effect of initial concentration (5–25 mg/L) on the adsorption capacity of *scolymus hispanicus* to dye is investigated. The removal efficiency (E) of BB41 on *scolymus hispanicus* and the sorption capacity, (q) were calculated from Eqs. (1)– (2):

$$E(\%) = \frac{Ci - Cf}{Ci} * 100 \quad (1)$$

$$q = \frac{(Ci - Cf) * V}{m} \quad (2)$$

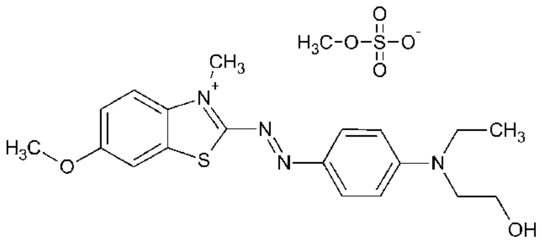

Fig. 1: Molecular structure of Basic Blue 41.

(a)

(b)

Fig. 2: (a) image of Scolymus hispanicus (b) Scolymus hispanicus powder.

where C_i and C_f are the initial and final concentrations of BB41 (mg/L) respectively, V the volume of the solution (L) and m the adsorbent weight (g).

Equilibrium studies

Adsorption *equilibrium* studies were conducted at initial dye concentration of 10 mg/L by adding a fixed amount of adsorbent (0.4g) into a series of conical flasks each filled with 100 mL of dye solution. Batch sorption experiments were performed at various aqueous phase pH (4-9). The pH value for test solution was adjusted by 0.1 N HCl or 0.1 N NaOH solutions Experiments were repeated for different adsorbent dose (0.4-6) g/L values. During the adsorption, the temperature is kept constant at 22°C.

Sorption isotherms

Adsorption experiments were carried out by adding a fixed amount of adsorbent (4 g) to a series of conical flasks filled with 100 mL diluted solutions (5–30 mg/L). The conical flasks were placed in a thermostatic shaker at 22 °C at pH 7.

RESULTS AND DISCUSSION

Surface characterization

Scanning Electron Microscope (SEM)

SEM is used to examine the morphologies and surface properties of an adsorbent made from *scolymus hispanicus* before and after BB41 adsorption; the results are shown in Fig. 3 (a) and (b), respectively. Fig.3 (a) shows that the adsorbent surface had an irregular heterogeneous, rough structure and many pores are clearly observed on the surface of the *scolymus hispanicus* indicating the possibility of its good adsorption properties. As a myriad of functional groups is often present on the sorbent surface, various sorption mechanisms may be involved in the sorption process. After BB41 adsorption, a significant change is observed in the structure of the *scolymus hispanicus* (Fig. 3(b)). Also, SEM image show clearly the BB41 loaded *scolymus hispanicus* coated by BB41 molecules over the whole surface. It can also be seen that some salt particles are released on the surface of the *scolymus hispanicus*, due to the presence of Al, Zn, Ca, Mg.

EDX analysis

Uptake of BB41 was confirmed by the EDX results. Elemental compositions of the sorbent before and after adsorption are tabulated in Table 1. The major components of the sorbent were found to be carbon (61.69%) and oxygen (35.93%). A decrease in elements concentration of the sorbent was noticed after the adsorption of BB41. Increase in carbon concentration after adsorption was noticed (72.42%), but a decrease in oxygen concentration was observed (25.36%). A decrease in the magnesium concentration was also noticed.

Table 1: Elemental composition of scolymus hispanicuss before and after BB41 adsorption.

Elements	C	O	Mg	Al	Si	Ca	S
Before adsorption (%)	61.69	35.93	00.34	00.21	00.26	01.15	00.07
After adsorption (%)	72.42	25.36	00.24	00.16	00.24	00.89	00.09

