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Study on a new adsorbent for biosorption of cadmium ion from aqueous solution by activated carbon prepared from *Ricinus communis*

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ABSTRACT

Adsorption of heavy metal ions from the aqueous solutions is an important environmental challenge. In this research, as a low-cost adsorbent, the activated carbon which was prepared from *Ricinus communis* leaves was applied to adsorb cadmium(II) ions from aqueous solution. The prepared activated carbon was characterized using Brunauer–Emmett–Teller, scanning electron microscope, energy-dispersive X-ray spectroscopy/Map, Fourier transform infrared spectroscopy, X-ray diffraction, and thermogravimetric analysis. Batch experiments were designed to investigate the significance of adsorption important parameters including solution pH, the dosage of adsorbent, adsorption time, temperature, and cadmium initial concentration on the Cd(II) ions removal efficiency. The highest adsorption efficiency was 97.71% which was achieved in the following conditions: pH = 8, the dosage of adsorbent = 0.6 g/L, adsorption time = 70 min, 25°C, and initial ion concentration = 70 ppm. Equilibrium studies showed that Langmuir isotherm performed better than the Freundlich model for fitting the data. Additionally, the kinetic behavior of the process was described by the pseudo-second-order model better than the pseudo-first-order model. Furthermore, based on thermodynamic calculations, the current process was exothermic, spontaneous with the decreased irregularities.

Keywords: Adsorption; *Ricinus communis*; Cadmium ion; Adsorbent; Adsorption isotherm; Activated carbon

1. Introduction

As a result of human industrial activities, emission of heavy metal contaminants in surface waters and swages has become a major environmental challenge, since such pollutants threaten the human and other creatures' health and life [1]. These heavy metals are introduced into the environment by the wastewater of industries such as mining, metal processing, fuel, and energy generation, electroplating, electrolysis, photography, nuclear plants, iron, and steel industries, etc. and disturb the ecological balance [2,3]. Heavy metals such as cadmium, nickel, lead, and mercury are non-biodegradable toxic at trace level concentrations and can accumulate in living organisms by entering the human food chain through the adsorption by water and soil which cause chronic diseases and various disorders [4]. The presence of excess cadmium ion in drinking water results in higher risks of diseases like kidney failure, hypertension, hepatitis, lung failure, bone deformation, and even cancer [5]. The maximum permissible concentration of cadmium ion in

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sewage and potable water is 0.1 and 0.005 mg/L, respectively. Considering the problems associated with the inappropriate discharge of such chemicals in the environment, the treatment of wastewaters containing heavy metal ions before their discharge into the environment or sewage collection network seems necessary [6].

In recent years, several attempts have been made to study the adsorption of heavy metals from wastewaters by the adsorption process, because this process is economically possible, effective, simple, fast, and biocompatible in comparison with other chemical or physical methods such as membrane separation, chemical precipitation, and ion exchange [7,8]. Recently investigators have examined the use of biological materials such as fungus, yeast, algae, and activated carbon as the adsorbent in adsorption processes [3]. One of the most common adsorbents in wastewater treatment researches is activated carbon, since it can be prepared from the leaves of plants [9]. A considerable amount of literature has been published on using the activated carbon adsorbents that have been produced from low valued materials [10–16].

In this work, activated carbon was produced from the leaves of *Ricinus communis* which are abundantly found in the local gardens of Boushehr province (Iran). It was characterized and used for cadmium(II) ions removal from synthetic aqueous solutions. The significance of solution pH, dosage of adsorbent, adsorption time, temperature, and initial ion concentration on the uptake percentage of Cd(II) ions were investigated. In addition, the achieved adsorption equilibrium, kinetic, and thermodynamic data were fitted with several models.

2. Experimental

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$-99.9%), sodium hydroxide (NaOH-99.9%), hydrochloride acid (HCl-37%), and phosphoric acid (H_3PO_4-28%) were all purchased from Merck Company (Germany) in analytical grade. It should be mentioned that double distilled water was utilized for the preparation of cadmium(II) ion solutions in all of the adsorption tests.

2.1. Preparation of activated carbon adsorbent

As the first step, the leaves of *Ricinus communis* tree were collected from the local grasslands and gardens of Boushehr province (Iran). Then dust and other probable impurities of the collected leaves were washed carefully using distilled water. In order to leaves be dried, they were placed in an oven (Memmert, UP400, Germany) for 3 h set at 100°C. The obtained dried leaves were immersed in phosphoric acid 28% (with the ratio of 1:4 for chemical agent/biomass) for 24 h and were dried again in the oven for 48 h. The next step, carbonization, was conducted using a nitrogen atmosphere furnace (ALARGE, ABF -1400T, China) for 4 h in 1,000°C under nitrogen atmosphere in the heating rate of 0–20°C/min. Finally, the carbonized material was powdered and sieved by no. 25 sieves (The nominal sieve opening 700 μm with a wire diameter of 0.33–0.48 mm) and stored in tightened cap bottles for further adsorption experiments. The steps of activated carbon preparation are depicted in Fig. 1.

2.2. Preparation of stock solution

As shown in Fig. 1, In order to prepare cadmium solutions with a concentration of 1,000 ppm, based on calculations using the molecular weight of cadmium nitrate tetrahydrate, 2.74 g of $Cd(NO_3)_2 \cdot 4H_2O$ was dissolved in distilled water. Double distilled water was applied for dilution of obtained stock solution in order to achieve solutions in the concentration range of 10–70 ppm for the designed adsorption experiments. It should be noted that during the experiments, NaOH and HCl were both utilized for the adjustment of the prepared solutions pH values using Metrohn digital pH meter.

2.3. Adsorption experiments

In this research, batch experiments were designed for assessing the importance of solution pH (3–10), a dosage of adsorbent (0.1–0.8 g/L), adsorption time (5–120 min), temperature (298–348 K), and initial cadmium concentration (10–70 ppm) on the adsorption efficiency of the prepared activated carbon from *Ricinus communis* leaves. Worthy to note that in all of the experiments the agitation speed was fixed in 200 rpm (Fig. 1).

In order to attain the significance of solution pH in the above-mentioned range, the adsorption experiments were conducted in a series of Erlenmeyer flasks containing solutions with the following conditions: an adsorbent dosage of 4 g/L, cadmium initial concentration of 40 ppm, the temperature of 298 K, and 50 min as the adsorption time. After the end of each experiment, the samples were filtered using the Whatman Grade 42 filter paper and the remained solution was analyzed using flame atomic adsorption device (VARIAN, USA) to determine the residual cadmium ions in the solution. In order to achieve the optimum values of other parameters, pH should be fixed in the prior optimized value while the effect of others was investigated in their corresponding ranges. The adsorption efficiency value (*R*%) for each experiment is then calculated using the following equation:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

In this equation C_i is the initial concentration and C_e is the equilibrium concentration of cadmium ions in the aqueous solution (mg/L).

The adsorption equilibrium capacity, q_e, which is the mass of adsorbed adsorbate on the adsorbent surface at equilibrium (mg/g) is determined using Eq. (2), in which W and V are the adsorbent mass (g) and solution volume (L), respectively:

$$q_e = \frac{C_i - C_e}{w} \times V \quad (2)$$

It is also worth noting that the adsorption capacity of the adsorbent depends on solution concentration, contact time, and solution pH. Consequently, the determination of the optimized values of the adsorption parameters seems necessary.

