Preparation and characterization of Chicory leaf powder and its application as a nano-native plant sorbent for removal of Acid Blue 25 from aqueous media: isotherm, kinetic and thermodynamic study of the adsorption phenomenon

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Received: 17 August 2019 / Accepted: 31 December 2019 / Published online: 29 January 2020
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Abstract

In this study, the Chicory leaf powder (CLP) was used as a native adsorbent to eliminate the Acid Blue 25 dye from aqueous media. The prepared native adsorbent was characterized by several techniques including the X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform spectroscopy (FTIR), Brunauer–Emmet–Teller essay (BET), and particle size analyzer (PSA). A collection of experiments was performed to distinguish the optimal conditions and to probe the effects of the different parameters such as initial concentration, contact time, adsorbent dosage, pH of solution, and temperature on the sorbent capacity. The attained optimal conditions for removal the Acid Blue 25 dye were pH = 3–4, contact time 50 min, dosage 0.1 g, and initial concentrations 10 (mg/L) at 30 °C. The adsorption data revealed that the adsorption procedure has more match with the Langmuir isotherm than others. The kinetic data were better fitted with the pseudo-second-order pattern with a trusty correlation coefficient. Finally, the thermodynamic parameters illustrated that the adsorption process is exothermal and spontaneous. Based on magnitude of the standard enthalpy change related to the studied adsorption, we may derive that the considered adsorption is physical adsorption.

Keywords Adsorption · Chicory leaf powder · Adsorbent · Acid Blue 25 · Kinetics · Thermodynamics · Isotherm

Introduction

Toxicity of dye compounds has been a major problem of human for several years [1]. Dyes are contaminants which are widely consumed in industrial operations such as textile, wood manufacturing, paper mills, and leather. It is necessary that the industrial wastewater be refined before it is discharged into the environment. A number of applied sciences have been developed over years for eliminating dye pollutants from aqueous solutions [2–4], as dyes are significant environmental pollutants and destroy natural eco-systems in particular. One of these methods is the adsorption process. In recent years, numerous studies have been accomplished to remove dyes from eco-systems using diverse adsorbents [5–7]; adsorbents with the superiorities of availability and

low cost of the processing [8, 9]. For example, the removal value of congo red by aloe vera leaf shell carried out with the maximum uptake capacity of CR dye by AV-AC was 1850 mg/g [10]. In another research, the Azollapinnata (AP) and soya bean waste (SBW) adsorbents were used for removing Acid Blue 25 from aqueous solutions [11]. Overall, there are extensive research works on the use of natural adsorbents to remove hazardous dyes to refine eco-systems [12].

In this study, we used Chicory leaf powder (CLP) as a native adsorbent to adsorb Acid Blue 25; it is referred to as CLP hereinafter.

Acid Blue 25 (AB25) belongs to the anthraquinone and anionic dyes class which is the most important dye following azo dyes with chemical formula $C_{20}H_{13}N_2NaO_5S$ and molecular mass 416.38 (g/mol). It is generally applied for dyeing wool, leather, detergents, wood, ink fur, and cosmetics [13].

Chicory plant is in two species; one kind is cultivated, while the other is savage and grows on its own. The main source of Chicory plant is central Europe, the western and central parts of Asia and north Africa, and has a vast

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scattering in different areas of Iran [14, 15]. The scientific name for this herb is *Cichorium intybus* and belongs to the category Asteraceae. Chicory has certain amount of vitamins, minerals (such as magnesium, phosphorus, C vitamin and B group vitamins) and active compounds such as inulin, fats and sesquiterpene lactones. In total, 20 components were identified in the aerial portions of this herb. Some of the chemical compositions are carvacrol (50.1%), thymol (13.3%), cinnamic aldehyde (12.4%), camphor (4.4%), linalool (3.9%) and terpineol (2.1%) [16, 17]. The discrepancy between this research and other studies is the use of a new natural adsorbent, which, in addition to its medicinal attributes, seems to be an eligible herbal adsorbent for adsorbing ionic pollutants. In articles [18], the effects of the drug and the adsorption of toxins in the liver were investigated by Chicory plant and its compounds.

