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Enhanced removal of Bismark Brown (BB) dye from aqueous solutions using activated carbon from raw Ziziphusspina-christi (ZSAC) Equilibrium, thermodynamic and kinetics

A. Koohmareh[1] and G. H. Vatan khah[1*]

[1] Department of Chemical Engineering, Islamic Azad University, Bushehr Branch, Bushehr, Iran

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ABSTRACT

In this study, carbon was easily made from walnut wood as a low-cost and non-toxic natural adsorbent. Ziziphusspina-christi (ZSAC), an excellent adsorbent, were successfully synthesized by an in chemical vapor deposition method and used for the removal of Bismark Brown(BB) dye from aqueous solution. The as-synthesized Ziziphusspina-christi (ZSAC) were characterized by FT-IR technique. Various operational parameters such as pH, initial dye concentration and contact time in batch systems were investigated on the use of Ziziphusspina-christi (ZSAC). Equilibrium data obtained have been fitted to the Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich adsorption isotherms. Langmuir isotherm best fits the experimental results. Kinetic modeling of pseudo -first order and pseudo-second order showed that the pseudo-second order equation was the most appropriate for the description of Bismark Brown(BB) dye adsorption by (ZSAC). The maximum sorption capacity q_{max} in Langmuir isotherm of (BB) 35.88 mg/g showed onto (ZSAC), The overall adsorption process was exothermic and spontaneous in nature. The thermodynamic functions (ΔSº, ΔHº, ΔGº) of the studied reaction are calculated using activated complex theory and show that adsorption (BB) dye onto (ZSAC) process requires heat. The results indicated that Bismark Brown (BB) adsorption onto Ziziphusspina-christi (ZSAC)might be a physical adsorption.

Keywords: Bismark Brown (BB); Isotherm; Kinetic; thermodynamic; Ziziphusspina-christi (ZSAC).

1. INTRODUCTION

Dyes have long been used in different types of industries such as, dyeing, textiles, paper, plastics, leather and cosmetics [1]. Color stuff discharged from these industries pose hazards and has an environmental impact[2].The presences of dyes in water are causing problems, such as, reducing oxygen levels in water; interfering with penetration of sunlight into waters; retarding photosynthesis and interfering with gas solubility in water bodies[3]. Azo dyes are divided according to the presence of azo bonds (–N=N–) in the molecule; these include mono azo, diazo, triazoetc [4]. Azo dyes resist the effect of oxidation agents and light, thus they cannot be completely treated by conventional methods of anaerobic digestion [5]. It is necessary to find an effective method for the treatment of Bismarck Brown. The degradation of Bismarck brown dye in the presence of aqueous zinc oxide suspension has been reported before [6]. The adsorption

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[*] Corresponding author: Gh.vatankhah@gmail.com

technique proved to be an effective and attractive process for removing dyes from aqueous solutions in term of initial cost, ease of operation, insensitivity to toxic substance, high efficiency, easy recovery and simplicity of design [7,8]. Conventional wastewater treatment protocol based on physicochemical, chemical, and biological processes includes coagulation and flocculation [9], adsorption [10], ozonation [11], electrochemical techniques [12], biosorption [13,14], and fungal decolonization [15]. Among them, adsorption is widely used for large scale biochemical, chemical, environmental recovery, and purification applications [16]. This technique benefits from simple design and ease of operation by efficient non-toxic and low-cost adsorbents. Characteristics and appropriate selection of the adsorbent are based on factors such as removal capacity, treatment cost, and operating conditions [17]. Chemical treatment and biodegradation procedure are based on expensive and complex processes that generate toxic by products. have been used for activated carbon production. Ziziphusspina-christi (ZSAC) is a plant that grows into a tree with thorny branches and is used as a hedge to form defensive fences for cattle. The fruit has a sweet edible pulp, the leaves are applied locally to sores, and the roots are used to cure and prevent skin diseases [18-20]. such as: Iran. Jujube fruits are consumed fresh or processed into beverage and food. The literature does not show research about preparation of activated carbon from Ziziphusspina-christi (ZSAC). On the other hand, Bismark Brown (BB), with complicated chemical structure, has high resistance to light and oxidizing agents. In addition, its removal based on biological treatment and chemical precipitation is not environmental friendly and has low efficiency [21]. Therefore, we were motivated to prepare walnut carbon as an alternative to expensive or toxic adsorbents for the removal of Bismark Brown (BB) from wastewater. FTIR, The experimental conditions, such as pH of solution, contact time, initial dye concentration, and adsorbent dosage as well as the dye removal percentage as response, were studied and optimized. Various isotherm models, such as Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich were used to fit the experimental equilibrium data. The results showed the suitability and applicability of the Langmuir model. Kinetic models, such as pseudo-first-order, pseudo-second-order diffusion models indicated that the pseudo-second-order model controls the kinetic of adsorption process. It was shown that the Ziziphusspina-christi (ZSAC) can be effectively used to remove the cationic dye of Bismark Brown (BB) from wastewater.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The chemical compounds and reagents used in this work were of analytical grade and purchased from Merck (Darmstadt, Germany). Bismarck Brown R, having molecular formula $C_{21}H_{24}N_8.2HCl$ was chosen as the adsorbate. Bismarck Brown R was purchased from Sigma Aldrich with water solubility as 11 g L^{-1} ($25^{\circ C}$) and molecular weight as 461.39 g mol^{-1}. The dye stock solution was prepared by dissolving Bismarck Brown R in distilled water to the concentration of 0.01M. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations. The IUPAC name of the Bismarck Brown is 4-[5-(2, 4-Diamino-5-methylphenyl) diazenyl-2-methylphenyl] diazenyl-6-methylbenzol-1, 3-diamin. The structure of Bismarck Brown is shown in fig. 1. The standard and experimental solutions were obtained by diluting the stock solutions with deionized water.