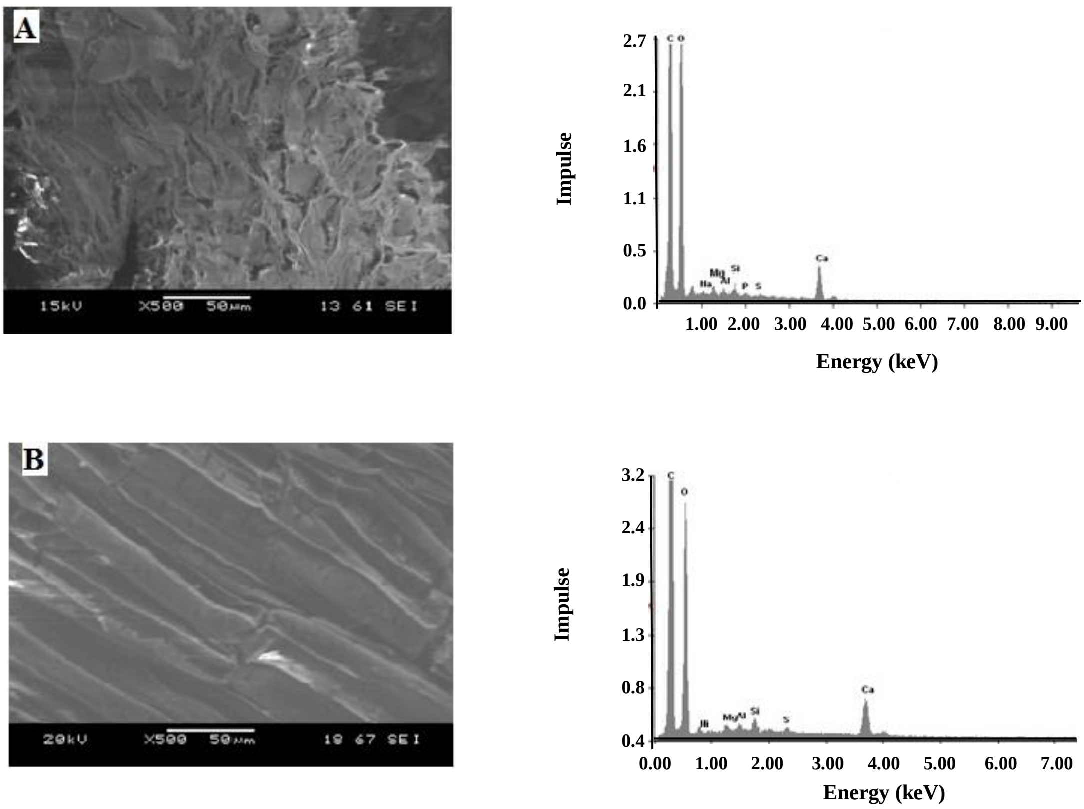

Fig. 3: (A) SEM image and EDX of the scolymus hispanicus adsorbent before adsorption. (B) After adsorption.

Fourier Transform InfraRed (FT-IR) spectra analysis

The FT-IR of *Scolymus hispanicus* in the range of 400-4000cm^{-1} is obtained to evaluate qualitatively the chemical structures of *scolymus hispanicus* before and after BB41 adsorption. Fig.4 shows the FT-IR spectrum of *Scolymus hispanicus*, which indicated various surface functional groups. The FT-IR spectrum of *scolymus hispanicus* presented in Fig. 4 shown broad and superposed bands around 3500 - 3200 cm^{-1} may be due to the overlapping of O-H and N-H stretching vibration. The spectra display absorption peaks at 2921.45 - 2923.50 cm^{-1} and 2851.99 – 2862.78 cm^{-1} are corresponding to C-H stretching vibration for CH_2 and CH_3 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} assigned to C-N for aromatic amine group the sorbent 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. Thus, these functional groups presented on the surface of *scolymus hispanicus* can be considered as the adsorption sites for BB41. In Fig.4, the spectra in their whole are similar, however, with a change in intensity. This is an indication that OH, C-H, C=C and C=O, carbonyl group could be involved in the adsorption of BB41 onto *scolymus hispanicus*

Equilibrium study

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 Fig. 5. Experiments were undertaken to study the effect of contact time at 22 °C on basic blue 41 removal by *scolymus hispanicus*. The rapid dye uptake for the first 20 min is due to the occurrence of molecule transfer ascribed to BB41–biosorbent interactions. The enhanced adsorption may also be due to the fact that initially, the sites on the *scolymus hispanicus* surface are vacant and the solute concentration gradient is high. The extent of BB41 uptake decreases over the contact time, because of the gradual decrease in the number of the surface sites. Besides, after lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid surface and the bulk phase. It was observed from Fig. 5 that the amount of dye adsorbed per unit mass of the adsorbent increased with increased initial dye concentration from 0.98 mg/g for 5 mg/L to 5.4 mg/g for 25 mg/L, revealing that the adsorption is highly dependent on initial concentration of dye.