The original target of the study is to test the adsorption treatment of Chicory savage powder as adsorbent with respect to Acid Blue 25 [19]. Remember that the technology of adsorption has been widely studied in last years. It is a suitable and effective technology for homemade and industrial wastewater therapy [20, 21]. The effects of different agents, such as initial concentrations of solution, contact time; pH values, adsorbent dosage, and temperature were investigated. The thermodynamics and kinetics of Acid Blue 25 adsorption onto the CLP were also studied.

Experimental

Chemical

All chemicals applied in this research were made a purchase from Merk Company and were of analytical standard. They were applied without further purification. Acid Blue 25, potassium hydroxide, hydrochloric acid, sodium hydroxide and sodium chloride were also from the same company and used as received.

Instruments

The adsorption of Acid Blue 25 in the desired studied solutions was quantified by a UV–Vis 1700 Simadzo model spectrophotometer at wavelength of 597 nm. The UV–Vis spectrophotometer was used to record the solution phase absorption. The measurement of the solutions' pH was done by A5500 model pH meter. A Neolab model shaker was used in the batch experiments which was thermostatic orbit incubator. The adsorbent specifications were investigated by X-ray powder diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) (varian 1000 Ft-IR Scimitar series). The specific surface area and total pore volume was determined by BET/BJH analyzer. The particle size analyzer

(PSA) was used for the particle size determination. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used for the size determination of CLP.

Preparation of adsorbent

At first, Chicory leaves were washed and dried in the laboratory and powdered by a milling device. The powder was sieved via a mesh number 100. Then, 5 g of CLP was placed in 0.01 M KOH solution for 15 h, and it was placed on ultrasonic bath for 2 h. Then, the product was filtered and rinsed multiple times with distilled water, and then it was dried about 3 h at 90° C in oven. After heating, the dried powder was put in a desiccator for 1 day. Then, it was gently compressed to turn into a tiny powder [22, 23].

Designing a typical adsorption experiment

The method of operation of an adsorption experiment is very momentous. In general, the ordinary procedure (batch method) is as follows: an adequate dosage of sorbent (e.g. 0.10 g) is mixed with the intended volume of sorbate solution with a investigated concentration (e.g. 50 mL with concentration of 10 mg L⁻¹). Then, the solution pH and temperature should be adjusted at the desired values (e.g. 3–4 and 30 °C, respectively). The obtained mixture should be stirred under the constant pH and temperature for suitable time interval (e.g. 50 min). The final mixture should be filtered, using a filter paper with a high quality. Finally, the concentration of the filtered solution (the obtained solution upon filtration) must be determined by an effective method, including spectrophotometric measurement, atomic absorption method, etc. In addition, the initial concentration should also be measured with the same instrument for promoting the measurement precision [24, 25].

The level, mg, of the adsorbed dye per gram of CLP at equilibrium, q_e (mg/g) or adsorption capacity, and the adsorption percentage, (% A), were computed applying the following equations [1, 26]:

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

$$\%A = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where C_0 (mg/L) is the initial concentration and C_e (mg/L) signified the equilibrium concentration of dye. m and V represent the mass of the sorbent (g) and the volume of the test solution (L), respectively. It is worthwhile to note that %A and q is a reliable criterion for evaluating the efficiency of an adsorption process.

Here, it should be noted that, several parameters including initial concentration of sorbate, pH solution, dosage of sorbent, temperature, contact time and some other conditions affect seriously the adsorption capacity of any adsorption process.

Therefore, determination of the optimum value of each mentioned parameter must firstly evaluate a discussed.

Results and discussion

Characterization of Chicory leaf powder

The chemical combination of CLP was determined by other researchers [16, 17]. In this study, some other characterizations were done. The X-ray diffraction pattern of the prepared CLP (Fig. 1) has no sharp peak and revealed that the prepared adsorbent is an amorphous material. Figure 2a and b displays the two images of the SEM and TEM of CLP indicating that the prepared CLP has a good quality as an adsorbent. The TEM image (Fig. 2b) indicates the gauge of the most native adsorbent particles was near 100 nm or somewhat smaller or larger.

