



On the performance of *Ballota undulata* biomass for the removal of cadmium(II) ions from water

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Received 15 August 2016; Accepted 19 November 2016

ABSTRACT

In this study, cadmium ions, Cd(II), were removed from aqueous solutions using *Ballota undulata*. Experimental data were exploited for kinetic and thermodynamic assessments related to adsorption processes. The different variables affecting the adsorption capacity such as pH, contact time, temperature, adsorbent particle size and mass of adsorbent have been studied. Adsorption isotherms were correlated well with the Langmuir isotherm model. The maximum monolayer adsorption capacity was 121.1 mg/g, which is higher than other adsorbents reported. The kinetic data were best described by pseudo-second-order model. The adsorption process was exothermic-spontaneous to indicate its feasibility.

Keywords: Biosorption; *Ballota undulata*; Kinetic models; Isotherms

1. Introduction

Currently, environmental pollution is considered as a major problem facing the societies [1]. One of the main reasons is that many industrial and metallurgical processes in addition to some human activities produce rapidly increasing amounts of wastewater containing harmful pollutants [2–5]. Heavy metal ions are among these pollutants since they are produced in appreciable concentration and therefore represent a significant threat to the ecosystem [4,6].

Most of heavy metal ions are characterized by their solubility and mobility in the liquid phase of the ecosystem. In addition to their toxicity to higher life forms even at low concentration [1], these ions are non-degradable and thus persistent in the environment, leading to both ecological and health problems. Accordingly, the presence of heavy metal ions in the environment at concentrations above critical values is unacceptable, and their removal from the wastewater is very essential [7]. It is familiar that cadmium (Cd), lead (Pb) and mercury (Hg) are the heavy metals with the greatest potential hazard to all humans and the environment due to their acute toxicity [8].

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Particularly, cadmium poses a serious threat to all biota including human health as it accumulates on the environment throughout the food chain. In addition, it is characterized by its high mobility in the terrestrial environment [9]. Consequently, cadmium has been classified as a human carcinogen and teratogen, bone damage, impacting the kidneys, lungs, liver, reproductive organs and the chromosome morphology [10]. Unfortunately, there are many sources of Cd(II) ions in the environment including: electroplating, paint pigments, urban traffic, plastics and stabilizers for PVC, waste incineration, alloy preparation, ceramics and researchable cells and phosphate rocks [11]. Accordingly, it is of primary importance to remove Cd(II) from water and wastewater prior to transport to prevent its accumulation in water, soil and the natural environment.

Conventionally, there is a variety of methods used for the removal of Cd(II) ions from industrial wastewater. These methods include chemical precipitation, chemical oxidation or reduction, ion exchange, electro flotation chemical treatment, evaporative recovery and adsorption using activated carbon [12]. However, most of these processes were found to be ineffective or expensive, and most of these processes are not eco-friendly, because of the production of sludge causing a solid disposal problem [2].

Furthermore, there has been a tremendous effort given to the use of bioadsorption processes by inexpensive biomaterials as a cost-effective, safe and sustainable alternatives for the removal of heavy metal ions including Cd(II) from contaminated areas [13]. These biomaterials include viable and dead biomass, agricultural wastes and plant tissues including neem bark [14], oil palm shell [15], olive cake [16], almond shells [17] and vermiculite [18].

Most of the previous studies have showed that agricultural wastes or plant tissues either in their natural forms or modified forms are highly efficient for the removal of cadmium ions. These materials are usually composed of lignin and cellulose as major constituents. They may also include other polar functional groups of lignin, which includes hydroxyl, carboxyl, carbonyl, phenolic and other groups. These functional groups have ability to bind heavy metal ions found in the wastewater to form relatively stable complexes [19]. It is familiar that *Ballota* represents a genus of about 35 species of flowering plants in the family of *Lamiaceae* that exists in Europe, North Africa and Western Asia, and with the highest diversity in the Mediterranean region. *Ballota undulata* is a perennial herb that grows in waste places and mountains [20]. This plant, which is abundant in many countries including Jordan, has not previously been used as a biosorbent. *Ballota undulata* was investigated chemically and found to contain different multi-hydroxylated compounds such as phenylpropanoidal glycosides (e.g., forsythoside B1, lysionotoside 2), flavones and flavonoidal glycosides (e.g., Gonsalitosin) [21]. Chemical structures of forsythoside B1, lysionotoside 2 and Gonsalitosin (luteolin 3',4',7-trimethyl ether) are shown in Fig. 1. Consequently, our study concentrated on the ability of the plant to combine with heavy metals either chemically or physically. This could be of great important, since the constituents contain a lot of vicinal hydroxyl groups.