Effect of the dose adsorbent

The adsorbent concentration is another factor that influences the adsorption kinetics. In order to determine the necessary biosorbent quantity for a maximal removal of BB41, the effect of the *scolymus hispanicus* dose on the adsorption equilibrium is illustrated in Fig. 6 which shows the uptake of BB41 for five doses over the range (0.5–6 g/ L). For a given dye concentration (5mg/L), 4 g/L of the adsorbent was observed to be the upper limit for the removal of BB41 (Fig. 6). This is probably because of the resistance to mass transfer of the dye from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading. Moreover, the percentage removal was decreased with the higher dosage (>4 g/L) and increased from 63.68 to 83.14 % when the adsorbent dosage increased from 0.5 to 4 g/L It might have happened that the higher dose causes particle aggregates and interference or repulsive forces between binding sites, and therefore decreases the interaction of the dye with the adsorbent and reduces the total surface area of the adsorbent; the optimal dose is used for further experiments. Similar behaviour for the effect of biosorbent dosage on the dye biosorption capacity was observed and discussed in the literature for different types of biosorbents [6,7].

Effect of solution pH

The adsorption is strongly dependent on pH through the functional groups of the sorbent. The pH of the dye

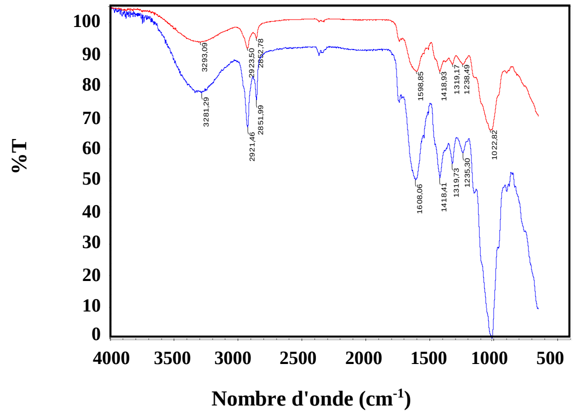

Fig. 4: FT-IR spectra of Scolymus hispanicus before and after adsorption.

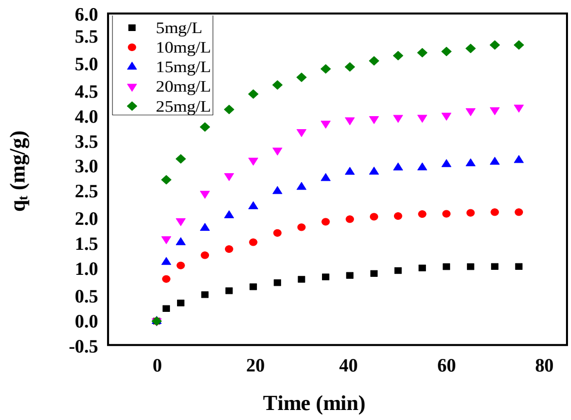

Fig. 5: Effect of contact time and initial dye concentration on sorption kinetic (22°C, pH 7.0, C_s=4 g/L).

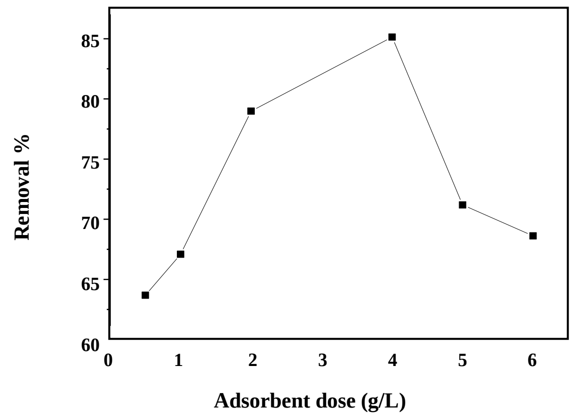

Fig. 6: Effect of dose adsorbent for the removal of basic blue 41.