Deionized water (DI-water) obtained was used throughout this study.

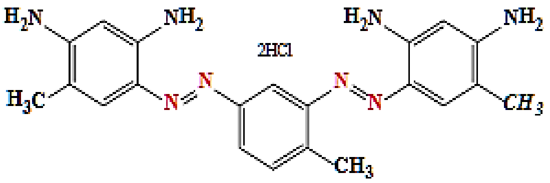

Fig. 1. Chemical structure of Bismarck Brown.

2.2. Preparation of ZSAC

Z.spina seeds were dried at 100 ^{0}C for 20 h, ground and granulometrically separated. The material, which had particle size between 0.9 and 1.5 mm, was placed in a vertical stainless steel reactor and heated in a furnace at a rate of 15^{0}C/min from room temperature to 500 ^{0}C and maintained at this temperature for 2 h. The obtained char was mixed with water and KOH with the weight ratio of water/KOH/char equal to 4/5/1, with constant mechanical stirring for 6 h and a temperature of 85^{0}C. The impregnated char was dried overnight at 100^{0}C. The reactor containing the dry mixture was set into a furnace under N_2 flow of 100 cm^3/min, and heated at a rate of 10^{0}C/min to the final temperature of 700 ^{0}C, which was maintained for 2 h. All the activated samples were washed with water, poured into 0.1 mol/L HCl and stirred for 1 h to eliminate the residual alkali [22]. Then, the samples were washed with hot distilled water until the pH of the filtrating solution was neutral [23]. The produced activated carbon was then dried at 100^{0}C overnight, ground and sifted to obtain a powder with a particle size smaller than 50µm; it was finally kept in a hermetic bottle for subsequent uses.

2.3. Batch adsorption experiments

Batch adsorption experiments were carried out to determine the Bismark Brown (BB) adsorption isotherm onto Ziziphusspina-christi (ZSAC) composite and its thermodynamic properties: 500 mL solution having 100 mg/L concentration of BB was prepared and Initial pH of the solution was adjusted with the help of 0.01N HCl / 0.01N NaOH aqueous solution without any further adjustments during the experiments. 10 samples of 50 mL solution were taken in ten 250 mL flasks containing fixed adsorbent dose of 25 mg/L. These flasks were agitated at a constant rate of 200 rpm in a temperature controlled orbital shaker maintained at 25^{oC} temperatures. One of the sample flasks was withdrawn from orbital shaker after fixed time intervals (10, 20, 30, 40, 50, 60, 70 min) and analyzed for remaining metal ions present in the adsorbate solution. Ziziphusspina-christi (ZSAC) was separated from aqueous solution by filtration through Whatman No. 42 filter paper. The BB concentration in the solution was measured using a double beam UV–vis spectrophotometer (jasco, Model UV–vis V-530, Japan) at 664 nm. The amount of adsorbed BB at equilibrium (qe(mg/g)) was calculated using equation:

$$\%A=\frac{C_0-C_e}{C_0}\times\ 100 \qquad (1)$$

Where C_0 and C_e are the initial and final concentration of Bismark Brown (BB) in solution(mg/L), respectively. The amount (mg/g) of (BB) adsorbed at equilibrium was calculated by using the following equation:

$$q_t=\frac{(C_0-C_t)V}{W} \qquad (2)$$

where, C_o and C_t are initial ion concentration and concentration of ion at any time‘t’, while V is volume of solution in litters and W is adsorbent dosage in g/L.