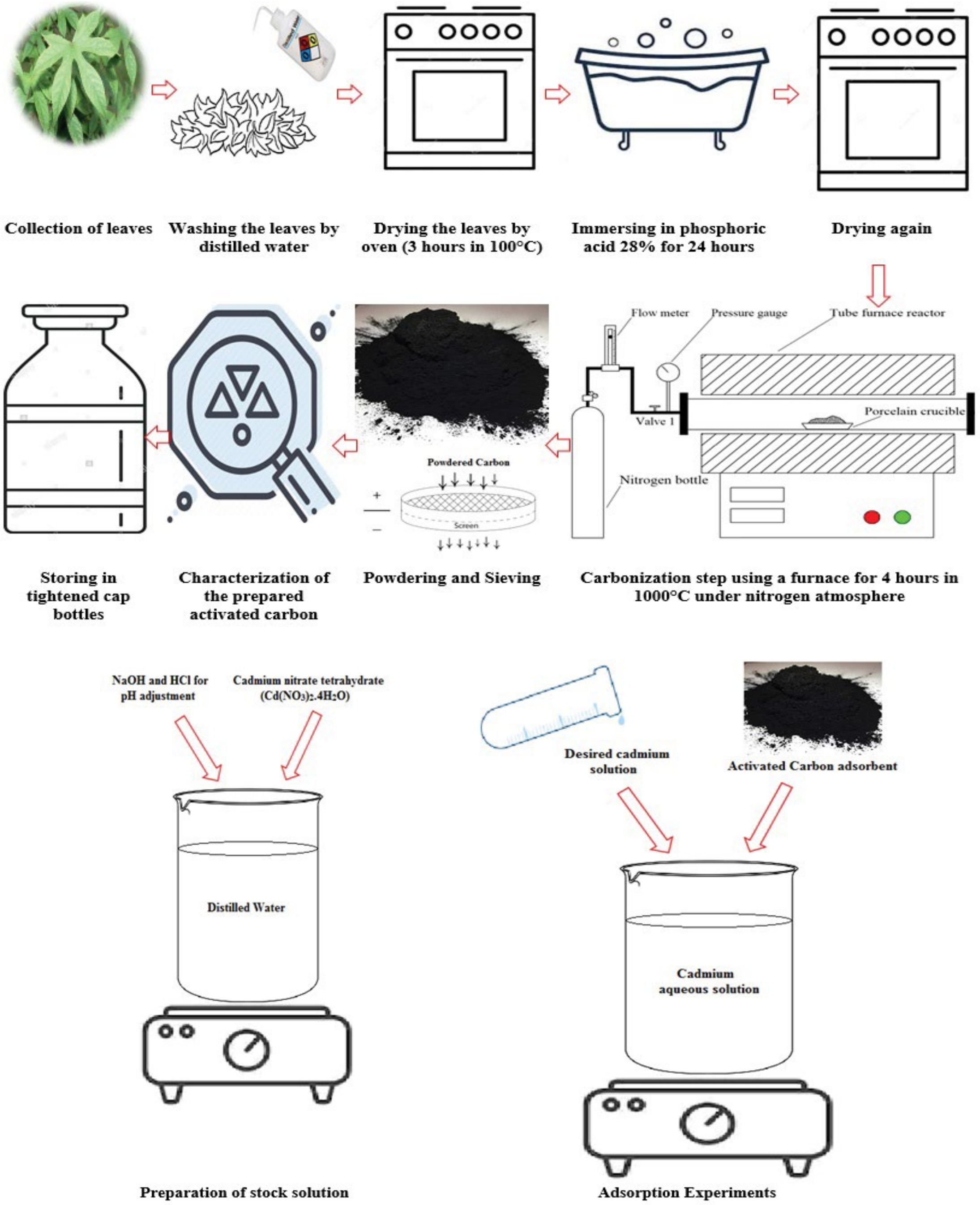

Fig. 1. Sketch of preparation of activated carbon, stock solution, and adsorption experiments.

2.4. Analysis and instruments

In this study, Brunauer–Emmett–Teller (BET) (Gemini 2375, USA), scanning electron microscope (SEM) (Tescan, Czech Republic), energy-dispersive X-ray spectroscopy (EDX)/Map (Tisteam SAM), Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, USA), X-ray diffraction (XRD) (Philips X'PERT 1 X-RAY, Netherland), and thermogravimetric analysis (TGA) (ADVANCE RIKO TGD-9800, Japan) instruments were applied to determine the adsorbent features including specific surface area, its morphology and structure, distribution of elements present on the adsorbent, adsorbent surface functional groups, its crystalline phases, and the thermal features, respectively.

3. Results and discussion

3.1. Activated carbon analysis

Based on BET analysis, the adsorbent specific surface area, pore-volume, and mean diameter of the pores were 88.5 m^2/g, 0.07 m^3/g, and 3.21 nm, respectively. Such a surface area value can partly reflect the porosity of the adsorbent surface which promotes its pollutant adsorption capability [17].

SEM images of the prepared activated carbon adsorbent before and after the adsorption of cadmium ions are presented in Fig. 2. As it can be clearly seen, the pores and cavities which were present on the adsorbent surface prior to the experiments were covered by the adsorbed cadmium ions. After the adsorption, the surface of activated carbon was changed and it can be seen that the aggregation of particles and surface roughness were reduced as the consequence of cadmium adsorption and the occupation of adsorbent active sites (Fig. 2b). Based on these micrographs, the obvious bumps and cavities which can be observed on the surface of the prepared adsorbent sample before the process can contribute to the adsorption of wastewater pollutants well, especially the larger ones.

EDX/Map analysis results are presented in Fig. 3a and Table 1 revealed that elements including C, N, O, P existed in the adsorbent structure and their corresponding weight percentages were 44.09%, 19.82%, 28.40%, and 7.62%, respectively. Meanwhile, Fig. 3b shows that cadmium ions with a weight percentage of 1.28% were detected on the adsorbent surface in addition to the other four above mentioned elements. This means that the cadmium ions have been attached to the prepared activated carbon active sites through the adsorption process. Additionally, the distribution of the constituents of the adsorbent prepared from *Ricinus communis* leaves shows that carbon is the major element of this adsorbent since it approximately covers the whole surface of the adsorbent.

The FTIR spectra of the prepared activated carbon in the range of 400–4,000 cm^{-1} before and after the adsorption Cd(II) ions are given in Fig. 4. Broad absorption band around 3,425 cm^{-1} shows the coincidence of peaks related to hydroxyl and amines (N–H) groups [18,19]. The peaks appeared at 1,113 and 1,434 cm^{-1} is the stretching vibrations of the C–C group in activated carbon structure, while the peak which is associated with C–CH$_3$ group is observed in 1,300 cm^{-1} [20–22]. Additionally, another weak band is seen around 1,030 cm^{-1} which can probably be related to stretching vibrations between Cd and C–O [23]. Furthermore, the band at about 482 cm^{-1} can probably correspond to C–O–H vibrations. In general, it can be said that changes in the activated carbon spectra after the removal of cadmium ions can be ascribed to the presence of Cd(II) ions in adsorbent's structure. Moreover, the other important result to emerge from the FTIR spectrum of the adsorbent before and after the adsorption experiments is that the functional groups play a major role in the adsorption process [24,25].