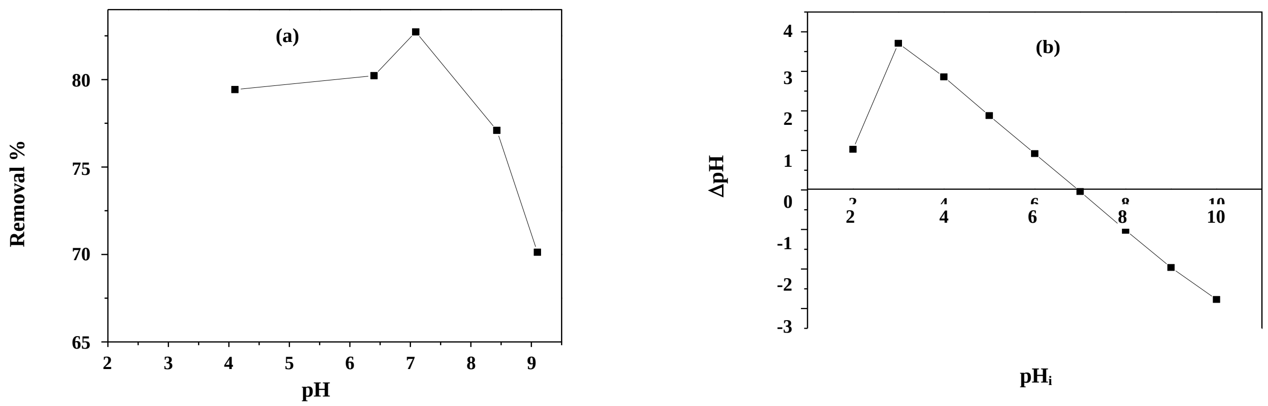

Fig. 7: ***(a) Effect of pH solution on adsorption of BB41 on Scolymus hispanicus (b) point of zero charges. of Scolymus hispanicus.***

solution plays an important role in the whole adsorption process and particularly in the adsorption capacity, influencing the surface charge of the sorbent, the degree of ionization of the dye present in the solution and the dissociation of functional groups on the active sites of sorbent, and the solution dye chemistries. The *scolymus* contains a high amount of polyphénols, polysaccharides, flavonoïdes and tanins and some of them are associated with proteins and other components [22]. These biomacromolecules on the *scolymus* surface have several functional groups such as amino, carboxyl, thiol, and sulfydryl groups [22] and the adsorption phenomena depends on the protonation or unprotonation of these functional groups on the surface of the biosorbent. Fig. 7 (a) indicates the removal of dye by *scolymus hispanicus* at various initial pH values ranging from 4 to 9 at 5 mg/L of dye solution. The results of percentage Basic Blue 41 removal versus equilibrium pH increased with increasing pH up to 7.09. This influence is due to the adsorbent surface charge which is positive for $pH < pH_{ZPC}$ (Electrostatic attraction adsorbate / adsorbent), and negative for $pH > pH_{ZPC}$ The isoelectric point of scolymus hispanicus was found to be at pH of 6.56 (Fig.7.b). The maximum BB41 removal (82.72 %) is obtained at pH 7.09 and decreases for higher pHs due to the ionic form of the BB41 (aromatic structure, polar groups) in solution and the electrical charge of *scolymus hispanicus.* The BB41 molecule has multiple functional groups and can be both protonated and deprotonated at a given pH. The protonated groups present on the surface of the adsorbent are mainly phenolic, carboxylic, and chromatic groups, whereas the deprotonated groups of the dye are probably sulphonated groups ($-SO_3^-$). Thus, BB41 anions move to positive charges on the surface of the adsorbent through electrostatic interactions. The weak removal at high pH may be due to the BB41 complexation or aggregation. The increase of aggregation of BB41 dye may form a bigger molecular form and become unable to enter into the adsorbent pore. So, the pH appears to be a key factor affecting the BB41 adsorption. The optimal pH leads to a high surface potential, allowing better adsorption.

Adsorption isotherm

In order to optimize the design of a sorption system to remove the dye from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curves Adsorption isotherm models are used to determine the adsorption mechanism and describe how BB41 molecules interact with the *S. hispanicus*. The isotherm data are analyzed using the Freundlich, Temkin, and Dubinin-Radushkevich. The Langmuir isotherm did not give good results, data is not shown.