3. RESULTS AND DISCUSSION

3.1. Characterization FTIR of WC

The surface functional groups and

structure were studied by FTIR spectroscopy. Fourier transform infrared (FTIR) spectra were recorded by a FTIR spectrophotometer (Bruker Optics) over the wave number range from 4000 to 500 cm^{-1}.

In this work, infrared spectroscopy was used to obtain information about the chemical structure and functional groups of the raw material and the prepared activated carbon [24,25]. The FTIR spectrum of the ZSAC is shown in Fig. 2.

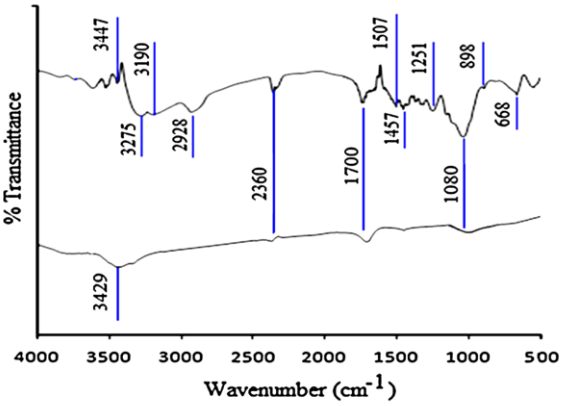

Fig. 2. FTIR spectrum of (a) ZiziphusSpina-christi and (b) ZSAC.

FTIR spectroscopic analysis:

In this work, infrared spectroscopy was used to obtain information about the chemical structure and functional groups of the raw material and the prepared activated carbon. The FTIR spectrum of the ZSAC is shown in Fig. 2. This spectrum is quite similar to that of other lignocellulosic materials such as pistachio-nut shell and rockrose [24,25]. The band located at 3447cm^{-1} corresponds to the intra-molecular H-bonded (–OH)[26]. The band observed around 2928 cm^{-1} is attributed to C–H stretching vibration of $^{-}CH_2$. The band at 1734 cm^{-1} is ascribed to carbonyl C,O groups. The skeletal C,C vibrations in aromatic rings cause two bands at 1507 and 1457 cm^{-1}. The band at 1251 cm^{-1} may be attributed to esters (R–CO–O–R$'$), ethers (R–O–R$'$) or phenol groups. The relatively intense band at 1036 cm^{-1} can be assigned to alcohol groups (R–OH) [25]. The C–H out-of-plane bending in benzene derivative vibrations causes the band at 898 cm^{-1} [26]. The FT-IR spectra of the activated carbon prepared at 700 ^{0}C was shown in Fig. 1b. The bands at 3429 and 1080 cm^{-1} were assigned to O–H bonds and C–OH stretching of phenolic groups, respectively [27]. the bands observed in the region between 1700 cm^{-1} and 1490 cm^{-1} were attributed to C,C symmetrical stretching of pyrone groups and C,O of carboxylic groups. Moreover [28]. noted that the alkaline treatment increased the amount of oxygen functional groups, especially, phenolic groups. In addition, carbon skeleton vibrations, which are characteristic in activated carbon, were observed.

3.2. Effect of pH on metal ion biosorption

The pH has been identified as one of the most important parameter that is effective on BB sorption. The effect of pH on the biosorption of BB onto (ZSAC) was studied at pH 2.0–8.0, Fig.3. The maximum biosorption was observed at pH 5.0 for BB. Therefore, the remaining all biosorption experiments were carried out at this pH value. The biosorption mechanisms on the Ziziphusspina-christi (ZSAC) surface reflect the nature of the physic chemical interaction of the solution[29]. At highly acidic pH, the overall surface charge on the active sites became. positive and BB and protons compete for binding sites on Ziziphusspina-christi (ZSAC), which results in lower uptake of BB. The biosorbent surface was more negatively charged as the pH solution increased from 5.0. The functional groups of the Ziziphusspina-christi (ZSAC) was more deprotonated and thus available for the BB. Decrease in biosorption yield at higher pH=5 is not only related to the formation of soluble hydroxylated complexes of the BB, but also to the ionized nature of the (ZSAC) of the biosorbent under the studied pH. Previous studies also reported that the maximum biosorption efficiency of BB on biomass was observed at pH 5.0.