Moreover, *Ballota undulata* attracts researchers to investigate its biological importance. For example, its

ethanolic crude extract (70%) was studied and found to have hypoglycemic, insulin-releasing and cholesterol-lowering effects on rats [22]. In addition, the effect of *Ballota undulata* on the reproductive system was studied recently [20]. Kinetic and isotherm models will be proposed to describe the experimental results. In addition, the effect of some operational parameters on the biosorption process will be investigated.

2. Materials and methods

2.1. Adsorbent preparation

The plant *Ballota undulata* used in this study as a bioadsorbent was collected from Jerash City located in the

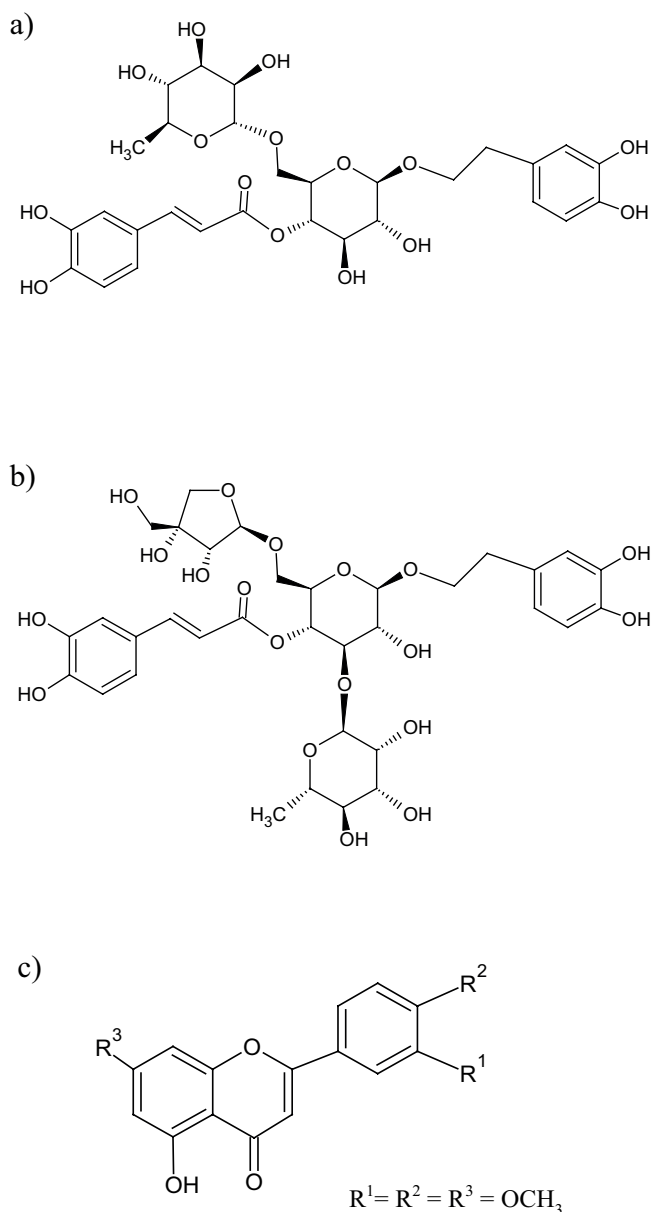


Fig. 1. Chemical structure of: (a) forsythoside B1, (b) lysionotoside 2 and (c) Gonsalitosin (luteolin 3',4',7-trimethyl ether) [21].

north side of Jordan. The flowers of this plant were cut to small parts and dried at temperature of about 30°C for 2 d, and then they were crushed to the desired particle size (D_p). The plant parts were then washed several times using distilled water then with sterile deionized water, and finally filtrated using Buchner funnel. The washing process continued until the filtrate gave approximately zero electrical conductivity value to ensure that there are neither residual heavy metal ions nor soluble salts in the *Ballota undulata* biosorbent. After that, the biosorbent was dried again for 2 d. The dried biosorbent was sieved into several size fractions using standard sieve mesh 18, 30 and 50). Three particle sizes were considered in the present study $D_p = 297, 595$ and $1,000 \mu\text{m}$ that accumulated on sieve of mesh number 50, 30 and 18, respectively.

