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Co^{2+} ion adsorption behavior on plum stone carbon prepared by a solid-combustion process

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ABSTRACT

Co^{2+} ion adsorption behavior on plum stone (*Spondias purpurea*) carbon (PSC) prepared by a solid-combustion process in batch mode was studied. The effects of various important adsorption parameters, such as the contact time, cobalt concentration, pH, and temperature were investigated. The as-prepared powders were characterized using X-ray diffraction, scanning electron microscopy, and N_2 physisorption measurements. Porous and amorphous PSC was obtained with a BET-surface area of 286.06 m^2/g and a maximum Co^{2+} ion adsorption capacity of 4.23 mg/g. The kinetic data, analyzed by non-linear regression, obeyed a pseudo-second-order model with intra-particle diffusion as one of the rate determining steps and showed that the equilibrium behavior can be well described by a Langmuir isotherm. The obtained thermodynamics parameters indicate that the adsorption process is endothermic, spontaneous, and has a chemical adsorption mechanism. The present study revealed that the PSC material can be used as an alternative to more costly adsorbents and that the outcome of this study may be helpful in the design of treatment plants for treatment of Co^{2+}-rich effluents.

Keywords: Plum stone carbon; Co^{2+} adsorption; Solid-combustion process; Kinetics; Thermodynamic parameters

1. Introduction

It is well known that the efficiency and cost-effectiveness during a wastewater adsorption process is determined by choosing suitable adsorbent particles [1]. Recognizing this in the search for materials with appropriate physicochemical characteristics to be used as efficient and low-cost adsorbents [2–6], many researchers around the world have studied numerous potential solid materials as adsorbents, and several efforts, including the development of chemical processes, have been developed to reduce the hazardous effects of toxic pollutants. Abbas et al. [7] show a critical review of adsorption applied to the water pollution caused by heavy metal discharge. The methods that have been employed for the removal of heavy metals from water are mentioned, focusing on the adsorption capacity of carbon nanotubes. However, in search of cheap and efficient adsorbents, silica and carbon from

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agricultural waste have been used [8–14]. For instance, activated carbon has been widely recognized as the oldest and most versatile adsorbent used in wastewater treatment to remove diverse organic and inorganic pollutants due to its large specific surface area, high adsorption capacity, porous structure, and good selective adsorption characteristics, which depend on their precursors as well on the synthesis method [15]. Currently, agricultural waste materials are good precursors for the preparation of carbonaceous adsorbents for water pollution control because they are readily available and are low-cost materials, which are factors that play a major role in precursor selection. Various fruit stones, such as apricot stones [16], waste olive stones [17], cherries [18] and others, have already been studied and tested as agricultural waste raw materials as effective carbonaceous materials for the removal of aqueous contaminants. These stones are abundant and cheap, have a high organic (carbon) content and low inorganic content, and can easily be activated [19]. In this context, materials prepared by the combustion method have attracted increasing interest because of their novel characteristic properties and potential technological applications; typically, products of combustion synthesis have large specific surface areas and porosity, and are chemically homogeneous materials [20]. In particular, plum stone carbon (PSC) from solid-combustion has not been studied. The plum (*Spondias purpurea*) is a small red fruit with an ovoid shape and is 3 cm long and 1.5 cm wide. It has a yellow pulp, is juicy and sweet and sour, and has a large and fibrous stone that is 0.5–0.75 cm long. It is an abundant fruit from Michoacán State in México and has a high production of 18,740 tons per year. Therefore, given this perspective and current efforts toward the development of low-cost alternative adsorbents, carbonaceous plum stones (*S. purpurea*) are an agro-based waste that has been emerged as a valuable source with potential utilization as an adsorbent for wastewater treatment.

Cobalt has both beneficial and harmful effects on human health. Cobalt is beneficial for humans because it is component of vitamin B12, which is essential to maintain human health, and because it has been used as a treatment for anemia, including in pregnant women. However, at high concentrations, cobalt can have toxic or harmful effects on the lungs, including asthma, pneumonia, and wheezing, which have been observed in people exposed to cobalt [21]. Cobalt is regularly ingested through water, causing damage mainly in the digestive tract due to its corrosiveness, but the major cobalt toxic factors are its carcinogenic and teratogenic characteristics [22]. Cobalt is widely used in many industries, and its most important applications are in the electronic, metallurgical, and paint industries. As a result, cobalt can be dispersed into different ecosystems and cause serious problems. The permissible limits of cobalt for irrigation and drinking water are set at 0.05 and 0.05 mg/L, respectively [23]. Therefore, cobalt removal from wastewater is of primary concern.