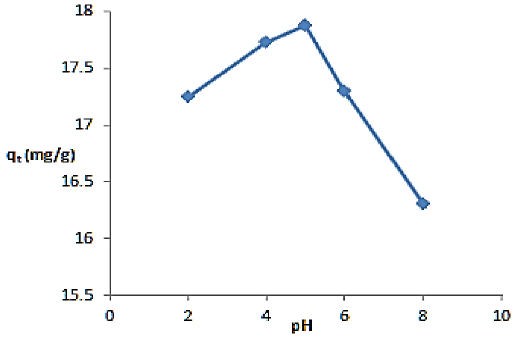

Fig. 3. Effect of initial solution pH on the adsorption amount of BB onto Ziziphusspina-christi (ZSAC).

3.3. Effect of biosorbent dose

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for BB as a function of biosorbent dosage was investigated. The percentage of the metal biosorption steeply increases with the biosorbent loading up to 25mg Fig. 4. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction, whereas the number of sites available for biosorption site increases by increasing the biosorbent dose [30]. The maximum biosorption was attained at biosorbent dosage, 25mg. Therefore, the optimum biosorbent dosage was taken as 25mg for further experiments. This can be explained by when the biosorbent ratio is small, the active sites for binding metal ions on the surface of Ziziphusspina-christi (ZSAC) is less, so the biosorption efficiency is low. As the biosorbent dose increased, more active sites to bind BB, thus it results an increase in the biosorption efficiency until saturation.

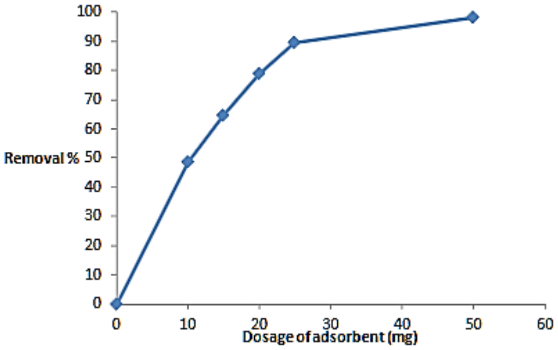

Fig. 4. Effect of Ziziphusspina-christi (ZSAC) dose on the adsorption percentage of BB.

3.4. Effect of contact time

The effect of contact time on the adsorption capacity of BB onto (ZSAC) is shown in fig.5, When the initial BB concentration is increased from 5 to 100 mg/L the amount of BB adsorbed onto (ZSAC), 10 at 70 min contact time, pH value 5, 25mg adsorbent dose and the constant temperature 298.15 K, increased 35.88 mg g^{-1}. The increase of loading capacity of (ZSAC) with increasing initial BB concentration may be due to higher interaction between BB dye and adsorbent [31,32]. These results show that rapid increase in adsorbed amount of BB is achieved during the first 20 minutes. Similar results were reported before for removal of hazardous contaminants from wastewater.

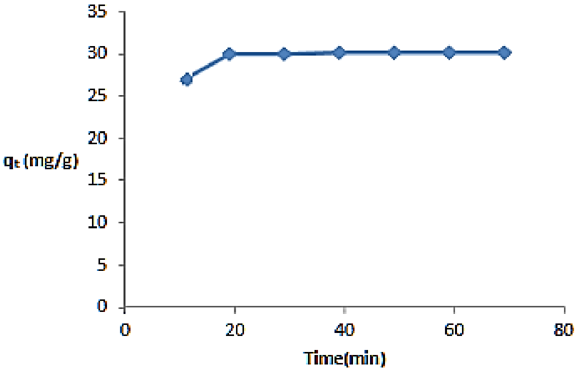

Fig. 5. Effect of contact time on the adsorption of BB dye by Ziziphusspina-christi (ZSAC).

