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Kinetic and Thermodynamic Study of Co^{2+} and Pb^{2+} Ions Adsorption onto Chicory Leaves Powder as a Native Plant Sorbent

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Abstract

In this study, chicory leaves were used as a native adsorbent to remove Pb (II) and Co (II) ions from aqueous solutions. A set of experiments were carried out to determine the optimal conditions and to explore the effects of various parameters such as contact time, pH, adsorbent dosage, initial concentration and temperature. The obtained optimal conditions for removing both ions were: pH 7-8; contact time 20 minutes, dosage 40 mg and initial concentrations 10-20(mg / L). The adsorption data showed that the adsorption process is more consistent with Langmuir isotherm. The kinetic data were matched better with the pseudo second order model with a reliable correlation coefficient. The calculation of thermodynamic quantities showed that the adsorption process was spontaneous and exothermal.

Keywords: Adsorption; Chicory leaves powder; Adsorbent; Isotherm; Kinetics and thermodynamics

Introduction

Heavy metals in water have been a major preoccupation for many years because of their toxicity towards aquatic-life, human beings and environment [1]. Two such contaminants are cobalt and lead, which are widely used in industrial activities such as electronic components manufacturing, paint manufacturing, mechanical alloying, metallurgical alloying. A number of technologies for the removal of inorganic and organic contaminants from aqueous solutions have been developed over years. One of these methods is the adsorption process. In this study, we used chicory leaves powder as a native adsorbent to adsorb cobalt and lead ions.

Chicory is in two types; one species is cultivated; the other is wild and growing on its own. The main origin of this plant is Central Europe, the western and central parts of Asia and North Africa, and has a large dispersal in different parts of Iran. It has many medicinal properties and its mechanism of action in the liver. It seems that to be suitable for adsorbing ionic pollutants. The main objective of the study is to examine the adsorption behavior of chicory wild powder as adsorbent with respect to Co (II) and Pb (II) ions. The effects of the various factors, such as initial concentrations of solution, contact time; adsorbent dosage, temperature, and pH values were investigated. The kinetics and thermodynamics of Co (II) and Pb (II) ions adsorption onto the adsorbent were also studied.

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Materials and Methods

Preparation of adsorbent

Chicory leaves were washed and dried in the laboratory and powdered by a milling machine. Then they passed through the mesh number 100. Then 5 g of chicory leaves powder was placed in 0.01 M (KOH) solution for 15 hours. After this time, the solution was filtered and rinsed with distilled water, and then it was dried for 3 hours at 90 ° C in oven and placed in a desiccator for one day. Then it was tapped to become powder [2,3].

Apparatus and materials

All chemical materials used in this study were of analytical grade. Lead nitrate and cobalt nitrate, were purchased from Merck Company. An AA 3000 model atomic absorption spectrometer (CAT Co.) was used for measuring the concentrations of Co^{2+} and Pb^{2+} ions in the studied solutions. A 5500 model pH meter (EUTECH Co.) was used to measure pH of the solutions and the pH of the solutions were adjusted using 0.01 N HCl or 0.01 N NaOH. A thermostatic orbit incubator shaker Neolab model was used in the studied experiments. The characteristics of the adsorbent were analyzed by X–ray powder diffraction (XRD).

Adsorption experiments

The desirable solutions were prepared by diluting Pb (II) and Co (II) ions solutions (1000 mg L^{-1}). It was obtained by dissolving an adequate amount of $Pb(NO_3)_2$ or $Co(NO_3)_2.6H_2O$ salts into the sufficient deionized water respectively, so to achieve the concentrations of 1000 mg L^{-1} in each case. Different initial concentrations of the metal ions were prepared by diluting the obtained stock solution [4].

Through the initial experiments, 20 mg of the adsorbent were mixed with 50 ml of the appropriate metal ion solution of appropriate concentration. The initial metal ion concentrations were checked from 10 to 80 mg/L at room temperature, so the adsorbent dosage was fixed and pH not changed. After shaking the appropriate mixture for 20 minutes, the adsorbent was removed from the solution by filtering the solution on the appropriate filter paper, and then the metal ion concentration in the filtered aqueous solution was determined by atomic absorption spectrometer [3]. (Since the atomic absorption spectrum is measured with the low concentration solutions, all filtered solutions were diluted in the limits of the standards of the desired ions. Finally, after reading the absorbance of the solutions, the concentrations were multiplied by the dilution factor).