Freundlich isotherm

The empirical Freundlich model [23] is especially applied for multilayer adsorption with possible adsorbed/molecules interactions and is expressed by:

$$q_e = k_F . C_e^{1/n} \quad (3)$$

The Freundlich constants k_f and n, related to sorption capacity ($mg\ g^{-1}$) and the heterogeneity factor respectively are deduced from the plot log q_e plotted versus log C_e (Fig.8 a):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{4}$$

The high correlation coefficient (r^2 = 0.998) value indicate that the high affinity between Scolymus. hispanicus surface and BB41 plays the major role in the adsorption mechanism in Freundlich model. That implies that heterogeneous surface conditions exist under the used experimental conditions [24]. Also, the adsorption is multilayer and there are interactions between adsorbed molecules of BB41. K_F and 1/n, the mono-component Freundlich constants are indicators of adsorption capacity and adsorption intensity, respectively. The slope 1/n, ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity [25]. According to *Treybal* [26] it has been shown using mathematical calculations that n values between 1 and 10 represent beneficial adsorption. The value of 1/ n obtained for the removal of BB41 is found less than one (0.94) this value indicates that the BB41 is favourably adsorbed on scolymus hispanicus. Otherwise, a value of (1/n) < 1 represents a convex, L type, isotherm, where the sorption energy decreases with increasing surface concentration for the sorption of BB41. Also, K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto scolymus hispanicus for a unit equilibrium concentration, the K_F magnitude of 1.069 indicated high adsorption capacity and easy uptake of dye molecules from aqueous solutions by scolymus. hispanicus.

Temkin isotherm

The Temkin isotherm model [27] assumes that (i) heat of adsorption of all the molecules in the adsorbed layer decreases linearly with coverage due to adsorbate– adsorbent interaction and (ii) adsorption is characterized by a uniform distribution of binding energies up to a maximum binding energy. Temkin isotherm is expressed as follows:

$$q_e = \left(\frac{RT}{b}\right) \ln(k_T C_e) \tag{5}$$

The linearized form is:

$$q_e = B \ln k_T + B \ln C_e \tag{6}$$

Where B = RT/b, T is the absolute temperature. The fitted Temkin constants, *b* (kJ/mol) and k_T (L/g), denote heat of adsorption and maximum binding energy, respectively, the value of the adsorption energy, *b* is obtained as 0.861 kJ/mol (Fig. 8b), which is positive indicating a physiosorption process. The coefficient