Fig. 5 shows the XRD patterns of the activated carbon adsorbent prepared from *Ricinus communis* leaves. The outstanding peak that is obviously seen at 2θ = 25°, is the characteristics of activated carbon structures, therefore it can be concluded that the prepared adsorbent exhibited the double-layered structure of the activated carbon [26].

The TGA thermal curve of biomass is presented in Fig. 6.TGA analysis demonstrated that the process of mass loss contained four sections. In the first one, the mass loss 4.13% resulting in moisture elimination. Secondly, the process of decomposition attains 48.67% load loss, while in the third stage the load loss of 41.92%. Finally in the last one, there is a loss of 1.6% of the mass. As it can be observed, in the current activated carbon sample, the temperature of around 1,000°C can be regarded as the decomposition threshold temperature.

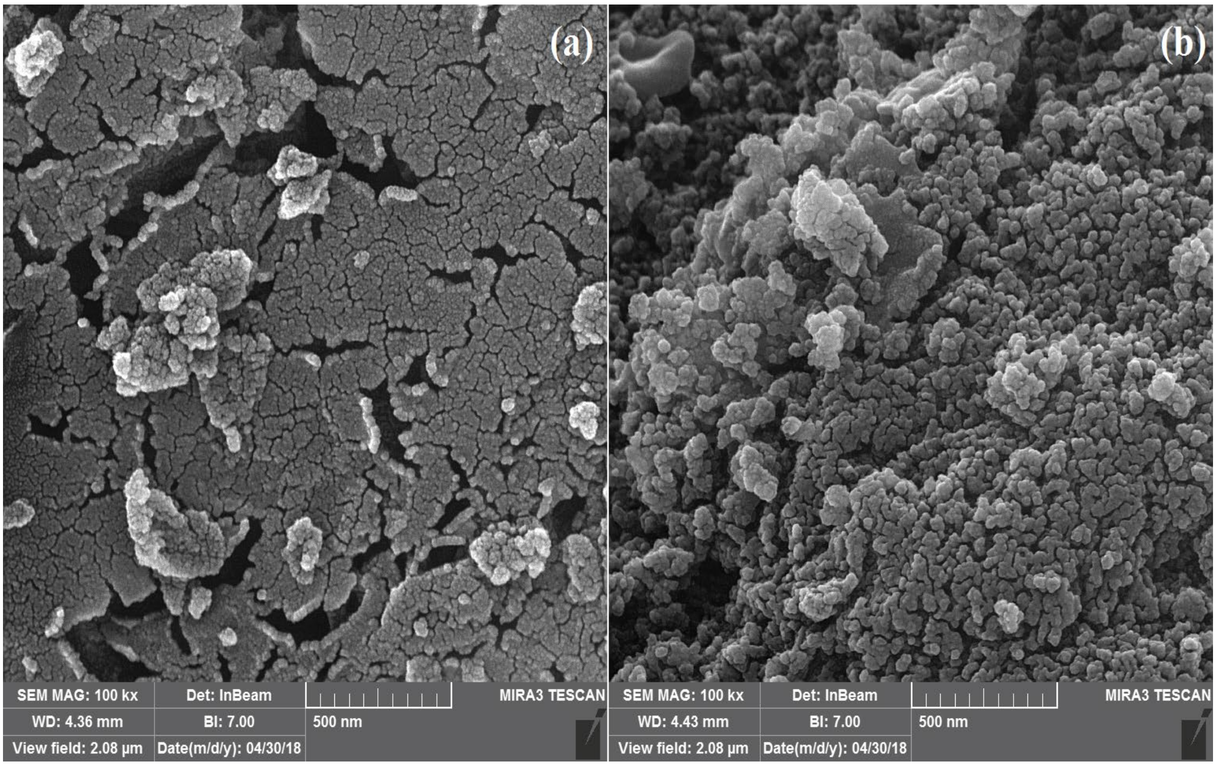

Fig. 2. SEM photographs of activated carbon (a) before and (b) after the adsorption of Cd(II) ions.