In this work, we present the preparation of a carbonaceous material by the solid-combustion of plum stones (*S. purpurea*) as local agricultural waste and investigate their Co^{2+} ion adsorption properties in batch mode as a function of various adsorption parameters (contact time, initial metal concentration, pH, and temperature).

2. Experimental

2.1. Materials

Plum stones that were washed, dried, and powdered were used as precursors for a further solid-combustion process to prepare a carbonaceous material. The following analytical grade reagents were used as starting chemical precursors without further purification: NH_4NO_3 (Sigma Aldrich, 99–100 wt.% purity) and NH_2CONH_2 (Sigma Aldrich, 99–100 wt.% purity). A stock solution of Co^{2+} ions was prepared by dissolving an exact quantity of $Co(NO_3)_2{\cdot}6H_2O$ (Baker, 100 wt.% purity) in distilled water. Solutions of 0.1 M NaOH and 0.1 M HCl were used for pH adjustment.

2.2. Preparation and characterization of the carbonaceous adsorbent

A PSC adsorbent was prepared from red plum stones; collected from local agricultural fields around Jungapeo, Michoacán, México; and were washed with water and dried in an oven for 24 h at 120˚C. Then, the dry plum stones were milled in an agate mortar, and the powders were treated through a solid-combustion process according to the following method: 3.6 g of dried-milled plum stones powders with 9 g of urea and 9 g of NH_4NO_3 were mixed. The solids were transferred directly into a 50-mL porcelain capsule and mixed with 3 mL of distilled water to obtain a homogeneous solution. The slurry was heated with a hot plated until most of the water evaporated, resulting in a water-integrated solid. The muffle furnace was heated at 620˚C and then the resulting solid was introduced in the muffle, and left was allowed to stand at 600˚C for 5 min more. Finally this sample was removed and allowed to cool down.

The composition and crystalline structure of the PSC was analyzed by X-ray diffraction (XRD) using a powder diffractometer (Siemens analytical D-5000, Madison, WI) attached to a copper anode X-ray tube with Cu Kα radiation ($\lambda = 10.154$ nm). The diffraction data were recorded from 5° to 70° (2θ) with a step size of 0.02° and at a rate of 0.07 s/step. The Brunauer–Emmet–Teller (BET) specific surface area, total pore volume, and mean pore diameter were obtained by nitrogen physisorption measurements using a Belsorp Max analyzer (Bel Japan, Osaka, Japan) at 77 K. The samples were previously degassed at 200°C for 2 h in vacuum. The morphology was determined using a scanning electron microscope (SEM) (Jeol JSM-5900LV, Tokio, Japan) at 25 kV equipped with a microprobe (EDS Oxford). The sample elemental chemical composition was determined by energy-dispersive X-ray spectroscopy (EDS).

2.3. Co^{2+} adsorption experiments

Batch experiments were performing to study the effect of diverse physicochemical parameters, such as the contact time, concentration, pH, and temperature. The studies were conducted in typical experiments at room temperature, during which 0.1 g of PSC with 10 mL of a cobalt solution (50 mg/L) were mixed in closed glass vials.

Adsorption kinetics experiments were performed at different pre-determined time intervals between 10 min and 24 h. After each time point, suspensions were centrifuged for 5 min at 3,000 rpm. Aliquots of 1 mL of the liquid phases were extracted for cobalt concentration measurements. The cobalt concentration in solutions was determined by ultraviolet/visible spectroscopy (UV/vis) using a Perkin–Elmer Spectrometer Lambda 10 previously calibrated at $\lambda = 265$ nm and a previously calibrated curve. The hydrogen peroxide and sodium bicarbonate methods were used to achieve green color complex development, with a cobalt concentration detection limit of 4 ppm [24]. All of the experimental data were the averages of duplicate determinations and had good reproducibility (the standard deviations were less than 5% of the mean values). The results showed that the equilibration time was 3 h.

To investigate the initial cobalt concentration effect, batch experiments were also conducted by using a procedure similar to the kinetic studies and varying the initial cobalt concentration (5–100 mg/L) at an equilibrium pH of 5.5 over 3 h at room temperature. The equilibrium data obtained from these studies were tested with the most common adsorption isotherm models: Langmuir and Freundlich, and their applicability was compared. The pH study was conducted in a pH range of 2–10 under ambient conditions with a pH 05669-20 instrument (Cole-Parmer, Tinley Park, IL) using 0.1 g of solid and 10 mL of a fixed initial cobalt ion concentration in solution (50 mg/L).