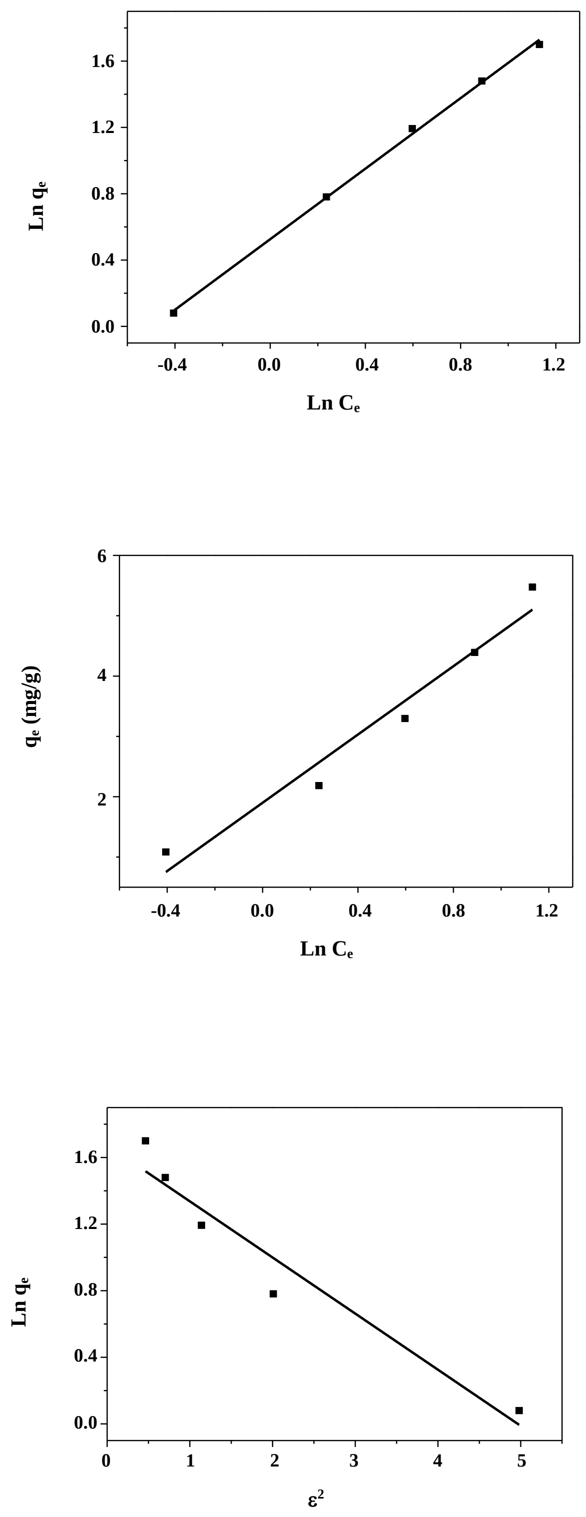

Fig. 8: Adsorption isotherm models of basic blue 41on scolymus hispanicus a)Freundlich isotherm b)Temkin isotherm c) D-R isotherm.

Table 2: Isotherm Parameters for the adsorption of basic blue 41 dye on scolymus hispanicus.

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	94/0	1.0691	0.946	861.5	1.957	0.92	5.332	0.337	1.218

of determination (r^2=0.946) (Table 2) reflects a poor fit to the experimental equilibrium data compared to the Freundlich model.

Dubinin-Radushkevich (D-R) isotherm

The Dubinin-Radushkevich (D-R) [28] model is generally used to explain the adsorption mechanism and focus on the heterogeneity of the surface. The adsorption equilibrium relation for a given adsorbate-adsorbent combination can be expressed independently of temperature by using the adsorption potential (ε) (Eq. (7))

$$\varepsilon = RT\ln(1 + \frac{1}{C_e}) \tag{7}$$

The D-R isotherm assumes a Gaussian-type distribution for the characteristic curve and the model can be described by Equation (8):

$$\ln q_e = \ln(q_{DR}) - \beta\varepsilon^2 \tag{8}$$

Where q_{DR} is the D-R constant (mol /g) and β gives the mean sorption free energy E (kJ/mol) per molecule of sorbate at the moment of its transfer to the solid surface from the bulk solution and can be computed using Eq. (9):

$$E = \frac{1}{\sqrt{2\beta}} \tag{9}$$

Values of q_{DR} and β can be determined through linearization of the D-R isotherm. Plotting ln qe versus ε^2, using Eq. (7) (Fig. 8c), results in a straight line of slope B and intercept q_{DR}

The (D-R) model can also be applied to give more explanations about the adsorption nature (chemical ion-exchange or physical sorption) through the apparent energy E, given in Eq. (9).

For E values between (8-16 kJ/mol), the sorption occurs by chemical ion-exchange, while the apparent energy values (< 8 kJ/mol), the adsorption is of physical nature. It is expected that large organic molecules would be adsorbed by physical interactions and small inorganic ions could be complexed with nitrogen or oxygen atoms of amines, amides, phenols, alcohols, and so on, being an interaction with adsorbent, which is a chemical adsorption process [29].

The estimate values of energy E is obtained as 0.882 kJ/mol, which confirms that the adsorption of basic blue 41 on *scolymus hispanicus* is a physical in nature [30].

Table 2 assembles the parameters of all isotherm models calculated for the equilibrium data of BB41 adsorption onto *S. hispanicus* and their regression coefficient r^2 and indicates that the adsorption process adequately follows the Freundlich isotherm models.

The classification of the models according to the simulation of the adsorption isotherms is: Freundlich (r^2=986) > Temkin (r^2=.946) > Dubinin-Radushkevich (r^2=920)

Adsorption Kinetic

In order to investigate the adsorption processes of BB41 on the *scolymus hispanicus*, pseudo-first-order and pseudo- kinetic models were used.

Pseudo-first-order model

The *pseudo-first-order* equation is given as [31]:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 \times t}{2.303} \tag{10}$$

Where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min).

The values of adsorption rate constant (k_1) for BB41 adsorption on *scolymus hispanicus* were determined from the plot of log (q_e q_t) against t (Fig.9 a).

Pseudo-second-order model

The *pseudo-second-order model* is represented as [32, 33]:

$$t/q_t = 1/((K_2 * q_e^2)) + t/q_e \tag{11}$$

Table 3: Kinetic parameters for the adsorption of BB41 onto Scolymus hispanicus adsorbent.