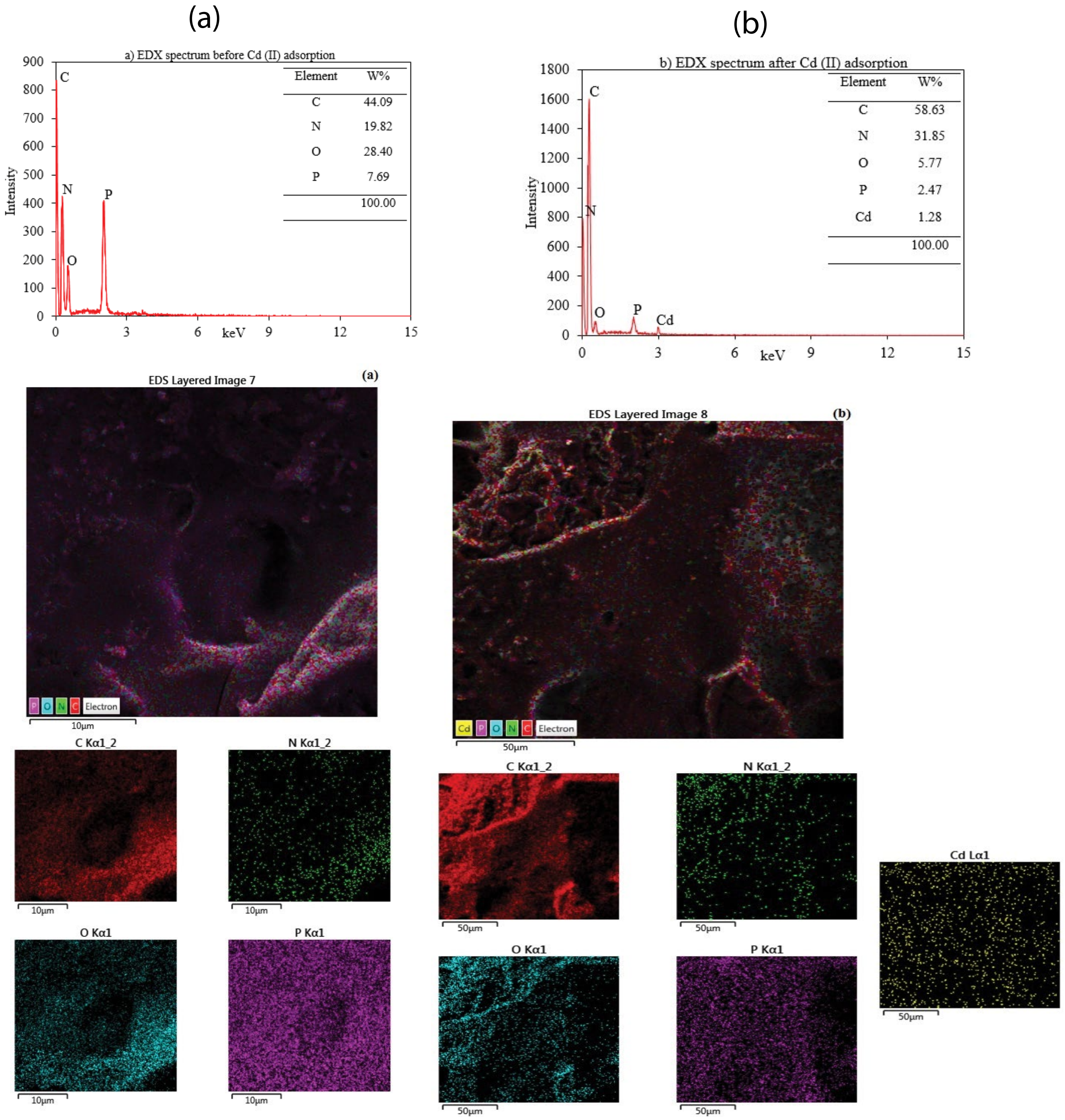

Fig. 3. EDX spectrum percentage and map images of the activated carbon adsorbent (a) before and (b) after the adsorption of Cd(II) ions.

3.2. Adsorption studies

3.2.1. Effect of solution pH

Solution pH is a significant factor since it controls the adsorption process. Fig. 7 demonstrates the significance of this parameter on the adsorption efficiency of the prepared adsorbent in the range of 3–10. As it can be seen, the uptake efficiency was increased from 65% to 97% and any further increase was not observed after this pH value. Such a trend has been reported in others previously [27]. The reason for low adsorption efficiencies in initial pH values is the high concentration of H^+ ions which overcome the cadmium ions for relocating on the adsorption active sites. After the initial pH values, the adsorbent surface charge became negative and the removal efficiency increased as the result of adsorption of Cd(II) ions by attractive forces between them and the adsorbent surface. This rising trend is continued until the uptake efficiency of 97% at pH = 8. In addition,

Table 1
EDX analysis of the activated carbon adsorbent

Element	Activated carbon (wt.%)	Adsorbent after Cd(II) adsorption (wt.%)
C	44.09	58.63
N	19.82	31.85
O	28.40	5.77
P	7.69	2.47
Cd	–	1.28
Total	100.00	100.00

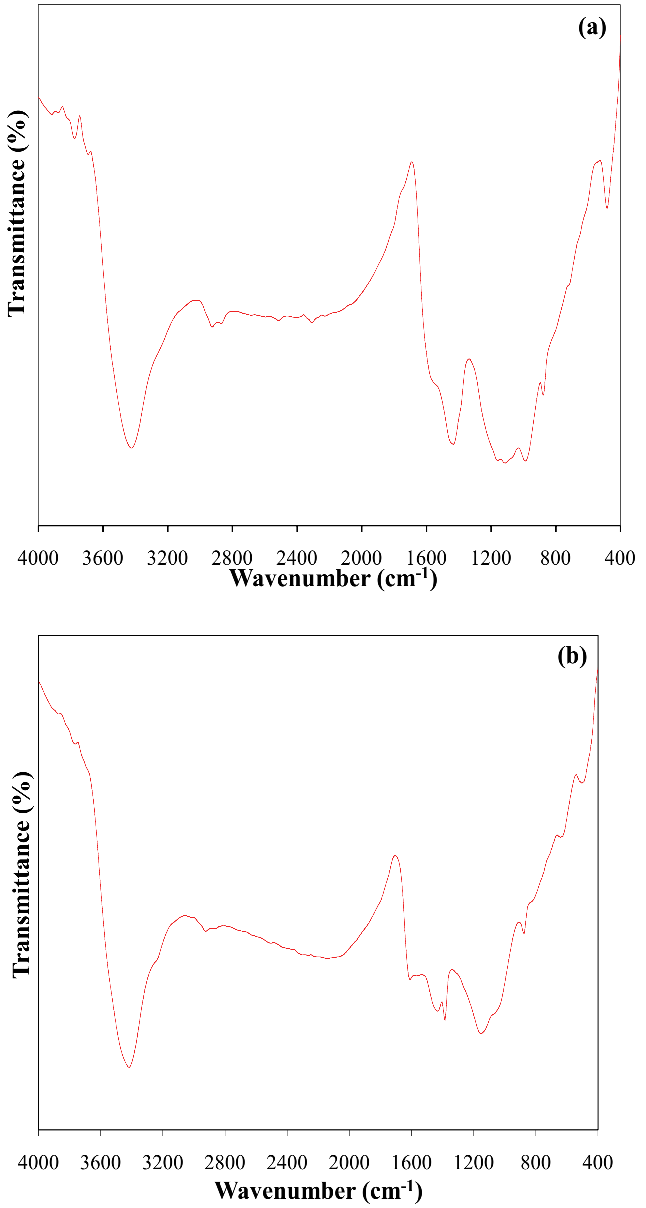

Fig. 4. FTIR spectra of the activated carbon (a) before and (b) after the adsorption of Cd(II) ions.

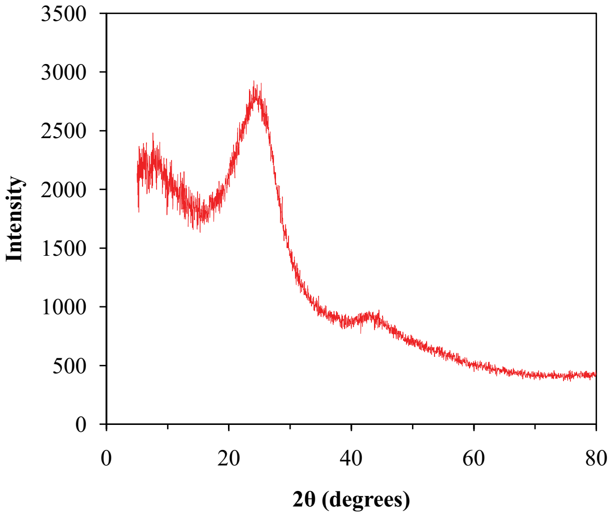

Fig. 5. X-ray diffractogram of the prepared activated carbon adsorbent from *Ricinus communis* leaves.

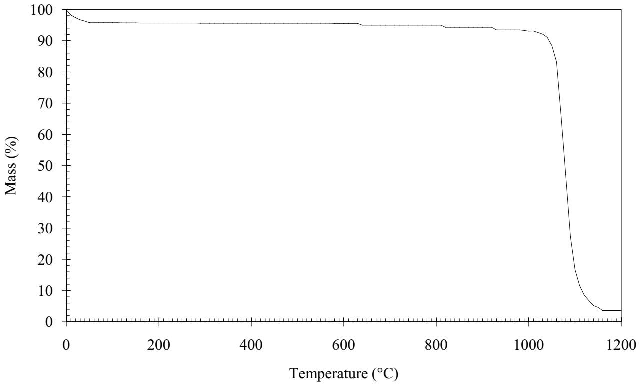

Fig. 6. TGA curves of biomass.