The amount, mg, of the adsorbed Pb (II) and Co (II) ions per gram of Chicory leaves powder at **e**quilibrium, q_e (mg/g) or adsorption capacity, and the removal percentage, (% A), were calculated using the following equations [1,5]:

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

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ions respectively (mg/L). V is the volume of Pb (II) or Co (II) solution (L) in the batch experiment and m is the mass of the sorbent (g). The results of the preliminary experiments are presented in **FIG. 1** (Leading to achieve the optimal concentration). The maximum removal percentage for Pb (II) ion is at a concentration of 30 (mg L^{-1}) and for Co (II) ion at a concentration of 15(mg L^{-1}). In order to determine the other optimal conditions, based on the result of the preliminary experiment, the effects of the other parameters such as contact time, pH solution, adsorbent dosage, temperature and initial concentration were examined [6]. **FIG. 1** shows the plot of the removal percentage of the ions versus the initial concentration and in **FIG. 2**, the capacity of adsorption, q_e is the amount (in mg) of the sorbate that is adsorbed on one gram of the sorbent, is plotted versus the initial concentration.

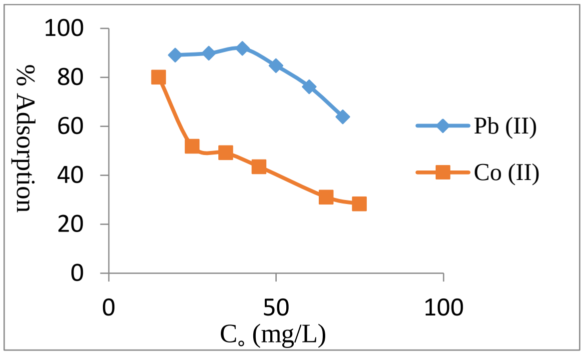

FIG. 1. **The removal percentage of the studied ions versus the initial concentration through the initial conditions.**

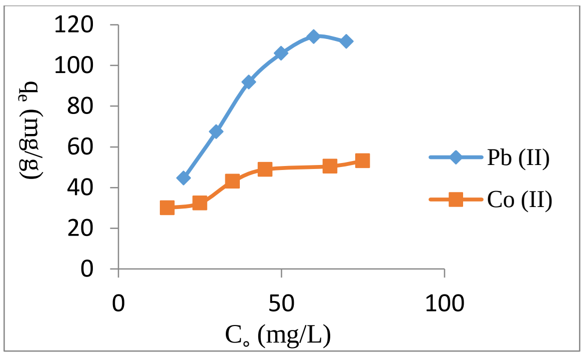

FIG. 2. **The plot of the adsorption capacity versus the initial concentration on the basis of the initial experiments.**

Results

The effect of contact time

One of the most meaningful and significant parameters in the adsorption process is the equilibrium contact time. The effect of contact time on the adsorption process was well studied and evaluated [7,8]. Each experiment was performed using 20 mg of adsorbent at normal pH solution and at temperature 25°C. The initial concentrations were 15 (mg/L) and 30 (mg/L) for Co (II) and Pb (II) respectively. The obtained results are shown in **FIG. 3**, it is clear that the adsorbent exhibited a gradual increase for the metal ions adsorption, when the contact time was increased. It was observed that after 20 min there is no change in the uptake of metal ions. Hence, 20 min was chosen as the optimum contact time for both ions.