2.2. Cadmium solution

The cadmium(II) metal salt, cadmium nitrate-4-hydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck Millipore, Darmstadt, Germany), was used as received without further purification. Individual stock metal Cd^{2+} ion solutions of 2,000 ppm concentration were prepared. 5 mL of 0.1 M HNO_3 were added to each stock solutions to prevent the adsorption of the heavy metal ions on the glass wall, to prevent the formation of metal hydroxide and to return the metal ion to dissolved state. Solutions of 50, 100, 150, 250, 300, 350, 400 and 500 ppm were prepared by dilution and kept for further use. 0.1 M HCl and 0.1 M NaOH were used to adjust pH values and to study the effect of pH values on the removal efficiency of *Ballota undulata*.

2.3. Measurements

The conductivity was measured using Lf 537 MWT conductivity meter with MWT Tetracon 96 conductance cell. The pH was measured using 3151 MWT pH meter (MWT GmbH, Germany). Electrical shaker was used for shaking the solution with adsorbent and to adjust the speed in (rpm). The metal ion concentrations were measured using Analyst 300 atomic absorption spectrophotometer equipped with AS-72 autosampler (PerkinElmer, USA).

2.4. Adsorption studies

The adsorption isotherm experiment were carried out initially by adding 100 mg of dried *Ballota undulata* biosorbent to 200 mL of different metal ion solutions with initial concentrations of $C_0 = 50, 100, 150, 250, 300, 350$ and 400 ppm . The mixtures were placed on a rotary shaker (Gallen Kamp, UK) and left overnight. Then, the solutions were filtrated, and the metal ion concentration in the filtrate was analyzed using the atomic absorption spectrophotometer. This procedure was repeated at four different temperatures of 20°C, 30°C, 40°C and 50°C. In this work, each experimental run was carried out in triplicate to rule out the uncertainty in the measurements. Mean and root mean square (RMS) values were calculated and presented in results and discussion section.

On the other hand, the kinetic study experiments were conducted using a stirred batch adsorber. It consists of a baffled Plexiglas tank with 1.7 L working volume, which was mounted with a variable speed mixer (Stuart Scientific, UK).

A two-third of batch adsorber was immersed in a water bath with $\pm 1^\circ\text{C}$ accuracy to ensure isothermal conditions over the period of each experiment. In each experiment, 1.7 L of the $\text{Cd}(\text{II})$ solution was continuously stirred with a certain amount of the plant *Ballota undulata*. Samples of the solution were continuously withdrawn from the adsorber by a suitable syringe at certain intervals. Each experiment continued until equilibrium conditions were reached when no further decrease in the Cd^{2+} concentration was recognized. The effect of several operational parameters on the cadmium equilibrium concentrations in the solution was studied. These parameters include: initial concentration, solution pH, adsorbent dose and temperature. The amount of cadmium ions adsorbed per unit mass of adsorbent, q (mg/g), was calculated using [23,24]:

$$q = \left[\frac{C_0 - C_e}{M} \right] \times V \quad (1)$$

where C_0 and C_e (mg/L) are the concentration of adsorbate at initial and equilibrium states, respectively; M is the mass of adsorbent (g) and V is the volume (dm^3). The percentage removal efficiency was calculated using [25]:

$$\eta (\%) = 100 \left[1 - \frac{C_e}{C_0} \right] \quad (2)$$

2.5. Isotherm and kinetic modeling

In this investigation, two of the most common sorption models were used to fit the experimental data. These are Langmuir and Freundlich isotherm models [26,27]. Langmuir model usually assumes the formation of a monolayer of the adsorbate molecules when equilibrium is attained and the adsorbent is saturated. The general and linear forms of Langmuir model are given by:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (3)$$

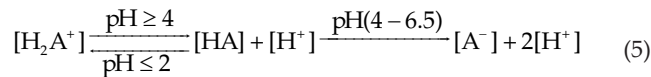
where q_{\max} (mg/g) is the Langmuir constant related to adsorption capacity, and b (L/mg) is a constant related to the affinity between the adsorbent and the adsorbate. The Freundlich model usually represents a process of initial adsorption at the surface followed the formation of multi-layers of the adsorbate as a result of the condensation effect caused by the extremely strong solute–solute interaction. The general form of Freundlich model is:

$$q_e = K_f C_e^n \quad (4)$$

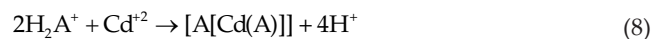
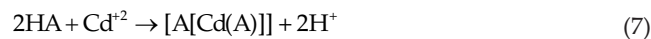
where K_f ($\text{L/mg})^{1/n}$ and n are Freundlich constants. K_f is correlated to the maximum adsorption capacity, and n gives an indication of how favorable the adsorption process.