Figure 3 displays the FTIR spectrum of CLP. The peaks at 2900 cm^{-1} and $3000\text{--}3700\text{ cm}^{-1}$ are related to the C–H (sp^2) and O–H functional groups, respectively, while $1600\text{--}1680\text{ cm}^{-1}$ represents C=C bond. The peak at around 1700 cm^{-1} is associated with C=O stretch. The weak peak at 1425 cm^{-1} confirms a C–C aromatic bond. Also, there are several strong peaks at $1050\text{--}1255\text{ cm}^{-1}$ which are C–O–C stretching functional group and the last broad peak indicates C–Br at 580 cm^{-1} . From these peaks, we can conclude many organic and inorganic compounds

Fig. 2 The SEM image (a) and TEM image (b) of CLP

Fig. 1 X-ray powder diffraction (XRD) of CLP

Fig. 3 FTIR spectrum of Chicory leaf powder (CLP)

are found in CLP [16]. The obtained specific surface area of CLP by BET essay was $6.09 \text{ m}^2/\text{g}$ (at ambient pressure: 1 atm and detector temperature: 100°C), which is relatively larger than that of flax, cotton and cellulose fibers. Our value is near to the values reported in [27, 28] and the total pore volume of CLP was $0.0692 \text{ m}^3/\text{g}$.

Charge essay: to investigate the CLP electrical behavior, we performed a simple experiment by an assembly consisting of two electrodes in a mixture of CLP and distilled water plus a battery in the electrical circuit. We found that the CLP particles do not migrate toward any electric charge. The pH of zero point charge (pH_{pzc}) of the adsorbent was determined by the salt addition method applying 0.01 mol L^{-1} NaCl solutions [29]. The pH of the NaCl solutions was adjusted with 0.1 mol L^{-1} HCl and NaOH to initial pH of 2.0–10.0. The pH was measured using a pH meter. Specifically, 0.02 g of the adsorbent was added to 20 mL of pH-adjusted NaCl and shaken for 24 h at 250 rpm applying an orbital shaker and the ultimate pH was measured. The final pH versus initial pH was plotted to determine the pH_{pzc} . The pH_{pzc} of CLP was found to be at 7.1.

In addition, the particle size analyzer experiment was also performed where the results demonstrated that the size of the most native adsorbent particles was near 100 nm or somewhat larger. The intensity distribution graph (Fig. 4) shows the particle size of Chicory leaf powder (CLP).

The effect of adsorbent dosage

Sufficient levels of adsorbent are a main parameter to be considered, since it specifies the number of free adsorption sites for a given initial concentration of the dye [30]. The experiments were accomplished at the normal pH (5.5) of the dye solution, the initial concentration 30 mg/L , and the contact time 30 min at 25°C . The quantity of CLP dosage was altered from 10 to 100 mg. Figure 5a demonstrates the graph of CLP dosage versus the adsorption percentage of the Acid Blue 25 dye.

Based on Fig. 5a, with elevation of the adsorbent dosage (or adsorbent' mass), the adsorption percentage increased, and the optimum dosage was chosen 100 mg.

The effect of temperature

The effect of temperature on the sorption of Acid Blue 25 onto CLP was tested at 25°C , 30°C , 40°C , and 50°C , while the other parameters including the initial concentration, contact time, and solution pH were 30 mg/L , 30 min and normal pH, respectively. As Fig. 5b illustrates, the removing percentage of the Acid Blue 25 dye increased gradually from 25 to 30°C and then diminished with increment of temperature. The reason is that by raising the temperature, dye molecules

Fig. 4 The intensity distribution graph of the particle size of Chicory leaf powder (CLP)

Fig. 5 The graph of examination of adsorbent dosage (a), the graph of investigation of temperature (b), the graph of inspection of contact time (c), and the graph of studying pH (d) versus the Acid Blue 25 dye adsorption percentage

move more vigorously, and the adsorption capacity is also increased; however, at a higher temperature, desorption may

take a prevailing role [31]. The optimum temperature may be chosen as 30 °C.