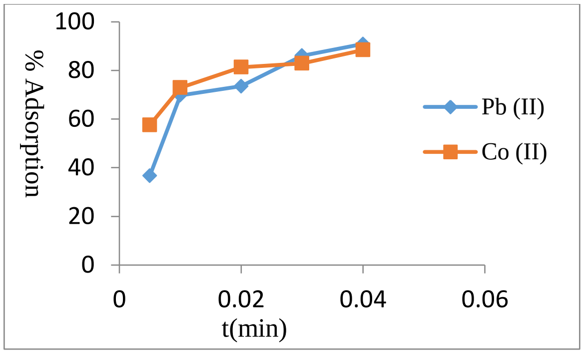

FIG. 3. **The effect of contact time on the removal percentage.**

The effect of ph

The pH value plays an important role with respect to the adsorption of particular ions on various adsorbents [9]. In order to evaluate the effect of pH on the adsorption of metal ions Pb (II) and Co (II) onto the adsorbent (Chicory leaves powder), the experiments were conducted under constant experimental conditions, whit an initial concentrations 15 (mg/L) and 30 (mg/L) for Co (II) and Pb (II) respectively and the amount of the adsorbent was chosen 20mg for both ions and the contact time was set at 20 minutes. The results are represented in **FIG. 4**.

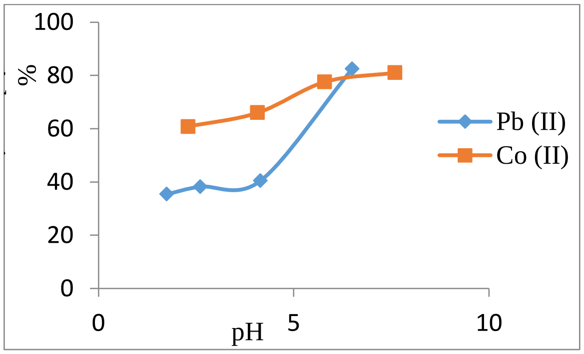

FIG. 4. **The effect of ph on the removal percentage.**

The obtained results indicate that the removal degree for two ions was pH dependent. We choose the value of pH 6-8 as the optimal pH (at higher pHs, the studied ions may be precipitated as own hydroxides).

The effect of adsorbent dosage

The availability of sufficient adsorbent is an important parameter to be considered because it determines the number of free adsorption sites for a given initial concentration of ions [10]. The experiments were carried out at pH 6 for Pb (II) and pH 7 for Co (II), contact time 20min and initial concentration 30 (mg/L) for Pb (II) ion and 15 (mg/L) for Co (II). The amount of adsorbent dosage was changed from 5 to 40 mg for both ions. **FIG. 5** shows the effect of Chicory dosage on the removal percentage of desired ions.

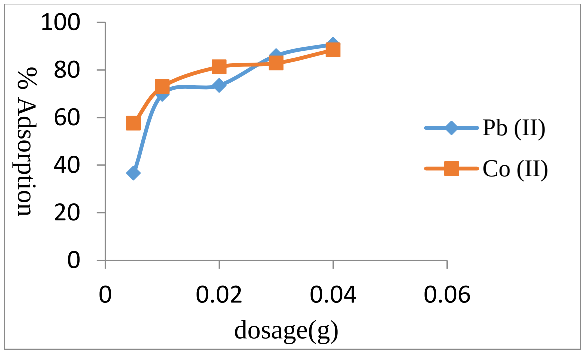

FIG. 5. **The effect of adsorbent dosage on the ions removal percentage.**

According to the **FIG. 5**, with increasing the adsorbent dosage, the removal percentage is increased, and the optimal dosage was 40 mg.

The effect of initial concentration

The initial ion concentration is another remarkable variable that can affect the adsorption process. The effect of initial concentration on the removal percentage of Pb (II) and Co (II) ions was investigated by changing the initial concentration from 10 to 70 mg/L. The obtained results are represented in **FIG. 6 and 7**. As we can see, the removal percentage (% adsorption) decreases with increasing the initial concentration, but the adsorption capacity, q_e (mg/g), increases with increasing the initial concentration. The maximum removal percentage occurred at initial concentration of 20 (mg/L) for Pb (II) ion, and 10 (mg/L) for Co (II) ion.