The kinetic behavior of cadmium ion adsorption by *Ballota undulata* biosorbent was studied. *Ballota undulata* cell surface is expected to be complex nature as it could contain

different active functional groups including carboxyl and hydroxyl groups. The availability of these functional groups as well as their ability to bind metal ions such as Cd^{2+} is strongly affected by the pH of the medium [28,29]. A reaction model is proposed by Mukhopadhyay et al. [1] to describe algal surface functional groups reaction with H^+ to produce several surface active sites that depending on pH value. This chemical reaction model, which could be applied in the case of *Ballota undulata* cells, is expressed as:



As shown in Eq. (5), three different species of active sites: A^- , HA and H_2A^+ are formed on the algal surface depending on the pH value. The reactions of these active species with Cd^{2+} are described by the following chemical equations [1]:



Eqs. (6)–(8) represent chemisorption processes between a divalent Cd^{2+} ions with three different ligands. However, most literature have indicated that the optimum pH for the bioadsorption of Cd^{2+} is in the range 5–6 since $\text{Cd}(\text{OH})_2$ starts to precipitate beyond a pH value of 6 [2]. For this reason, most of the active sites in optimum pH range will be in the form A^- , and its reaction is represented by Eq. (2). For this reason, only this reaction will be considered in this investigation. Accordingly, the rate equation for these reactions could be described by the pseudo-second-order rate equation. However, the pseudo-first-order equation will be tested for comparison purposes. The pseudo-first-order model equation is given as [30,31]:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (9)$$

while the pseudo-second-order equation is given as:

$$q_t = \frac{k_2 q_e^2}{(1 + k_2 q_e t)} t \quad (10)$$

where k_1 (1/min) and k_2 (g/mg min) are the rate constants for first-order and second-order models, respectively. The quantity, q_t , the amount of $\text{Cd}(\text{II})$ ions adsorbed in mg/g of adsorbent was calculated using Eq. (1) by replacing the equilibrium concentration by the concentration, C , at time t .

2.6. Thermodynamic modeling

The thermodynamic parameters, the standard enthalpy (ΔH°) and the standard entropy ΔS° were calculated using [32]:

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where b is the Langmuir equilibrium constant; R (8.314 J/molK) is the universal gas constant and T is the absolute solution temperature in K. The values of ΔH° and ΔS° were calculated from the slope and intercept of plot between $\ln b$ vs. $1/T$. In addition, the standard free energy (ΔG°) can be calculated using:

$$\Delta G^\circ = -RT \ln b \quad (12)$$

where b is the distribution coefficient which can be calculated as:

$$b = \frac{C_{Ae}}{C_e} \quad (13)$$

where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium, and C_e (mg/L) is the equilibrium concentration.

3. Results and discussion

3.1. Effect of adsorbent mass

The effect of varying *Ballota undulata* mass on the adsorption of $\text{Cd}(\text{II})$ ions is shown in Fig. 2. It can be observed that the removal efficiency increases as the *Ballota undulata* mass increases. This is attributed to the availability of the surface area and the increased number of binding sites for the ions [33]. For example, the mean removal efficiency of *Ballota undulata* contacted with initial concentration of $\text{Cd}(\text{II})$ solution of 150 mg/L increases from 19.8% to 95.0% as the mass of adsorbent increases from 50 to 300 mg. However, the $\text{Cd}(\text{II})$ sorption rate declined as the dosage of *Ballota undulata* increased. Similar trends were reported for the biosorption of cadmium using rice straw [34]. At adsorbent mass of 300 mg, the removal efficiencies of the three solution concentrations