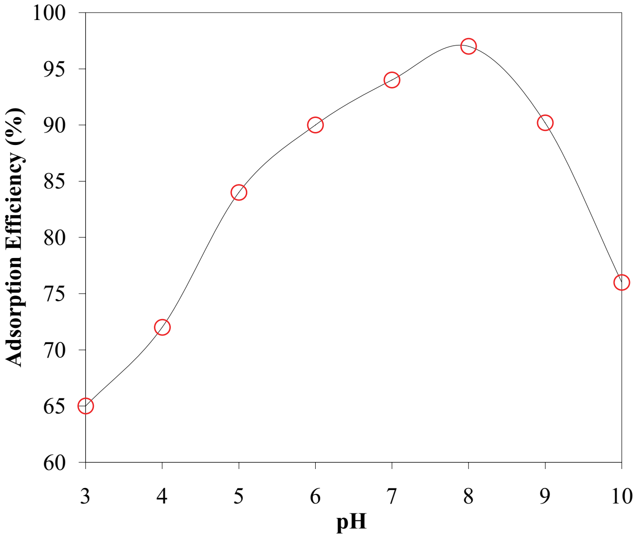

Fig. 7. Effect of solution pH on cadmium ions adsorption efficiency (adsorbent dosage = 0.4 g/L, t = 50 min, T = 298 K, initial concentration = 40 mg/L, and stirring rate = 200 rpm).

The results showed the drop of the adsorption efficiency in the range of 8–10 was because of high concentration of OH^- ions and formation of complexes of hydroxyl and cadmium ions which occupy the active adsorption sites of the adsorbent and decreased contacts between the cadmium and the adsorbent active sites, as well as the competition between OH^- ions and the remained metal ions for relocation on active sites, which result in a decline of adsorption efficiency. Considering these data, it can be concluded that the optimum pH value for the removal of cadmium ions by the prepared adsorbent was 8 [28]. Taken together, the effect of solution pH on the adsorption efficiency of the current adsorbent can be justified through the surface charges.

3.2.2. Effect of adsorbent dosage

The result of adsorbent dosage change effect on the uptake efficiency of Cd(II) ions by the prepared activated carbon in the range 0.1–0.8 g/L is presented in Fig. 8. This figure is quite revealing that the adsorption efficiency increased in the range of 0.1–0.6 g/L from 45% to 91.2%. The observed increase in the adsorption efficiency in initial values of adsorbent dosage could be attributed to the fact that by increasing the adsorbent dosage, the surface area and number of active sites of the adsorbent were increased, which results in higher adsorption and diffusion of pollutants into the active sites of the applied activated carbon [29]. Additionally, for dosages higher than 0.6 g/L, the uptake percentage was not increased. The probable reason for the cease of increase in adsorption rate is the occupation of the adsorbent active sites as the result of adsorption of cadmium ions [29]. These findings can be compared to other works [30–33]. After the optimum point of adsorbent dosage, the adsorption efficiency became constant, since there is not a considerable amount of pollutants available in the solution to promote the removal percentage and no significant adsorption was found for the residual cadmium ions after this point. Based on these data, the adsorbent dosage of 0.6 g/L is the optimum value under the current conditions of adsorption experiments.

3.2.3. Effect of contact time

The effect of contact time in the range of 5–120 min on the efficiency of removal of Cd(II) ions was studied and its results are illustrated in Fig. 9. As indicated in this figure, high rates of adsorption were occurred in initial steps, because of the abundance of active sites on the surface of the adsorbent that can be occupied by the free ions in the solution. However it was decreased gradually and became approximately constant after 70 min since most of the ions of the initial solution were adsorbed on the activated carbon adsorbent so far [34]. It could be conceivably hypothesized that higher active sites were available on the surface of the adsorbent in the initial stages of adsorption which yielded high adsorption efficiencies. After a while it became constant as the result of saturation of active sites by the cadmium ions [35]. It should be noted that the highest adsorption efficiency (96%) was achieved in 70 min, and there was not any significant increase in the uptake percentage from 70 to 120 min. Consequently, it can be considered as the equilibrium time of adsorption.

3.2.4. Effect of temperature

The thermal nature of the adsorption process can be determined by investigating the temperature effects [24]. Therefore, in the current work its effect on the removal efficiency percentage of cadmium ions was investigated in the range of 298–348 K and its results are shown in Fig. 10. It is observed that the uptake efficiency decreased remarkably by temperature which denotes that this process was exothermic and no chemical bonds were formed

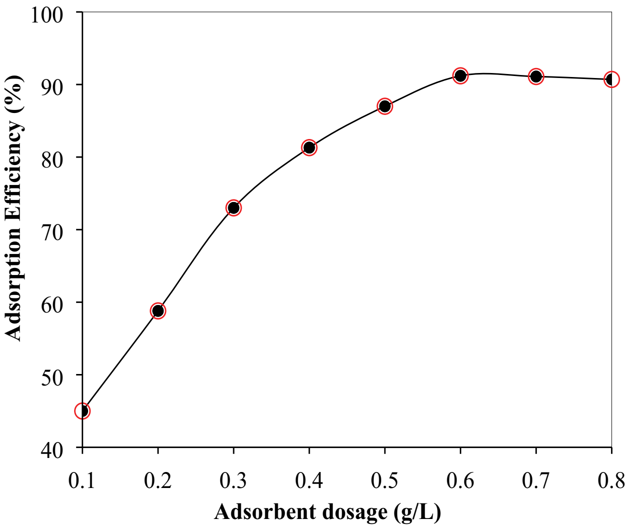

Fig. 8. Effect of adsorbent dosage on cadmium ions adsorption efficiency (solution pH = 8, t = 50 min, T = 298 K, initial concentration = 40 mg/L, and stirring rate = 200 rpm).

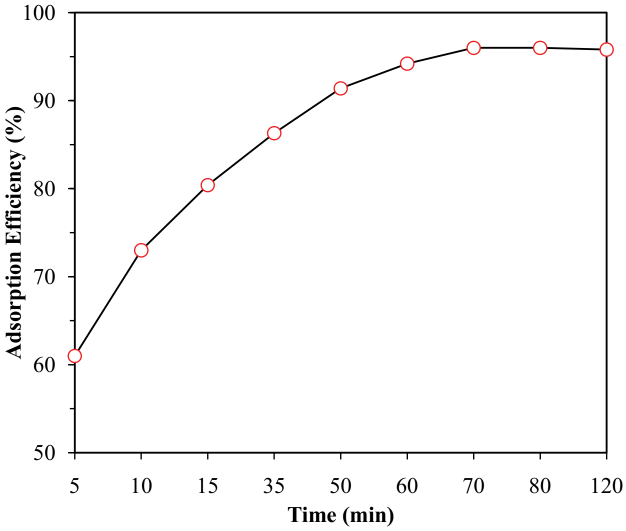

Fig. 9. Effect of contact time on cadmium ions adsorption efficiency (solution pH = 8, adsorbent dosage = 0.6 g/L, T = 298K, initial ion concentration = 40 mg/L, and stirring rate = 200 rpm).