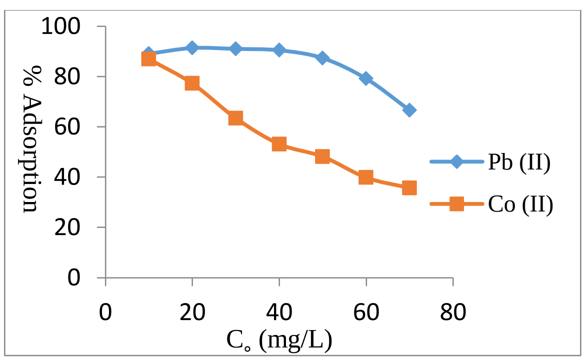

FIG. 6. **The effect of initial concentration on the ions removal percentage under optimum conditions.**

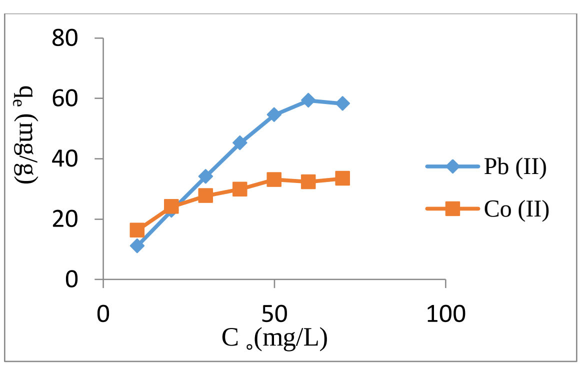

FIG. 7. **The effect of initial concentration on the adsorption capacity, q, under the optimum conditions.**

Adsorption isotherms

Adsorption isotherms are essential for the description of the interactive behavior between adsorbate and adsorbent, and they are critical in optimizing the application of an adsorbent. Several isotherm equations are available but two important of them were applied to fit the equilibrium data in this study [11-15]. The mathematical expressions of these two isotherms are as below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right)\frac{1}{C_e} \quad \text{"Langmuir isotherm"} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \text{"Freundlich isotherm"} \quad (4)$$

where q_e (mg/g) is the amount of ions adsorbed per unit mass of the adsorbent at equilibrium; C_e (mg/L) is the liquid phase concentration of ions at equilibrium; q_m (mg/g) is the maximum adsorption capacity according to the Langmuir monolayer adsorption; K_L (L/mg) is the equilibrium constant of the Langmuir isotherm; K_F $(mg/g)(L/mg)^{1/n}$ and n are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. To obtain the Langmuir isotherm parameters, using the experimental data, the plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ was drawn. According to equation (3), the slope and intercept of the plot are $\frac{1}{q_m K_L}$ and $\frac{1}{q_m}$ respectively, which enable us to calculate the values of q_m and K_L. The Langmuir linear equation and the Freundlich linear equation for Pb (II) and Co (II) ions removing are drawn in **FIG. 8 and 9** respectively. From the Freundrich equation, the values of K_F and n can be deduced from the slope $\left(\frac{1}{n}\right)$ and the intercept (Log K_F). The obtained Langmuir and Fr eundlich parameters based on the results of this research are listed in **TABLE 1**.

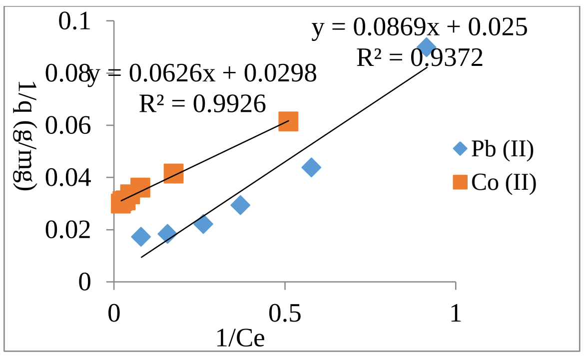

FIG. 8. **The linear Langmuir isotherm for removing Pb (II) and Co (II) ions by Chicory leaves powder adsorbent.**

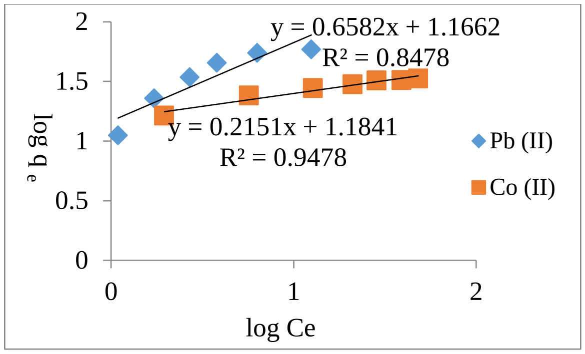

FIG. 9. **The linear Freundlich isotherm for removing Pb (II) and Co (II) ions by Chicory leaves powder adsorbent.**