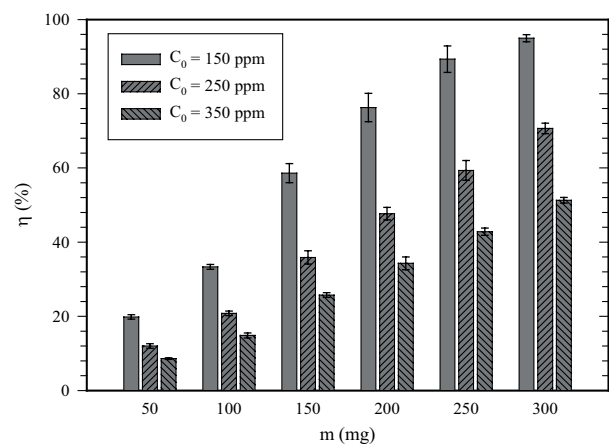


Fig. 2. Effect of adsorbent dosage on the removal of $\text{Cd}(\text{II})$ heavy metal ions from aqueous solutions by batch adsorption at different initial concentrations: $V = 200$ mL, $D_p = 297$ mm, $\text{pH} = 6.0$ and $t = 2$ h.

150, 250 and 350 mg/L are: 95.0%, 70.7% and 51.3%. This difference could be referred to the fact that the adsorbent mass is the same in the three solutions and limited adsorption sites are available for concentrated solutions.

3.2. Effect of pH

The effect of pH on Cd(II) adsorption was studied at various solutions of different concentration. Other parameters like temperature, adsorbent mass and adsorbent particle size were maintained constants. The results were expressed as removal efficiency as shown in Fig. 3. It is clear from the figure that for certain values of Cd(II) initial concentrations, there are an optimum value of pH where the removal efficiency has a maximum value. For three initial concentrations considered ($C_0 = 150, 250$ and 350 ppm), Fig. 3 depicts that the optimum pH value was 6. The corresponding mean removal efficiencies were 33.3%, 20.8% and 14.9% for $C_0 = 150, 250$ and 350 ppm solutions, respectively. The decrease of removal efficiency at low pH values could be attributed to the high mobility of hydrogen ions compared with Cd(II). This means that hydrogen ion will react with active sites before adsorbing the metal ions. The relatively high adsorption capacity at $\text{pH} > 6$ may be a combination of both adsorption and precipitation on the surface of the adsorbent. Similar trend has also been reported for the removal of Cd(II) ions by Bamboo charcoal adsorbent [35]. Cd(II) exists predominantly in the ionic state at pH value > 7 , and the precipitation of $\text{Cd}(\text{OH})_2$ and other Cd(II) species for example $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_3^-$ takes place at pH value < 7 [36]. Consequently, the experiments were carried out at pH 6.

3.3. Effect of particle diameter

Fig. 4 illustrates the variation of removal efficiency with the adsorbent particles diameter at different initial Cd(II) ion concentrations. Three different fractions of *Ballota undulata* particles with particle diameter of $D_p = 297, 595$ and $1,000 \mu\text{m}$ were used. The results shown in Fig. 4 indicate that the extent of Cd(II) ions adsorption by *Ballota undulata* slightly decreased by increasing the particle size. For example, the removal efficiency decreases from 14.9% to 12.1% as the adsorbent particles diameter increases from 297 to $1,000 \mu\text{m}$ when Cd(II) concentration is 350 ppm. It decreases from 33.3% to 30.0% when Cd(II) concentration is 150 mg/L. This behavior can be attributed to the relationship between the effective specific surface area of the adsorbent particles and the particles size. In general, the smaller the adsorbent particles, the greater the amount of metal ions could be adsorbed to the surface [2].

3.4. Adsorption isotherms and thermodynamics

The adsorption isotherm experiments are very important since their results show how the adsorbate molecules are distributed between the adsorbent and the solution at the equilibrium conditions [37]. Fig. 5 illustrates the adsorption isotherms for removal of cadmium ions from aqueous solution using *Ballota undulata* at different operating temperatures ($20^\circ\text{C}, 30^\circ\text{C}, 40^\circ\text{C}$ and 50°C). It is clear from Fig. 5 that the loading capacity, q_e , increases sharply at