3.5. Effect of temperature

To study the effects of temperature on the adsorption of dye by Ziziphusspina-christi (ZSAC), the experiments were performed at temperatures from 278.15 to 298.15 K. Fig.6. shows the influence of temperature on the adsorption of dye on Ziziphusspina-christi (ZSAC). As it was observed, the equilibrium adsorption capacity of BB onto (ZSAC) was found to increase with increasing temperature. This fact indicates that the mobility of dye molecules increased with the temperature, additionally the viscosity of dye solution reduces with rise in temperature and as a result, it increases the rate of diffusion of dye molecules. The results were in agreement with the effect of the solution pH, and temperature on adsorption behavior of reactive dyes on activated carbon [33].

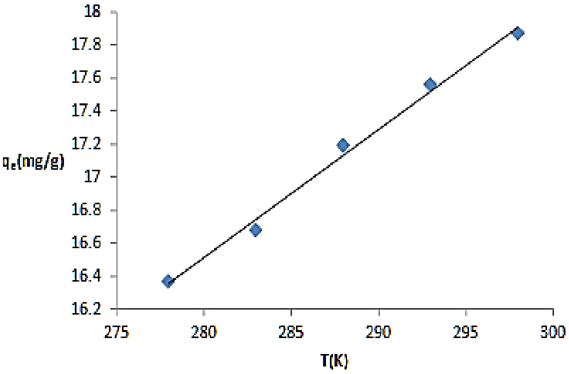

Fig. 6. Effect of temperature on the adsorption amount of BB on Ziziphusspina-christi (ZSAC).

3.5. Biosorption isotherms

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Bismark Brown (BB) onto Ziziphusspina-christi (ZSAC) was modeled using four adsorption isotherms: Langmuir, Freundlich, Temkin, and Dubinin - Radushkevich isotherms.

3.5.1. Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites [34]. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [35]:

$$\frac{C_e}{q_e} = \frac{1}{K_{Lqmax}} + \frac{1}{qmax} C_e, \quad (3)$$

where K_L is the Langmuir constant related to the energy of adsorption and qmax is the maximum adsorption capacity (mg/g). Values of Langmuir parameters, qmax and K_L were calculated from the slope and intercept of the linear plot of Ce/qe versus Ce as shown in Fig. 7. Values of qmax, K_L and regression coefficient R^2 are listed in Table1. These values for Ziziphusspina-christi (ZSAC) biosorbent indicated that Langmuir model describes the biosorption phenomena as favorable. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L, expressed as in the following Eq. [36]:

$$R_L = \frac{1}{(1 + K_l C_o)}, \quad (4)$$

where K_L is the Langmuir constant and Co is the maximum initial concentration of BB dye. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) or unfavorable (R_L<1). The R_L for BB biosorption by (ZSAC) was found to be 0.31–0.86 for concentration of 5–100 mg/L of BB. They are in the range of 0 - 1 which indicates the favorable biosorption.

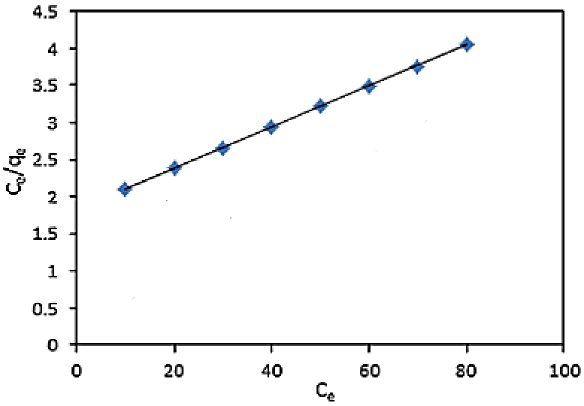

Fig. 7. Langmuir isotherm for BB onto Ziziphusspina-christi (ZSAC).

3.5.2. Freundlich isotherm

Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [37]:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e, \qquad (5)$$

Where K_F is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption[38].

Freundlich equilibrium constants were determined from the plot of lnqe versus lnCe, Fig.8. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if n = 1, then adsorption is linear; if n>1, then adsorption is a chemical process; if n<1, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.48 for BB, respectively, Table 1. Since n lie between 1 and 10, this indicates the physical biosorption of BB onto Ziziphusspina-christi (ZSAC). The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm model.