	Pseudo premier order			Pseudo second order			
Concentration (mg/L)	K_1 (min^{-1})	q_e(mg/g)	r^2	K_2 (g/mg.min)	q_e (mg/g)	$h=K_2q_e$	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
25	0,1303	0,6256	0,976	0.053	5.714	0.302842	0.999

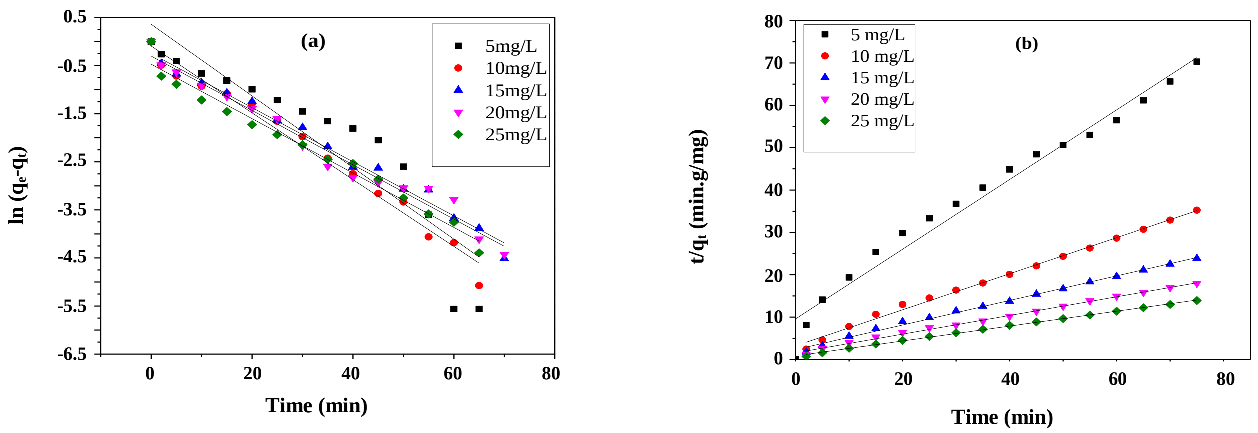

Fig. 9: Kinetic model for the BB41 adsorption on the Scolymus hispanicus a) pseudo first order b) pseudo second order..

where K_2 is the pseudo-second-order rate constant (g/mg min).

The initial sorption rate, h (mg/g min), at t=0 is defined as:

$$h = K_2 qe \quad (12)$$

The q_e is obtained from the slope of the t/qt versus t (Fig. 10 b) and h is obtained from the intercept. Since q_e is known from the slope, the k_2 can be determined from the value of h. The best-fit values of h, q_e and K_2 along with correlation coefficients for the pseudo-first-order and pseudo-second-order models are shown in Table 3. According to r^2 values (Table 3), the BB41 adsorption is well described by the pseudo second order kinetic model. , it was found that the variations of the rate constant, K_2, seem to have a decreasing trend with increasing initial dye concentration. Similar results were obtained par several authors [33-35].

Thermodynamic parameters

Thermodynamic parameters such as enthalpy$\Delta H°$, entropy $\Delta S°$ and free energy of Gibbs $\Delta G°$ were determined using the following equations:

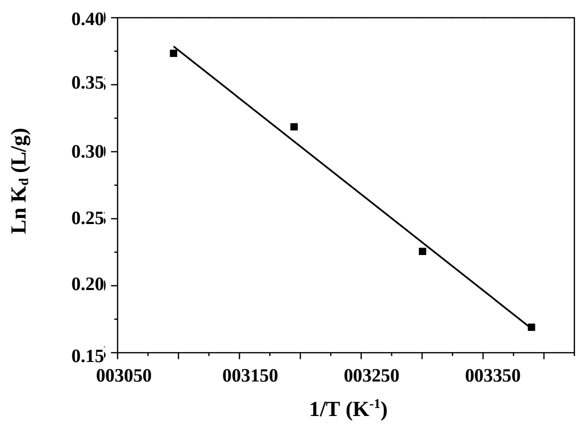

Fig. 10: The plot of for ln K_D vs. 1/T for Basic Blue 41 adsorption onto scolymus hispanicus.

$$K_d = \frac{q_e}{C_e} \quad (13)$$

$$\Delta H° = -RT \times LnK_d \quad (14)$$

$$\Delta G° = \Delta H° - T\Delta S \quad (15)$$

Table 4: Thermodynamics parameters for the adsorption of the BB41dye onto Scolymus haspanicus.