The effect of contact time

The equilibrium contact time is one of the most basic parameters of the adsorption procedure. The effect of contact time on the adsorption procedure was investigated [32, 33]. Every experiment was carried out using 100 mg of adsorbent at normal pH (5.5) of the dye solution and at temperature 30 °C. The initial concentration of Acid Blue 25 solution was 30 (mg/L). According to Fig. 5c, the adsorbent displays an imperceptible growth for the dye adsorption, as the contact time increased. Note that beyond 50 min, there is no considerable growth in the dye uptake. At first, the number of adsorbent sites of available is high, so the adsorption percentage increases gradually, as the time passage the adsorbent sites is occupied by a great number of the molecules of Acid Blue 25, and the adsorption rate does not change much and remains constant. Hence, 50 min was chosen as the optimized contact time. After this time, the removal percentage of the Acid Blue 25 dye fixed and not changed.

The effect of pH

The pH quantity participates a notable role in dye adsorption on the various adsorbents [34]. To appraise the effect of pH on the capacity adsorption, the experiments were directed under fixed experimental conditions, with an initial concentration 30 (mg/L), adsorbent quantity 100 mg, and contact time 50 min at temperature 30 °C. The effect of pH was investigated within the range of 3 to near 9. The solution pH was justified with 0.01 M HCl and 0.01 M NaOH solutions. Based on the concept of point of zero charge, if the solution pH is lower than the pH_{pzc} (which is 7.1 for CLP) value, it is mostly positively charged, while if the solution pH is greater than this value, it is mainly negatively charged. The results are shown in Fig. 5d.

The optimum pH was selected within the range of 3–4. The obtained data suggest that the removal percentage was pH dependent. The reason is that, more OH^- is available at

higher pH and competes with the anionic sulfonic groups (in the structure of Acid Blue 25) for the adsorption of the Acid Blue 25 dye, which results in a reduction in the number of the adsorption sites for the anionic Acid Blue 25 dye molecules [35] because the OH^- molecule is smaller than the Acid Blue 25 molecule and is better placed in the adsorbent pores in competition with Acid Blue 25. Also, H^+ ion is placed on the adsorbent surface thus the Acid Blue 25 anionic dyes attracts the adsorbent and the adsorption percentage increases at lower pH.

The effect of initial concentration

Another significant variable that can influence the adsorption capacity is the initial concentration of dye or ion [11]. The effect of the initial concentration on the adsorption percentage of the Acid Blue 25 dye was checked by altering the initial concentration from 10 to 70 mg/L, while the next parameters were as pursues: adsorbent dosage 100 mg, temperature 30 °C, solution pH 3–4, and contact time 50 min [36]. The results are shown in Fig. 6a and b. According to these data, the adsorption percentage (% removal) declines with the initial concentration elevation, but the adsorption capacity, q_e (mg/g), grows with increasing the initial concentration. The maximum adsorption percentage happened almost at the initial concentration of 10 (mg/L). Investigating the absorption capacity at different temperatures indicated that the maximum absorption capacity occurred at temperature of 30°C (Fig. 6b).

Adsorption isotherms

Adsorption isotherms are necessary for explaining the interaction that occurs between the adsorbent and the adsorbate, and are also critical in optimizing the usage of an adsorbent. Various isotherm equations are existing, but two major of them were utilized to represent the equilibrium data of this study, one Langmuir isotherm and another Freundlich model. Langmuir monolayer

Fig. 6 The effect of initial concentration on Acid Blue 25 adsorption percentage under optimum conditions (a); the effect of initial concentration on the desired dye adsorption capacity, q , under the optimum conditions at different temperatures (b)

adsorption has a reasonable theoretical basis which gives it a broad application [37]. Based on the statistical mechanical approach and using canonical partition function for a sample of ideal lattice gas (monolayer ideal gas on the solid surface), the molecular chemical potential, μ_{ad} , of an adsorbed gas molecule was obtained as

$$\mu_{\text{ad}} = kT \left(\frac{\theta}{(1-\theta)q} \right), \quad (3)$$

where θ is the coverage fraction of the solid surface and q is molecular partition function of the adsorbed molecule, T is temperature in Kelvin and k is Boltzmann constant. At equilibrium between the adsorbent phase and the gas phase, we have [38]

$$\mu_{\text{ad}} = \mu_g = \mu_g^\circ(T) + kT \ln \left(\frac{P}{P^\circ} \right). \quad (4)$$