TABLE 1. **The Langmuir and Freundlich isotherms model parameters.**

ion	Langmuir model K_L (L/mg) q_m(mg/g) R^2	Freundrich model K_F($mg^{1-(1/n)}L^{1/n}$ g^{-1}) n R^2
Pb (II)	0.287 40 0.9372	14.655 1.51 0.8478
Co (II)	0.476 33.55 0.9926	15.13 4.64 0.9478

Adsorption thermodynamics

The spontaneity and feasibility of the adsorption process can be determined by the related thermodynamic quantities, such as Gibbs free energy changes (ΔG)°, enthalpy changes (ΔH)° and entropy changes (ΔS)°, as follow [16]:

$$\Delta G^{\circ} = -RTLnK_C \quad (5)$$

$$LnK_C = -\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^{\circ}}{R} \quad (6)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (7)$$

where R is the ideal gas constant (0.008314 kJ/mol.K), and T is temperature (K). The enthalpy change and the entropy change were calculated from the slope and intercept of the plot of ln (K_c) versus 1/T (**FIG. 10**).

Thermodynamic studies were performed in the range of 298-343 K, under the optimum conditions (Pb (II) initial concentrations was 20(mg/L), pH 6-7, adsorbent dosage 40mg, and contact time 20 minutes and Co (II) initial concentration 10(mg/L), pH 7-8, adsorbent dosage 40mg, and contact time 20 minutes).

In order to extend the above equations, it may be assume a conditional equilibrium constant as follow:

$$K_C = \frac{q_e}{C_e} \quad (8)$$

where q_e and C_e are the amount, mg, of adsorbed ion per mass of adsorbent, g, (mg/g) and the concentration of considered ion in solutions (mg/L), respectively, while there is no a reliable thermodynamic criterion respect to the definition of equation 8. Nevertheless, this definition is used in the major research papers in connection with adsorption studied. Upon conditional K_C (eq.8) and thermodynamic equations (5 and 6) and **FIG. 10**, one can deduce the values of ΔG°, ΔH° and ΔS° related to Pb (II) and Co (II) ions adsorption onto the Chicory leaves powder as the sorbent. The obtained values are listed in **TABLE 2**.

In **TABLE 2**, the negative value of ΔH° shows the exothermic nature of the process. The free energy change, ΔG°, is negative, indicating a spontaneous process. The more negative the ΔG°, the more spontaneous the adsorption process, hence, it is expected a higher adsorption capacity. Finally, the negative values of the entropy show a decrease in randomness at the adsorbate/adsorbent interface during the adsorption [17,18].

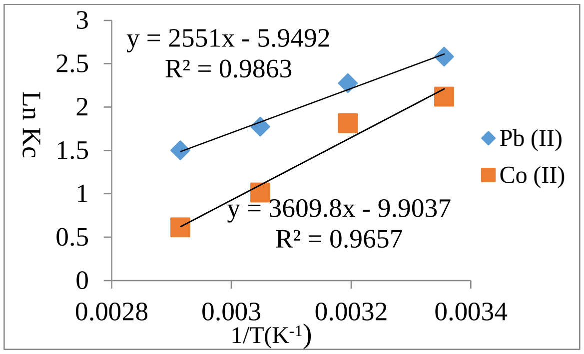

FIG. 10. **The plot of Ln K_C versus 1/T.**

TABLE 2. **Thermodynamic parameters for Pb (II) and Co (II) ions adsorption onto chicory leaves powder.**

T(K) ΔH° (kJ/mol) ΔS°(kJ/mol K) ΔG°(kJ/mol)	
Pb (II)	298 -21.065 -0.046 -7.190
	313 -6.492
	328 -5.794
	343 -5.095
Co (II)	298 -30.001 -0.082 -5.483
	313 -4.249
	328 -3.014
	343 -1.780