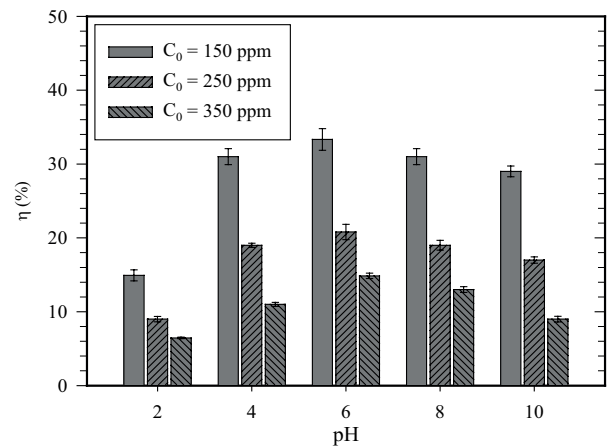


Fig. 3. Effect of pH on the removal of Cd(II) heavy metal ions from aqueous solutions by batch adsorption at different initial concentrations: $V = 200$ mL, $m = 100$ mg, $D_p = 297 \mu\text{m}$ and $t = 2$ h.

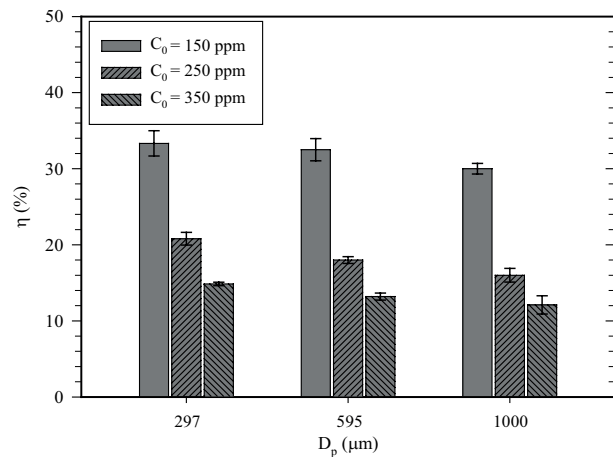


Fig. 4. Effect of adsorbent particle size on the removal of Cd(II) heavy metal ions from aqueous solutions at different initial concentration: $V = 200$ mL, $m = 100$ mg, $\text{pH} = 6$ and $t = 2$ h.

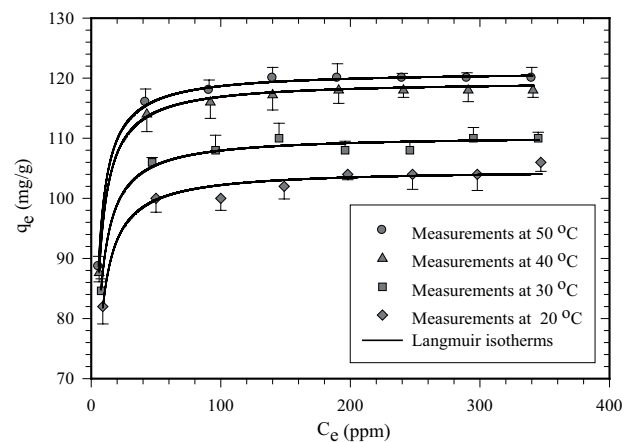


Fig. 5. Adsorption isotherms for Cd(II) adsorption onto *Ballota undulata* at different temperatures: $V = 200$ mL, $m = 100$ mg, $D_p = 297 \mu\text{m}$, $\text{pH} = 6$ and $t = 2$ h.

Table 1

Langmuir and Freundlich parameters at different temperatures for adsorption of cadmium ions from aqueous solution using *Ballota undulata* (experimental conditions: $m = 100$ mg; solution volume $V = 200$ mL; pH = 6; adsorbent particle size of $D_p = 297$ μm and contact time of $t = 2$ h)

T ($^{\circ}\text{C}$)	Langmuir isotherm model			Freundlich isotherm model		
	q_{max} (mg/g)	b (L/mg)	R^2	K_L (mg/g)	n	R^2
20	104.8	0.395	0.980	74.69	16.25	0.887
30	110.5	0.428	0.986	79.55	16.81	0.804
40	119.5	0.445	0.991	83.56	15.28	0.800
50	121.1	0.482	0.998	84.98	15.37	0.816

relatively low equilibrium concentrations. At relatively high values of Cd(II) equilibrium concentration, the loading capacity increases slightly until it reaches its maximum values. This type of adsorption is favorable and indicates high affinity between the adsorbent and the adsorbate. In addition, Fig. 5 shows that the adsorption capacity of *Ballota undulata* slightly increases with temperature at the same equilibrium concentrations. The maximum loading capacity at 20 $^{\circ}\text{C}$ and 50 $^{\circ}\text{C}$ were about 106 and 120 mg/g, respectively. The increase reaches about 20% as the temperature increases from 20 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$. This moderate increase could be referred to the reversible nature of the adsorption process. It is familiar that as the temperature increases the viscosity of the solution decreases that enhances the intraparticle diffusion of the Cd(II) ions inside the plant tissues.