So,

$$kT \left(\frac{\theta}{(1-\theta)q} \right) = \mu_g^\circ(T) + kT \ln \left(\frac{P}{P^\circ} \right) \quad (5)$$

Or,

$$\left(\frac{\theta}{1-\theta} \right) \frac{1}{P} = \frac{1}{P^\circ} q e^{\mu_g^\circ(T)/kT}. \quad (6)$$

The components in the right hand of Eq. (6) are only temperature dependent and so can be considered as a constant, $K(T)$, (or K_L) at constant temperature.

Therefore,

$$\left(\frac{\theta}{1-\theta} \right) = K(T) = K_L P, \quad (7)$$

which lead to the well-known Langmuir adsorption isotherm [39].

$$\theta(P, T) = \frac{K_L P}{1 + K_L P}, \quad (8)$$

By analogy, we may use the above equation the adsorption of the considered adsorbate from the solution phases onto the solid surface.

For Acid Blue 25, adsorption onto the Chicory leaf powder (CLP) surfaces, we can propose the below simple mechanism [40]:

With the equilibrium constant, K , (Eq. 10)

$$K = \frac{[\text{ABS}]}{[\text{AB}][\text{S}]}, \quad (10)$$

$[\text{ABS}]$ is the number of occupied sites per unit area of the adsorption surface, $[\text{AB}]$ is the concentration of the

adsorption in the solution phase and $[\text{S}]$ is the number of unoccupied site per unit area of the adsorbent surface. By analogy with the gas adsorption onto the solid surface (equilibrium), we can assume that the K constant in Eq. (10) can be written as [41]

$$K = K(T) = K_L = \frac{1}{[\text{AB}]^\circ} q_{\text{ABS}} e^{\mu^\circ/kT}, \quad (11)$$

where $[\text{AB}]^\circ$ is the standard concentration, q_{ABS} is the molecular partition function of ABS and μ° is the molecular standard chemical potential of AB in the solution phase. Based on the values of $K(K_L)$ and its dependent on the temperature, one can estimate the values of thermodynamic function of the adsorption process ($\Delta G_{\text{ad}}^\circ$, $\Delta H_{\text{ad}}^\circ$ and $\Delta S_{\text{ad}}^\circ$). By analogy, Eq. (8) at existing situation can be written as:

$$\theta = \frac{K_L C}{1 + K_L C}, \quad (12)$$

where C_e is the equilibrium concentration of the sorbate in the solution phase. By taking $= \frac{q}{q_m}$, we obtain the linear Langmuir equation [42–44]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L} \right) \frac{1}{C_e} \text{ linear Langmuir isotherm equation,} \quad (13)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{ linear Freundlich isotherm equation,} \quad (14)$$

where q_e (mg/g) is the value of adsorbed dye (mg) per unit mass (g) of the adsorbent at equilibrium; C_e (mg/L) denotes the equilibrium concentration; q_m (mg/g) shows the largest adsorption capacity supported by the Langmuir adsorption; K_L (L/mg) is the equilibrium constant of the Langmuir isotherm; n and K_F (mg/g)(L/mg)^{1/n} illustrate Freundlich constants affiliate to the adsorption intensity and adsorption capacity by the adsorbent, respectively. To attain the Langmuir isotherm parameters, applying the experimental results, the plot of $\frac{1}{q_e}$ was drawn versus $\frac{1}{C_e}$. Based on Eq. (13), the slope and the intercept of the plot are $\frac{1}{q_m K_L}$ and $\frac{1}{q_m}$, respectively, enabling us to compute the values of q_m and K_L . The Langmuir linear equation and the Freundlich linear equation for the studied dye removal are plotted in Fig. 7a and b, respectively. The values of K_F and n can be derived from the slope ($\frac{1}{n}$) and the intercept ($\log K_F$) from the linear Freundlich equation. The calculated values of the Langmuir and Freundlich parameters based on the outcomes of this study are represented in Table 1. The maximum adsorption capacity (q_m) is 22.222 mg/g for the Acid Blue 25 dye onto the CLP, Although this value is not high but it can be reliable enough, because it is near the values of some bio adsorbent like References [24, 46]. In the Table 2, the maximum