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

$$LnK_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (16)$$

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 slop and intercept of the plot $\ln K_d$ versus 1/T respectively (Fig. 10). The ΔH^o and ΔS° values are positive. The positive value of ΔH indicates the presence of endothermic process [36]. Generally, the magnitude of the ΔH^0 value lies in the range of 2.1-20.9 kJ/mol for physical and 80-200 kJ/ mol for chemical adsorption [37]. The ΔH^o value of 5.96 kJ/·mol is an indication that the nature of the dye adsorption is predominant physical, involving weak interaction forces. The positive value of entropy change ΔS° (0.094 kJ/ mol) reflects good affinity of dye ions towards the sorbent and the increasing randomness at the solid-solution interface during the adsorption process. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions. Moreover, a positive ΔS value corresponds to an increase in the degree of freedom of the adsorbed species [38]. In Table 4, it can be noticed that the Gibbs free energy has negative values. The negative values of ΔG° (Eq. (15)) reflect that the adsorption of BB41 in *scolymus hispanicus* is feasible and spontaneous. The variation of free energy for physical adsorption is generally between -20 and 0 kJ/mol, the physical adsorption together with chemical adsorption is at the range of ─20 to ─80 kJ/mol and chemical adsorption is at a range of ─80 to ─ 400 kJ/mol [39]. In our case, ΔG° (Table 4) is characteristic of a physical adsorption, ΔG° decreases from -0.415 to -1.02 kJ /mol when the temperature increases from 22 to 50 °C (Table 4), interaction BB41- *scolymus hispanicus* is mainly electrostatic (Coulombic interactions). The ΔG° values which were found to be in between -20 kJ/ mol and 0 kJ/ mol fall in the physisorption range [40].

CONCLUSIONS

Based on the experimental results, the following conclusions can be made: *Scolymus hispanicus* has shown excellent adsorption potential. Therefore, it can serve as an attractive low-cost alternate for costly activated carbon. The *Scolymus hispanicus* functional groups and surface texture were characterised using FTIR, SEM-EDX and *pHzpc* method. The optimum adsorption was found at around pH 7; contact time 75 min; adsorbent dose 4 g/L. The maximum percentage dye removal value was 81, 92 % with an initial dye concentration of 5 mg/L. The Adsorption of BB41 on *Scolymus hispanicus* increases until pH 7.09 and then decreases at higher pHs. The adsorption is strongly dependent on pH through the functional groups of the sorbent. The Freundlich isotherm model was found to be one of the best fitting isotherm models, suggesting the multilayer coverage of BB41 by *scolymus hispanicus*. Batch studies show that a simple model of pseudo-second-order kinetic equation can adequately predict the adsorption of BB41 on *Scolymus hispanicus*. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) showed that the adsorption process of BB41 was endothermic and spontaneous. The small values of the heat of adsorption confirms well that the adsorption of basic blue 41 on *scolymus hispanicus* is a physical in nature [22].

Nomenclature

BB41	Basic Blue 41
SC	Scolymus hispanicus
SEM	Scanning Electronic Microscopy
FTIR	Fourier Transformation Red Infra

EDX	Energy Dispersion rayon X
R%	Removal percentage, %
V	Volume of the solution, L
m	Mass of the adsorbent, g
C_i	Initial concentration, mg/L
C_e	Equilibrium concentration, mg/L
q_e	Equilibrium adsorption capacity, mg/g
K_F	Freundlich constant
n	Heterogeneity factor
b_T	Constant related to the adsorption heat, J/mol
A_T	Isotherm constant, L/mg
β	Coefficient related to the mean free The energy of adsorption, mol^2/J^2
ε	Polarity potential (J/mol)
r^2	Correlation coefficient
K_1	Constant of pseudo-first-order (min^{-1})
K_2	Constant of pseudo-second-order (mg/g.min)
ΔG°	Gibbs energy (kJ/mol)
ΔH°	Enthalpy (kJ/mol)
ΔS°	Entropy (kJ/mol)
R	Gas constant (8.314 J.mol/K)
T	Temperature (K)

Acknowledgments

The authors would like to thank the University of Science and Technology Haouari Boumadiene (Algeria).

Received : Sep. 23, 2019 ; Accepted : Dec. 23, 2019

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