In addition, the desorption rate of the Cd(II) is expected to be increased as the temperature increases [2]. The Langmuir and Freundlich isotherm models were used to describe the adsorption characteristics. The values of the model constants and squared correlation coefficients, R^2 , are given in Table 1. It is evident from Fig. 5 as well as the data in Table 1 that the Langmuir isotherm gives a better fit than Freundlich isotherm model, as indicated by the values of R^2 approach unity. This demonstrates that the adsorption of Cd(II) from aqueous solution using *Ballota undulata* is characterized by the formation of a monolayer coverage of the adsorbate molecules on the adsorbent outer surface. In addition, this adsorption has a homogenous nature or equal activation energy for each adsorbed molecule. These results are in agreement with those of Kadirvelu and Namasivayam [11] for the adsorption of cadmium(II) by modified agricultural wastes and Al-Qodah [2] for the adsorption of cadmium by activated sludge. Table 1 gives the values of the monolayer maximum loading capacity q_{max} predicted by Langmuir model. The higher value of q_{max} was 121.1 mg/g at temperature of 50 $^{\circ}\text{C}$. This value is compared with those found in the literature as shown in Table 2. It is clear that the maximum loading capacity obtained in the present investigation at 50 $^{\circ}\text{C}$ is quite high and promising [16,34,38,39,40].

On the other hand, by plotting a graph of $\ln b$ vs. $1/T$, see Eq. (11), the values ΔH° and ΔS° can be estimated from the slopes and intercepts [26]. Table 3 shows negative values of standard specific enthalpies (ΔH°), which indicates the exothermic nature of the adsorption process of Cd(II) with *Ballota undulata*. This fact was previously confirmed by the isotherm experiments at different temperatures. This means that as the temperature decreases more energy is available to

Table 2

Maximum adsorption capacity, q_{max} , for adsorption of cadmium ions from aqueous solution using different adsorbents

Adsorbent	q_{max} (mg/g)	C_0 (mg/L)	References
Olive cake	65.40	100	Al-Anber and Matouq [16]
<i>Pinus halepensis</i> sawdust	7.350	50	Semerjian [38]
Modified kaolinite	36.47	400	Sari and Tuzen [39]
Unmodified rice straw	13.90	350	Ding et al. [34]
Xanthated nano banana cellulose	154.3	300	Pillai et al. [40]
<i>Ballota undulata</i>	121.1	350	Present study

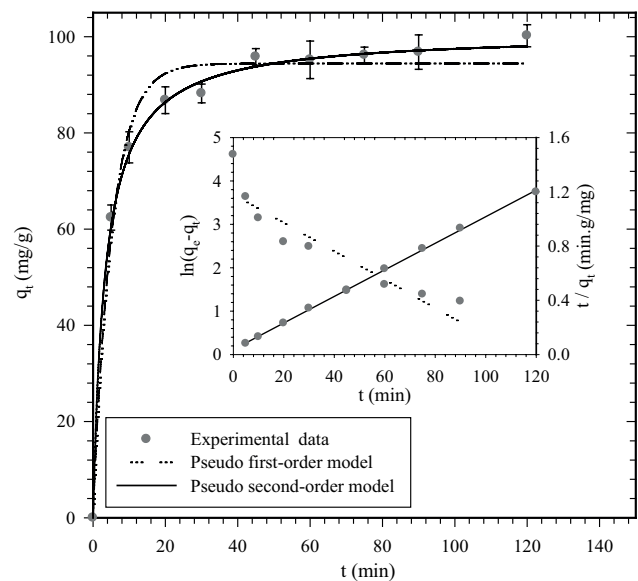


Fig. 6. Pseudo-first-order and pseudo-second-order kinetic models for Cd(II) ions adsorption onto *Ballota undulata* at $T = 20^{\circ}\text{C}$, $C_0 = 100$ ppm, $m = 100$ mg, $V = 200$ mL, $D_p = 297$ μm and pH = 6.0.