Fig. 7 The linear Langmuir isotherm (a), the linear Freundlich isotherm (b), for removing Acid Blue 25 by CLP adsorbent at 298 K

Table 1 Parameters of Freundlich and Langmuir isotherms at 298 K

Dye	Freundlich model			Langmuir model		
	K_F ($\text{mg}^{1-(1/n)}\text{L}^{1/n}\text{g}^{-1}$)	n	R^2	K_L (L/mg)	q_m (mg/g)	R^2
Acid Blue 25	3.0974	1.867	0.986	0.112	22.222	0.997

Table 2 The adsorption of Acid Blue 25 on various adsorbent under different conditions

Absorbent	q_m (mg/g)	Number of references
Calcined diatomite	9.41	[62]
Raw diatomite	21.41	[62]
Chicory leaf powder	22.22	This study
Base-treated <i>Shorea dasyphylla</i> sawdust	24.4	[19]
Cempedak durian peel	26.62	[32]
Phosphoric acid treated rubber leaf powder	28.09	[64]
Soya bean waste	38.3	[11]
<i>Azolla pinnata</i>	50.5	[11]
Quaternized kenaf core fiber	303.03	[63]
Crosslinked chitosan beads	443.3	[2]

adsorption capacity of Acid Blue 25 on Chicory leaf nanopowder was compared with some other bio adsorbent.

Adsorption thermodynamics

Thermodynamic quantities can specify the spontaneity and feasibility of the adsorption procedure. Standard Gibbs free-energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) can be evaluated as follows [45]:

$$\Delta G^\circ = -RT \ln K_C, \quad (15)$$

$$\ln K_C = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}, \quad (16)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (17)$$

where T is temperature (K) and R is the ideal gas constant (8.314 J/mol.K). The standard enthalpy change of the studied adsorption ($\Delta H^\circ_{\text{ad}}$) was calculated from the gradient of the chart of $\ln(K_C)$ versus $1/T$, while the standard entropy change ($\Delta S^\circ_{\text{ad}}$) was computed from the intercept of the plot (Fig. 8a).

Thermodynamic studies were accomplished within the temperature limit of 298–328 K, under the optimized conditions (the initial concentration of Acid Blue 25 was 10 (mg/L), pH 3–4, contact time and adsorbent dosage were 50 min and 100 mg, respectively).

To expand the thermodynamics of the studied adsorption, we may presume a conditional equilibrium constant as follows [46]:

Fig. 8 The plot of $\ln K_C$ versus $1/T$ (a), the kinetic investigation of the Acid Blue 25 adsorption capacity at different concentrations (b) at optimum conditions

Table 3 Thermodynamic parameters for Acid Blue 25 adsorption onto CLP

	T (K)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)
Acid Blue 25	298	-18.566	-0.056	-1.729
	303			-1.446
	313			-0.881
	328			-0.034

$$K_C = \frac{[\text{sorbate}]_{\text{(ad)}}}{[\text{sorbate}]_{\text{(aq)}}} = \frac{q_e}{C_e}. \quad (19)$$

This equilibrium constant (Eq. 19) is conditional and not so rigorous from the thermodynamic point of view, but it has been used in major research papers with regards to the adsorption process [47–51]. Based on the conditional K_C and the related thermodynamic equations (Eqs. 15–18) and Fig. 8a, one can derive the values of $\Delta H^\circ_{\text{ad}}$, $\Delta G^\circ_{\text{ad}}$ and $\Delta S^\circ_{\text{ad}}$ associated with Acid Blue 25 adsorption onto CLP as the sorbent. The acquired quantities are represented in Table 3.