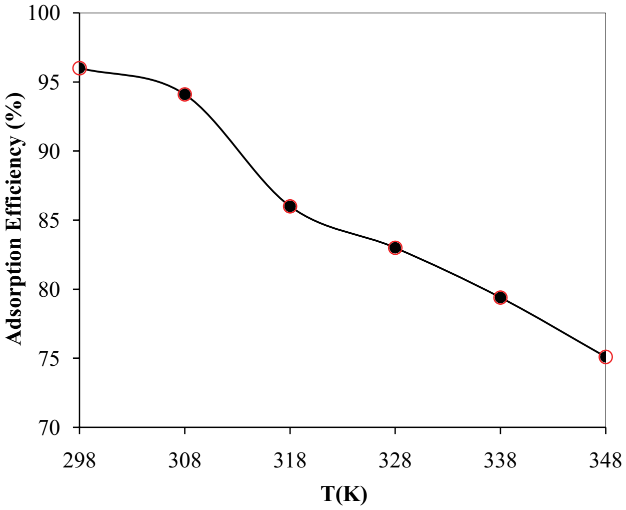

Fig. 10. Effect of temperature on cadmium ions adsorption efficiency (solution pH = 8, adsorbent dosage = 0.6 g/L, t = 70 min, initial ion concentration = 40 mg/L, and stirring rate = 200 rpm).

during the adsorption. These observations are in accordance with previous works [36]. The possible explanation for the decrease is the higher mobility of cadmium ions and their tendency for separation from the adsorbent surface in higher temperatures [37]. Considering these data, 298 K was the optimum temperature in which the adsorption efficiency peaked at 96%.

3.2.5. Effect of initial ion concentration

The initial concentration of ions plays a key role in the adsorption process for the generation of the driving force of solid-liquid mass transfer. Fig. 11 illustrates the effect of the initial concentration of cadmium ions on the uptake efficiency of the prepared activated carbon. It is clearly seen that there is a positive correlation between the removal percentage (89%–97.71%) and the ion concentration in the range of 10–60 mg/L. These results were also seen in other researches [30,38]. The reason for this observation can be attributed to the high ratio of the active sites to the cadmium initial concentration at the initial values of this parameter which results in high interactions between the adsorbent and Cd(II) ions [39]. As a result of such high interactions most of the cadmium ions were adsorbed on the adsorbent surface, which resulted in higher adsorption efficiencies. Additionally, the adsorption capacity rose with cadmium initial concentration. It seems possible that these results are due to an increase of collisions between cadmium ions and adsorbent which led to their rapid diffusion into the adsorbent structure [40]. The graph shows that there has been a fall in adsorption efficiency after 60 mg/L, which can be attributed to the saturation of adsorbent active sites, therefore there were not free sites for the higher pollutant concentrations. Considering these findings, it can be concluded that the optimum initial concentration value was 60 mg/L, where the adsorption efficiency was 97.71%.

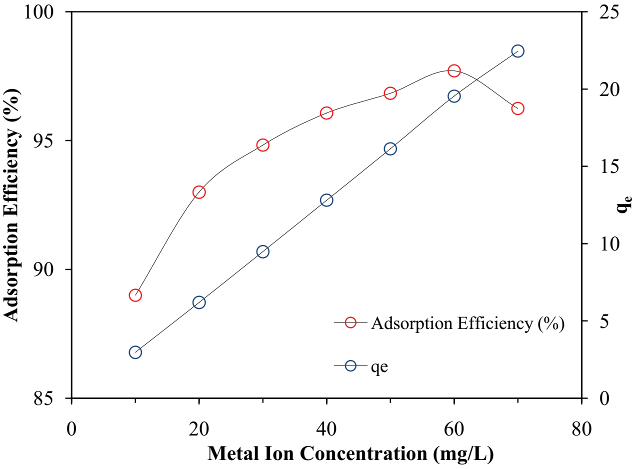

Fig. 11. Effect of initial cadmium ion concentration on its adsorption efficiency and capacity (solution pH = 8, adsorbent dosage = 0.6 g/L, T = 298 K, t = 70 min, and stirring rate = 200 rpm).

3.3. Desorption study

In order to investigate the regeneration capacity of the current prepared adsorbent, reusability experiments were conducted in six cycles in the optimum experimental conditions which were determined during the course of the current study, and the results are presented in Fig. 12. During the regeneration experiments the used adsorbent was recovered by vacuum filtration and then washed by methanol and dried in an oven at 120°C. Considering the data depicted in Fig. 12, the adsorption efficiency of the prepared adsorbent witnessed a gradual decline. The loss of efficiency of the recovered adsorbent can be attributed to the deposition of the cadmium ions on the adsorbent surface which may result in blockage of its adsorption sites and vacancies.

3.4. Adsorption isotherms

Having an adequate information about the adsorption equilibrium is significant since it can be applied for the design and optimization of the adsorption systems [41,42]. Adsorption isotherms describe the interactions between the adsorbent and adsorbate. Hence Langmuir [43,44] and Freundlich [45] isotherm models were utilized to specify the extent of maximum adsorption capacity of cadmium ions by the prepared activated carbon adsorbent from *Ricinus communis* leaves. The linear form of these two models and their related parameters are presented in Table 2 as Eqs. (3)–(6). Langmuir isotherm model is based on the hypothesis that the adsorption is a mono-layer process on a finite number of active sites of a homogeneous adsorbent, while, as an empirical model, Freundlich is applied to describe the adsorption on heterogeneous adsorbents [46].

In equations presented in Table 2, $q_{\max}$ and K_L are the Langmuir constants that represent the highest adsorption capacity (mg/g) and adsorption energy (L/mg), respectively and R_L is called the adsorption intensity parameter. It should be noted that for $0 < R_L < 1$, $R_L > 1$, $R_L = 1$, and $R_L = 0$, the process is favorable and reversible, unfavorable, favorable and linear, and reversible process, respectively

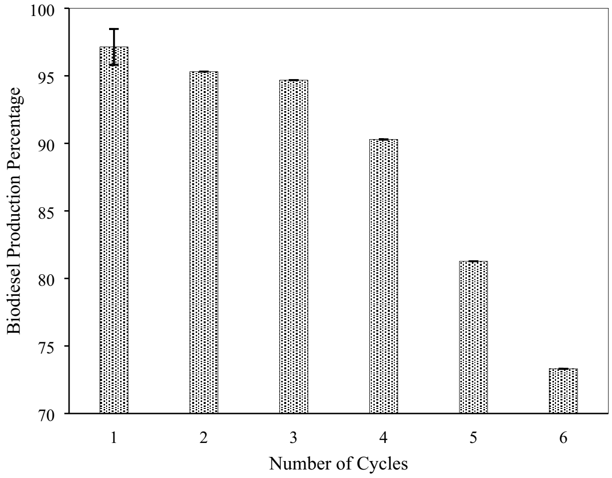

Fig. 12. Desorption study of the used adsorbent in the optimum adsorption conditions (pH = 8, a dosage of adsorbent = 0.6 g/L, adsorption time = 70 min, 25°C, and initial ion concentration = 70 ppm).