Adsorption kinetics

The kinetic experimental data of this study were compared with the widely used pseudo-first-order and pseudo-second-order models, which are generally expressed as follows [19-22]:

$$Ln\left(q_e - q_t\right) = Lnq_e - k_1 t \quad (9)$$

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

where q_e and q_t are the amount (mg/g) of adsorbed ions at equilibrium and at time t (min) respectively, k_1 is the rate constant of the pseudo first-order adsorption process (1/min), k_2 is the rate constant of the pseudo second-order adsorption process (g/mg. min) [23,24]. In this study, the kinetics of adsorption of Pb (II) and Co (II) ions onto Chicory leaves powder as adsorbent was investigated by taking 100 ml of each ion solution (20 mg/L) and monitoring each solution according to the previous procedure (solution pH 7-8 and adsorbent dosage 20mg, respect to the kinetic experiments). The time duration was chose in the range of 10-60 min. In **FIG. 11 (a, b),** the plots of adsorption kinetic models are depicted and the obtained kinetic parameters are listed in **TABLE 3**. Adsorption kinetics of the adsorbed ions were better fitted with pseudo-second order kinetics and respect correlation factors were fairly good.

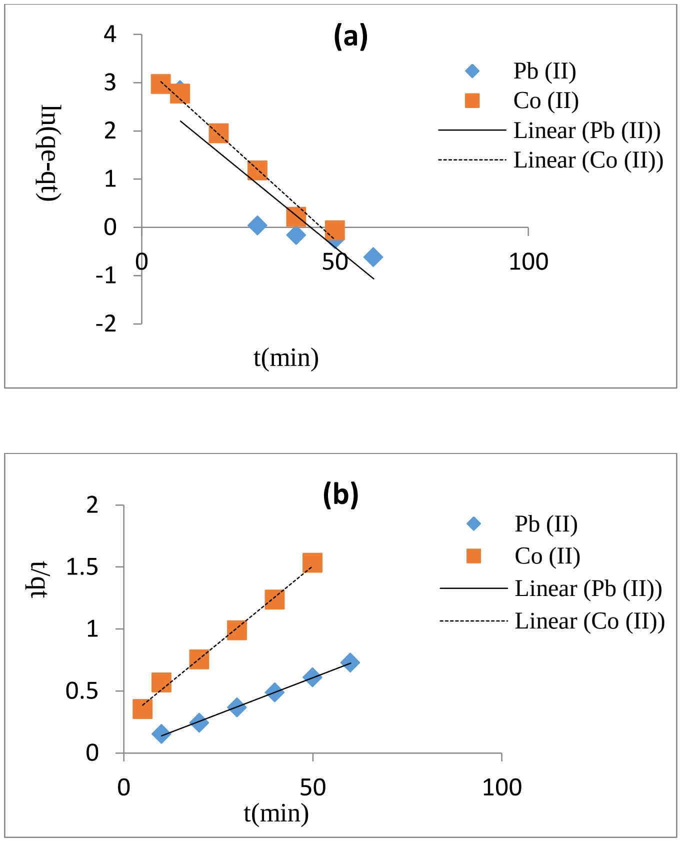

FIG. 11. **Pseudo-first order model (a), Pseudo-second order model (b), respect to the adsorption kinetics Pb (II) and Co (II) ions onto Chicory leaves powder.**

TABLE 3. **Kinetic parameters for Pb (II) and Co (II) ions adsorption onto chicory leaves powder.**

	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**
Pb (II)	7.767	0.065	0.804	0.988	1.02	0.998
Co (II)	9.189	0.0727	0.953	40.160	0.002	0.994

Conclusion

In this study, the thermodynamic and kinetic adsorption behavior of Pb (II) and Co (II) ions was investigated by using a native plant adsorbent (Chicory leaves powder). It was found that the optimal pH, contact time and adsorbent dosage are 7, 20 min and 40mg at 298 K for both Pb (II) and Co (II) ions respectively. The removal percentage was increase with decreasing the initial concentration. The obtained adsorption isotherms indicated that the Langmuir model can better fits our experimental data. The thermodynamic analysis revealed that the studied adsorptions were spontaneous and exothermic. The adsorption kinetic experiments showed that the adsorption of Pb (II) and Co (II) ions onto chicory leaves powder as a native plant adsorbent is finally, pseudo second-order kinetic model. In addition, from the experimental data of this work and analyzing them theoretically and experimentally, one can conclude the Chicory leaves powder as a native plant sorbent is fairly a good candidate for adsorbing some metal ions from the aqueous media.

Acknowledgments

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