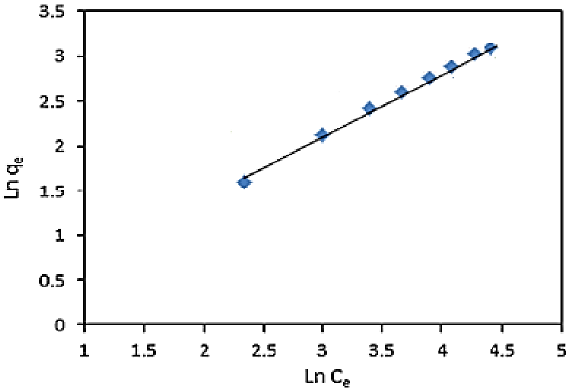

Fig. 8. Freundlich isotherm for BB onto Ziziphusspina-christi (ZSAC).

3.5.3. Temkin isotherm

Temkin isotherm equation [39] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy [40]. The Temkin isotherm has been used in the linear form as follows:

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e, \qquad (6)$$

A plot of qe versus lnCe enables the determination of the isotherm constants b_T and A_T from the slope and the ntercept, Fig.9. Where A_T(L/mg) is the equilibrium binding constant corresponding to the maxmium binding energy and constant b_T is related to the heat of biosorption, Table 1.

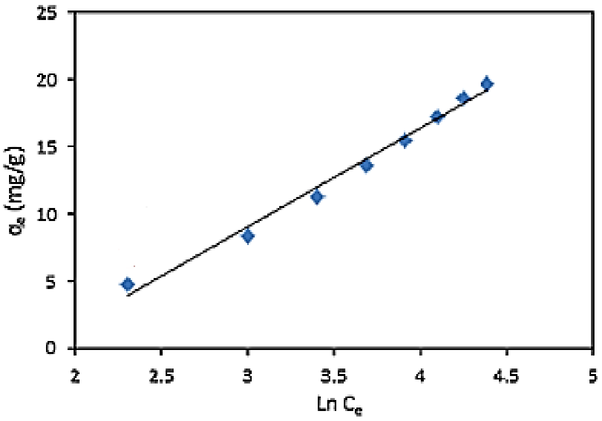

Fig. 9. Temkin isotherm for BB onto Ziziphusspina-christi (ZSAC).

Table. 1. Adsorption isotherms parameters and correlation coefficients

Isotherms	Bismark Brown (BB)		
Langmuir	q_{max}	K_L(L/mg)	R^2
	35.84	0.0149	0.9999
Freundich	K_F (mg/g)	n(g/L)	R^2
	1.06	1.48	0.9901
Tempkin	b_T(J/mol)	k_T(L/g)	R^2
	353.88	0.16	0.9881
Dubinin–Radushkevich (D–R)	q_{max}	β	R^2
	21.61	8.00	0.9096

3.5.4. Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich isotherm [41] describes the biosorption nature of the sorbate on the biosorbent and to calculate the mean free energy of biosorption.

$$\ln q_{\mathrm{e}} = \ln q_{\max} - \beta\varepsilon^2, \tag{7}$$

where e can be correlated

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right), \tag{8}$$

where R is the gas constant (8.314 J/mol K). T is the absolute temperature (K). The D–R isotherm constants b and qmax were obtained from the slope and intercept of the plot of ln qe against e^2, Fig.10. The calculated values are listed in Table1. The mean free energy of biosorption, E, defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution and calculated from the b value from:

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

If the magnitude of E is between 8 and 16 kJ/mol, then the sorption process is supposed to proceed via chemisorption reaction, while for values of E is\8 kJ/mol, the sorption process is of physical nature [42]. The value of E calculated from for the biosorption of BB by Ziziphusspina-christi (ZSAC) is 0.11 kJ/mol. This indicates that the biosorption process is of physical nature.

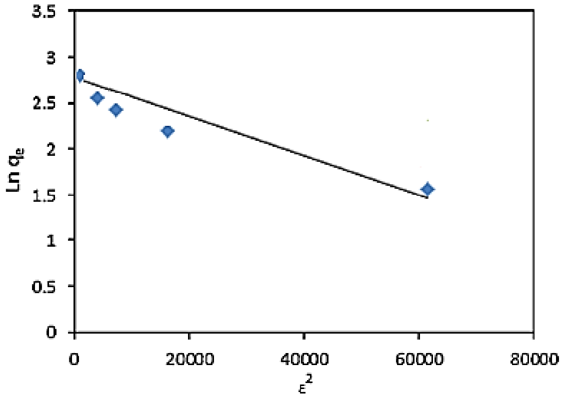

Fig. 10. Dubinin–Radushkevich (D–R) isotherm for BB onto Ziziphusspina-christi (ZSAC).