Table 3

Thermodynamic parameters for adsorption of cadmium ions from aqueous solution with different initial concentration with $m = 100$ mg, $V = 200$ mL, $D_p = 297$ μ m, pH=6.0 and contact time of 2 h

C_0 (ppm)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)			
			$T = 293$ K	$T = 303$ K	$T = 313$ K	$T = 323$ K
150	-7.07	-0.0185	-1.648	-1.464	-1.279	-1.094
250	-5.26	-0.0068	-3.266	-3.198	-3.130	-3.062
350	-4.70	-0.0016	-4.240	-4.225	-4.209	-4.193

Table 4

The biosorption kinetic model rate constants for Cd(II) onto *Ballota undulata* at $T = 20^\circ\text{C}$, $C_0 = 100$ ppm, $m = 100$ mg, $V = 200$ mL, $D_p = 297$ μ m and pH=6.0

C_0 (ppm)	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (L/min)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2
100	0.0327	39.6	0.820	0.0026	102.0	0.999

enhance the adsorption. Moreover, Table 3 depicts that the values of standard entropy of activation (ΔS°) are negative, which indicates low affinity of the *Ballota undulata* adsorbent for positive ions and results with a decrease in randomness at the interface between the solid liquid phases. However, the absolute values of both ΔH° and ΔS° were found to decrease as the initial concentration increases. Table 3 also shows the corresponding values of standard free energy (ΔG°) calculated using Eq. (12) at different temperatures. As can be shown in Table 3, all values of ΔG° were negative at all temperature considered, which indicates the spontaneous nature of adsorption and feasibility of such treatment process [41].

3.5. Adsorption kinetics

The effect of contact time, t , on the loading capacity, q_t , is given in Fig. 6 where the initial Cd(II) concentration was 100 mg/L, adsorbent mass 100 mg, V 200 mL, particles diameter, D_p 300 μ m, pH 6.0 and T 20°C. It can be observed from Fig. 6 that the contact time needed to reach equilibrium conditions was about 60 min. This indicates that there is a strong interaction between Cd(II) and *Ballota undulata*. In addition, Fig. 6 depicts that the amount of Cd(II) ion adsorbed increases with time until it approaches a pseudo-steady-state value known as the equilibrium loading capacity, q_e . When the equilibrium conditions are reached the adsorbate molecules in the solutions are in a state of equilibrium with the molecules adsorbed by the adsorbent. This state indicates negligible further removal of Cd(II) ions and referred to the continuous decrease in the concentration driving force. Fitting results of the experimental data to the pseudo-first-order and pseudo-second-order models are also shown in Fig. 6.

Table 4 summarizes the kinetic parameters resulted from fitting the experimental data using these two models. Such kinetics parameters were found by plotting $\ln(q_e - q_t)$ and t/q_t against the contact time, t , for pseudo-first-order and pseudo-second-order models, respectively (see Eqs. (9) and (10)). By comparing the values of the squared correlation coefficients in Table 4 and observing Fig. 6 demonstrate that the kinetic of adsorption process is best described by

the pseudo-second-order model. These kinetic results are in excellent agreement with those of John et al. [13] for the adsorption of cadmium on *Cassia siamea* bark and those of Awwad and Salem [42] for the adsorption of cadmium ions with loquat (*Eriobotrya japonica*) leaves. The above results suggest that the adsorption of Cd^{2+} into *Ballota undulata* is chemisorption process with a rate-determining step involving the formation of chemical bonds [1] via sharing of electrons between oxygen or nitrogen atoms of the plant with the Cd^{2+} metal ions.

4. Conclusions

Ballota undulata is an abundant plant that can be easily used as a cheap bioadsorbent for heavy metal ions such as Cd^{2+} . The maximum adsorption capacity of the *Ballota undulata* was found to be comparable with many bioadsorbents, and it reaches 121.1 mg/g. Langmuir was found to fit the experimental adsorption data of the heavy metal onto *Ballota undulata*. The maximum adsorption capacity of the sludge was found to be increased as the temperature increases. The maximum loading capacity at 20°C and 50°C were about 106 and 120 mg/g, respectively. The adsorption capacity was found to increase by increasing the adsorbent mass. On the other hand, it was found that there is an optimum value of the pH of about 6. The results obtained for the adsorption of Cd^{2+} by *Ballota undulata* indicate encourage to design a continuous adsorption column packed with *Ballota undulata* to be used to treat effectively wastewater treatment containing heavy metal ions.

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