Table 2
Langmuir and Freundlich isotherm models equations

Isotherm model	Definition	Equation	
Langmuir	Linear form	$\frac{1}{q_e}=\frac{1}{K_L q_m}\frac{1}{C_e}+\frac{1}{q_m}$	(3)
	Adsorption intensity	$R_L=\frac{1}{1+K_L C_i}$	(4)
Freundlich	Linear form	$\ln q_e=\frac{1}{n}\ln C_e+\ln K_f$	(5)

[47]. Additionally, n and K_f which are Freundlich constants represent the adsorption rate and degree of nonlinearity of the adsorption process [48]. The values of $q_{\max}$ and K_L are calculated from the values of slope and intercept of the $1/q_e$ vs. $1/C_e$ linear form, while the slope and intercept of the $\ln q_e$ vs. $\ln C_e$ diagram is applied to determine K_f and $1/n$. Fig. 13 and Table 3 represent Langmuir and Freundlich linear isotherm plots and their related parameters for cadmium adsorption by the prepared activated carbon adsorbent from *Ricinus communis* leaves.

According to the achieved data, R_L is between zero and one, which indicates that the adsorption of cadmium was optimal and reversible. In addition the value of $q_{\max}$ is reported equal to 20.9 mg/g, which can be considered as a significant maximum adsorption capacity [49]. Furthermore, the equation of the trend line for Langmuir model was achieved as $y = 0.1944x–0.1087$ and its correlation coefficient (R^2) was 0.9775, which is obviously higher than that of Freundlich (R^2 0.8585), indicating that the equilibrium behavior of cadmium adsorption by the current adsorbent was defined better by the former. In addition, n was 0.26 ($n < 1$), therefore the adsorption of cadmium on the activated carbon prepared from *Ricinus communis* leaves is undesirable. These results would seem to suggest that the Langmuir isotherm model was more capable of describing the cadmium adsorption from the synthetic wastewater using the activated carbon prepared from *Ricinus communis*

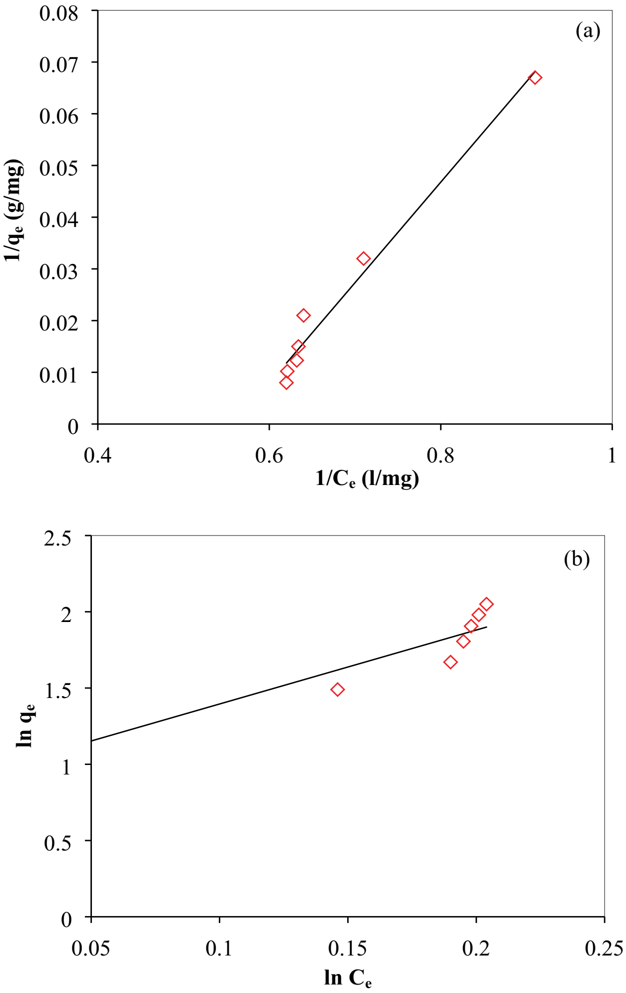

Fig. 13. Linear plots of (a) Langmuir and (b) Freundlich isotherm models for the adsorption of cadmium ions from aqueous solution by the activated carbon adsorbent.

Table 3
Langmuir and Freundlich adsorption isotherms parameters for the adsorption of cadmium ions from aqueous solution by the activated carbon adsorbent

Models	Parameters	Value
Langmuir	q_m (mg/g)	20.9
	K_L (L/mg)	0.56
	R^2	0.9775
	R_L	0.029
Freundlich	n	0.21
	K_f $(\text{mg})^{1-n}$ L^n/g	8.13
	R^2	0.8583

leaves in comparison with the Freundlich isotherm model. Therefore these findings suggest that the current adsorption process was a single layer process on a heterogeneous adsorbent [50,51].

3.5. Adsorption kinetics

Adsorption kinetics has received considerable critical attention since it provides critical information about the mechanism of the adsorption process, therefore the kinetic behavior of cadmium ions adsorption by the produced adsorbent from the leaves of *Ricinus communis* was investigated as a function of time using pseudo-first-order and pseudo-second-order kinetic models [52–55] (Table 4) and its data are presented in Fig. 14 and Table 5. Based on these results, a fast adsorption process was observed in the first 60 min. The observed fast trend might be attributed to the abundance of adsorption active sites on the adsorbent structure at the initial steps of the adsorption before the achievement of equilibrium [56].

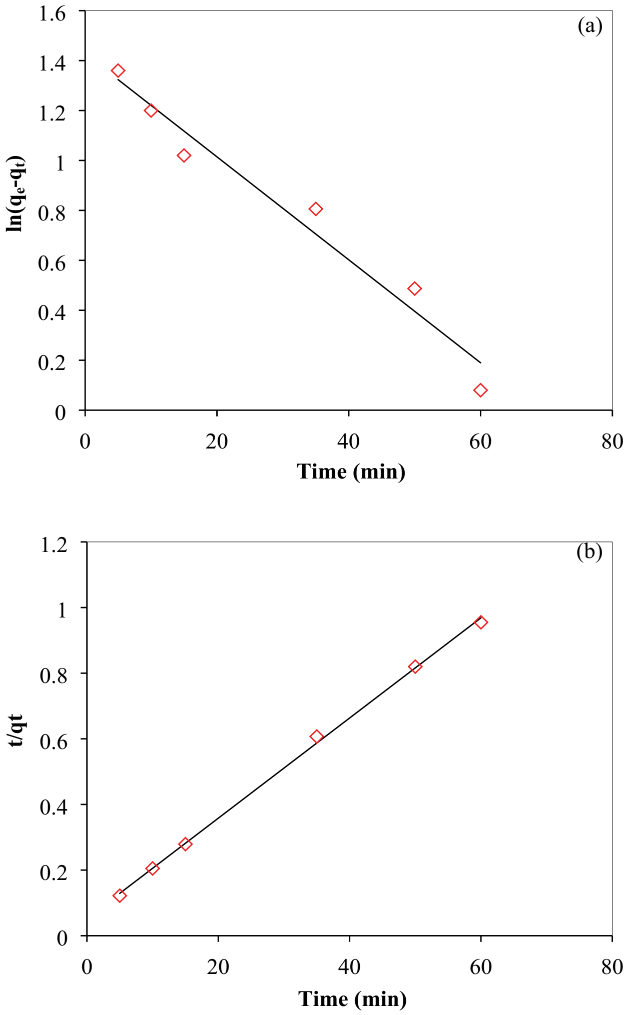

Fig. 14. (a) Pseudo-first-order and (b) pseudo-second-order kinetic model diagrams for the adsorption of cadmium ions from aqueous solution by the activated carbon adsorbent.