3.6. Biosorption kinetics

Parameters from two kinetic models, pseudo-first-order and pseudo-second-order, were fit to experimental data to examine the biosorption kinetics of BB uptake onto Ziziphusspina-christi (ZSAC).

3.6.1. Pseudo-first-order kinetics

The pseudo-first-order equation of Lagergren [43] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \qquad (10)$$

Where qe and qt are the sorption capacities at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions, qt=0 to qt=qt at t=0 to t=t, the integrated form of equation becomes [44]:

$$\ln(q_e - q_t) = \ln q_n - \frac{k_1}{2.303}t, \qquad (11)$$

The equation applicable to experimental results generally differs from a true first-order equation in two ways: the parameter k_1(qe-qt) does not represent the number of available sites; and the parameter ln qe is an adjustable parameter which is often not found equal to the intercept of a plot of ln (qe - qt) against t, whereas in a true first-order sorption reaction log qe should be equal to the intercept of ln(qe - qt) against t. To fit the equation to experimental data, the equilibrium sorption capacity, qe, must be known.

In many cases is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 10–80 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to t = ∞ on treating qe as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, to analyze the pseudo-first-order model kinetics.

The pseudo-first-order rate constant can be obtained from the slope of plot between log (qe-qt) against time (t), Fig. 11. The calculated values and their corresponding linear regression correlation coefficient values are listed in Table 2. R^2 Was found to be 0.926, which shows that this model cannot be applied to predict the adsorption kinetic model.

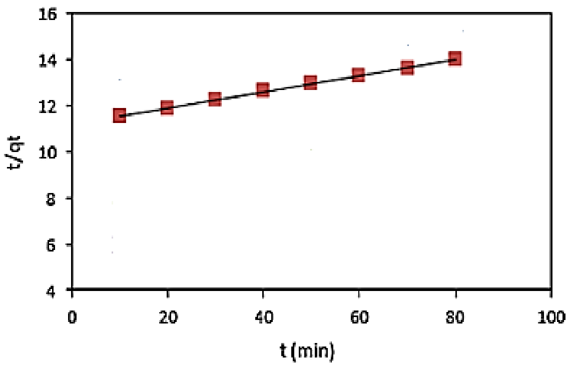

Fig. 11. Pseudo-first-order kinetics for Mn (VII) onto Ziziphusspina-christi (ZSAC).

3.6.2. Pseudo-second-order kinetics

The pseudo-second-order rate expression, which has been applied for analyzing chemisorption kinetics rate, is expressed as[45]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \qquad (12)$$

where qe and qt are the sorption capacity at equilibrium and at time t, respectively (mg/g), and k is the rate constant of pseudo-second-order sorption, (g/mg min). For the boundary conditions to qt=0 to qt=qt at t=0 to t=t, the integrated form of Eq. (13) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \qquad (13)$$

where t is the contact time(min), qe(mg/g) and qt(mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. If pseudo-second-order kinetics is applicable, the plot of t/q t versus t of Eq. (13) should give a linear relationship, from which qe and k_2 can be determined from the slope and intercept of the plot, Fig. 12. The pseudo- second-order rate constant k_2, the calculated e value and the corresponding linear regression correlation coefficient value are given in Table 2. At all initial metal concentrations, the linear regression correlation coefficient R^2 values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second-order kinetics.

3.7. Adsorption thermodynamics

The thermodynamic parameters, namely Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change ΔS°, for the adsorption processes were determined using the following equations [46-48]:

$$\Delta G^{\circ} = RT lnK_{ad} \qquad (14)$$

$$lnK_{ad} = \frac{ÄH^{\circ}}{RT} + \frac{ÄS^{\circ}}{R} \qquad (15)$$

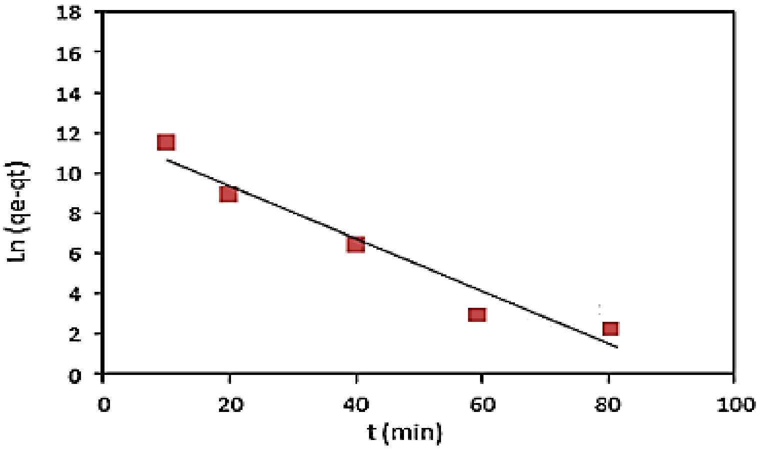

Fig. 12. Pseudo-second-order kinetics for BB onto Ziziphusspina-christi (ZSAC).

Table 2. Adsorption rate constants by kinetic equation

Kinetic Model dye	Pseudo first - order kinetic			Seudo second-order kinetic		
	q_e(mg g^{-1})	k_1(1/min)	R^2	q_e(mg g^{-1})	k_2(g/mg min)	R^2
Bismark Brown (BB)	7.93	0.383	0.9903	28.49	1.1	0.9999

where R is universal gas constant (8.314J mol^{-1}K^{-1}), and T is the absolute temperature in Kelvin. Thermodynamic parameters were summarized in table 3. The negative values of ΔG° indicate that the adsorption process was a spontaneous process. The decrease in ΔG° with the increase of temperature indicates more efficient adsorption at higher temperature. The positive values of ΔH° confirm that the sorption of BB onto (ZSAC) is endothermic in nature. Fig. 13 shows the Van’t Hoff plot for the adsorption of BB on Ziziphusspina-christi (ZSAC).

4. CONCLUSION

The Ziziphusspina-christi (ZSAC) has been synthesized and used as an effective adsorbent for the removal of Bismark Brown(BB) dye from aqueous solutions. The effects of adsorbent dosage, pH, contact time, and initial dye on the removal of BB were investigated through batch experiments. Isotherm models such as Langmuir, Freundlich, Temkin, and Dubinin - Radushkevich for the adsorption process were evaluated and the equilibrium data were best described by the Langmuir model. The process kinetics was found to be successfully fitted to the pseudo-second-order kinetic model. Adsorption of BB was found to be spontaneous at the temperatures under investigation. The positive value of ΔH° confirmed the sorption process was endothermic. The goal for this work is to develop inexpensive, highly available, effective BB dye adsorbents from natural waste as alternative to existing commercial adsorbents. Ziziphusspina-christi (ZSAC) has a high adsorption capacity when compared to other adsorbents for Bismark Brown (BB) dye removal from an aqueous medium.

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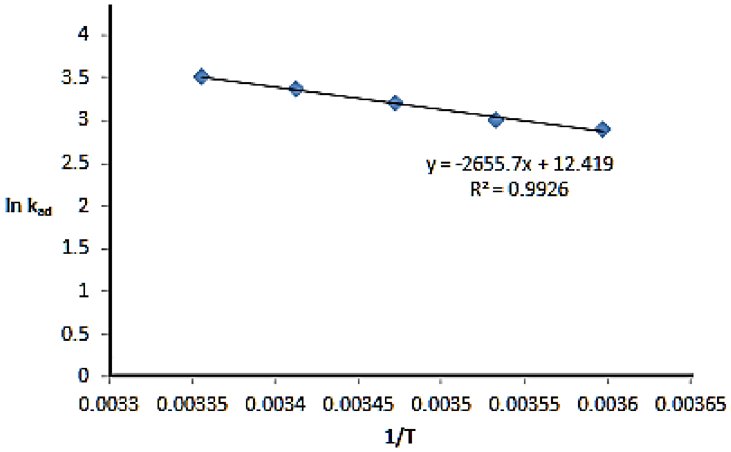

Fig. 13. Plot of lnK$_{ad}$ vs. 1/T for the estimation of thermodynamic parameters.

Table 3. Thermodynamic data for the adsorption of BB onto Ziziphusspina-christi (ZSAC)

Initial Bismark Brown (BB) concn.(mg/L)	ΔH°(kJ/mol)	ΔS°(J/mol K)	ΔG°(kJ/mol)				
			5^{oC}	10^{oC}	15^{oC}	20^{oC}	25^{oC}
20	22.08	103. 2	6.68-	-7.05	-7.65	-8.18	-8.70

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