In Table 3, the negative quantity of ΔH° indicates the exothermic character of the adsorption process. The free energy change, $\Delta G^\circ_{\text{ad}}$, is negative, informing a spontaneous process. The more negative the $\Delta G^\circ_{\text{ad}}$, the more spontaneous the adsorption process will be; thus, a higher adsorption capacity is anticipated. Finally, the negative quantity of the entropy change discloses a decrement in

randomness at the adsorbate/adsorbent interface during the adsorption process [52].

Adsorption kinetics

In this research, the kinetic empirical parameters were evaluated via the vastly applied pseudo-first-order and pseudo-second-order models, which are usually defined as follows [53–56]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (20)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (21)$$

where q_e (mg/g) is the value of the adsorption capacity at equilibrium and q_t (mg/g) represents the value of q at time t (min), k_1 (1/min) and k_2 (g/mg.min) shows the rate constants of the pseudo first-order and the pseudo-second-order adsorption procedures, respectively [57–64]. In this work, the kinetics of the adsorption of Acid Blue 25 dye onto CLP as adsorbent was tested by taking 50 mL of the dye solution with a concentration 10 mg/L and the solution was monitored according to the prior method (solution pH 3–4, adsorbent dosage 100 mg, for the kinetic experiments at 25 °C). The time period was selected within the range of 10–70 min. In Fig. 9a and b, the plots of adsorption kinetic data are drawn and the acquired kinetic data are reported in Table 4.

The adsorption kinetic data of the adsorbed dye were better fitted with pseudo-second-order kinetics where the correlation coefficient was fairly good. Also, the kinetic study was done in optimum conditions at different concentrations, as shown in Fig. 8a. The main results of this investigation showed that the adsorption capacity rose with increasing time for all concentrations.

Fig. 9 Pseudo-first-order model (a), pseudo-second-order model (b), and the adsorption kinetics of the studied dye onto CLP

Conclusion

The results of this research revealed that the prepared CLP as a very fine powder of a native plant has a fairly good ability for removing Acid Blue 25 from aqueous media and acts as a good adsorbent for Acid Blue 25 removal. The optimum condition for removal of the Acid Blue 25 dye onto the CLP adsorption were investigated and reported as: dosage mass = 0.1 g, pH = 3–4, contact time = 50 min, temperature = 30 °C and initial concentration = 10 mg/L. The result showed that all the parameters influence the removal percentage but the pH effect was more interesting. The adsorption experimental results showed that the Freundlich and Langmuir isotherms could represent almost all results of this study, but Langmuir isotherm fitted the results better. Furthermore, pseudo-first-order kinetics and pseudo-second-order kinetics were performed to test the kinetic data, where Pseudo-second-order kinetics proved better for representing the kinetic data. The thermodynamic examinations revealed that the studied adsorption process is exothermic and showed a reduction in randomness ($\Delta H_{ad}^{\circ} < 0$, $\Delta S_{ad}^{\circ} < 0$). In addition, the adsorption of Acid Blue 25 dye onto the prepared nano-native powder, under the experimental conditions was spontaneous because of $\Delta G_{ad}^{\circ} < 0$. Finally, given the magnitude of ΔH_{ad}° , we may conclude that the studied adsorption is a physisorption phenomenon. The advantage of using this adsorbent is its simple and low cost preparation method with relatively good results. If other processes are performed on the adsorbent or it becomes functional, the

amount of dye removal and its thermodynamic quantities may be improved.

Acknowledgements The authors would like to appreciate Islamic Azad University, Science and Research Branch for all their supports.

Author contribution statement HM Designed and performed experiments, analyzed data and co-wrote the paper. AH Designed experiments and co-wrote the paper. ZK Supervised the research. MM analyzed data.

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Table 4 Kinetic parameters for Acid Blue 25 adsorption onto CLP

Pseudo first-order model			Pseudo-second-order model		
q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
2.490	0.039	0.972	4.454	0.136	0.993

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