Table 4
Pseudo-first-order and pseudo-second-order kinetic models equations

Kinetic Model	Equation	
Pseudo-first-order linear form	$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t$	(6)
Pseudo-second-order linear form	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	(7)

Table 5
Pseudo-first-order and pseudo-second-order kinetic models parameters for the adsorption of cadmium ions from aqueous solution by the activated carbon adsorbent

Kinetic models	Parameters	Value
Pseudo-first-order	$q_{e,\mathrm{cal}}$ (mg/g)	26.71
	K_1 (1/min)	0.047
	R^2	0.9632
Pseudo-second-order	$q_{e,\mathrm{cal}}$ (mg/g)	65.35
	$K_2 \times 10^{-3}$ (g/mg min)	4.41
	R^2	0.9899

In Eqs. (6) and (7), q_t, K_1, and K_2 are the value of the adsorbed ion per gram of adsorbent at time t (mg/g), pseudo-first-order (1/min), and pseudo-second-order (g/mg g) kinetic rate constants, respectively. It should be noted that K_1 and q_e are determined from the values of slope and intercept of the $\ln(q_e\text{-}q_t)$ vs. at t diagram, while q_e and K_2 are calculated from the slope and intercept values of t/q_t vs. t linear form.

As presented in Fig. 14 and Table 5, the calculated R^2 values were 0.9632 and 0.9989 for pseudo-first-order and pseudo-second-order models, respectively. Consequently, the pseudo-second-order model performed better than the other model for describing the kinetic behavior of cadmium ions removal from aqueous solution by the produced adsorbent. In addition, the calculated adsorption capacities by the applied models were 26.71 and 65.35 mg/g, respectively. These results are in accordance with previously published data [31]. It should be noted that the value of the pseudo-first-order kinetic rate constant, K_1, was equal to 0.047 min^{-1}.

3.6. Adsorption thermodynamics

The spontaneous nature of the adsorption process can be studied through thermodynamic parameters such as Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes considering the variations of equilibrium constant (K_e) vs. time (Table 6) [57]. In addition, the equilibrium constant may be expressed as a function of temperature, $\Delta H°$, and $\Delta S°$ by van't Hoff equation [Eq. (10)].

In equations presented in Table 6, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (Kelvin). The $\Delta H°$ and $\Delta S°$ values can be calculated from the slope and intercept values of lnK_e vs. 1/T line [58]. Fig. 15 and Table 7 illustrate the thermodynamic behavior and parameters of the cadmium adsorption process by the produced adsorbent. According to the achieved data, $\Delta G°$, $\Delta H°$, and $\Delta S°$ changes were all negative. Therefore, the removal of cadmium ions was possible and spontaneous and it can be considered as a desirable process from the thermodynamic viewpoint. Additionally, negative enthalpy values denote that the process adsorption efficiency decreased with temperature, therefore the process was exothermic. Furthermore, the entropy changes were also negative. Consequently, according to the Le-chatelier's principle, irregularities decreased with temperature as the result of the decline of adsorption [59].

Table 6
Thermodynamic parameters equations

Definition	Equation	
Equilibrium constant	$K_e = \frac{q_e}{C_e}$	(8)
Gibbs free energy	$\Delta G° = -RT \ln K_e$	(9)
Van't Hoff equation	$\ln K_e = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$	(10)

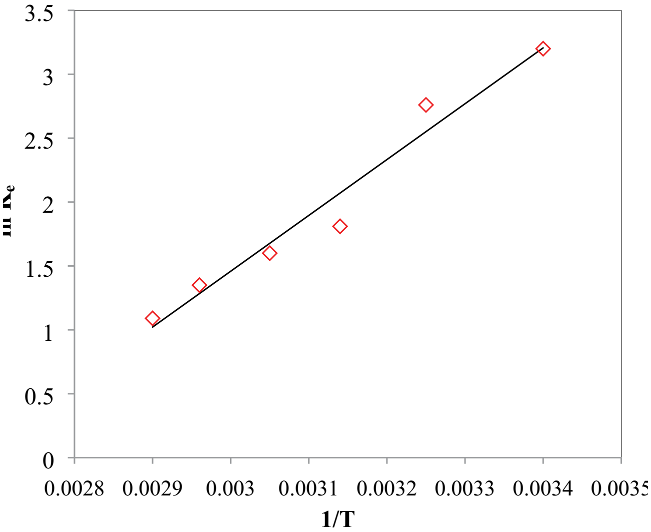

Fig. 15. Thermodynamic diagram for the adsorption of cadmium ions from aqueous solution by the activated carbon adsorbent.

Table 7
Thermodynamic parameters for the adsorption of cadmium ions from aqueous solution by the activated carbon adsorbent

T(K)	$\Delta G°$(KJ/mol)	$\Delta H°$(KJ/mol)	$\Delta S°$(J/mol K)
298	–7.92	–36.325	–96.8
308	–7.04		
318	–4.78		
328	–4.36		
338	–3.79		
348	–3.15		

4. Conclusion

In the current work activated carbon was prepared from the leaves of *Ricinus communis* and was applied for cadmium ions adsorption from aqueous solution. Various analyses including BET, SEM, EDX/Map, FTIR, XRD, and TGA were used to study features of the prepared activated carbon. Moreover, the effect of solution pH, adsorbent dosage, adsorption time, temperature, and initial concentration of cadmium ion on its uptake efficiency was investigated. The maximum removal percentage was 97.71% which was achieved in the following conditions: pH = 8, an adsorbent dosage of 0.6 g/L, 60 min, 298 K, and cadmium concentration of 60 mg/L. Adsorption equilibrium studies approved the higher capability of the Langmuir model in comparison with the Freundlich model for describing the equilibrium behavior of Cd(II) ions removal. Therefore, it suggests that the adsorption of cadmium ions by the produced activated carbon adsorbent was mono-layer. In addition, pseudo-second-order kinetic model described the kinetic behavior of the process better in comparison with pseudo-first-order model. Consequently, chemical sorption may be the rate-limiting step of the process rather than diffusion. Finally, thermodynamic investigations showed that the current adsorption process was feasible, spontaneous, and highly exothermic with decreased irregularities.

Symbols

C_i — Initial concentration of metal ions, mg/L
C_e — Equilibrium concentration of metal ions, mg/L
K_1 — Pseudo-first-order model rate constant, min^{-1}
K_2 — Pseudo-second-order kinetic rate constant, g/mg g
K_e — Adsorption equilibrium constant
K_f — Freundlich model constant, L/mg
K_L — Adsorption energy, L/mg
n — Freundlich model constant
q_e — Equilibrium capacity, mg/g
q_m — Maximum adsorption capacity, mg/g
q_t — Value of the adsorbed ion per gram of adsorbent at time t, mg/g
R — Universal gas constant, J/mol k
%R — Adsorption efficiency
R_L — Adsorption intensity
T — Absolute temperature, K
t — Time, minutes
V — Volume of the solution, L
W — Adsorbent mass, g
$\Delta G°$ — Gibbs free energy, kJ/mol
$\Delta H°$ — Enthalpy, kJ/mol
$\Delta S°$ — Entropy, J/mol K

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