A thermodynamic study was also conducted using a wide range of temperatures (293, 303, 313, and 323 K) with an initial cobalt concentration of 50 mg/L, equilibrium pH of 5.5, and equilibrium time of 3 h. The number of milligrams of Co^{2+} ions adsorbed by one gram of PSC sample was calculated using the following equation:

$$q_t = [(C_i - C_t)V]/m \tag{1}$$

where q_t is the amount of Co^{2+} ions in (mg/g) adsorbed on the adsorbent at time t, C_i is the initial cobalt concentration (mg/L), C_t the cobalt concentration at time t (mg/L), m is the mass of adsorbent used (g), and V is the volume of cobalt ions solution (L).

3. Results and discussion

3.1. Characterization of PSC

The XRD pattern of the as-prepared carbonous material (PSC) reveals the presence of a wide band due to the absence of any ordered crystalline structure, indicating that the amorphous material has some degree of non-arrangement in the molecular chain, which is an advantageous property for well-defined adsorbents. The diffused haloes (imperfect developing of photographs) appearing at 2θ values among 5 to 70° confirm this disordered typical amorphous solids structure (Fig. 1).

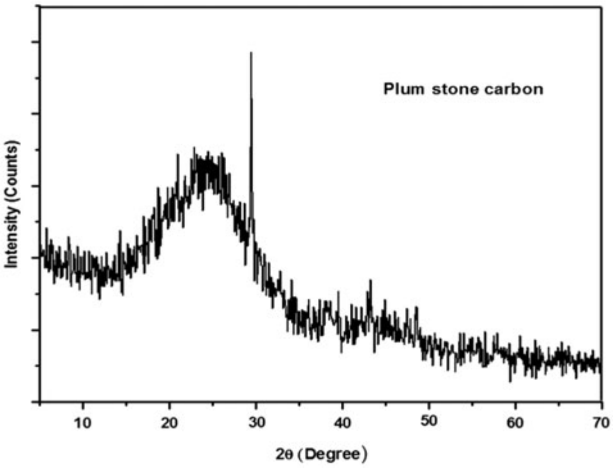


Fig. 1. XRD pattern of the PSC obtained by the solid-combustion process.

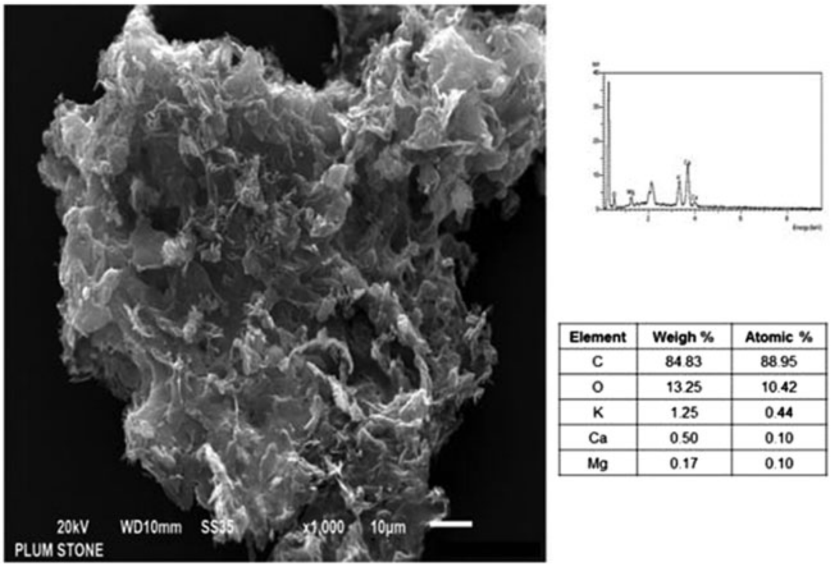
The SEM micrograph of the synthesized material (PSC) (Fig. 2) shows that this adsorbent is a compact agglomerate formed by smaller particles with an irregular morphology and rough surfaces, with a higher porous structure that contains many craters formed by the hot gases produced during the solid-combustion process as observed by Granados et al. [25]. The elemental analysis spectra of the (PSC) samples show energies that correspond to oxygen, potassium, calcium, magnesium, and mainly, carbon elements that are present in the carbonaceous sample (see inset in Fig. 2). The BET specific surface area of the prepared carbonaceous material was 286.06 m^2/g, the mean pore diameter was 2.5746 nm, and the total pore volume was 0.1841 cm^3/g.

Indeed, the N_2 adsorption–desorption isotherm of the PSC sample (Fig. 3) exhibited type IV behavior with a very large hysteresis-loop at p/p_o between 0.1 and 1.0, denoting the porous characteristics of this sample. According to the International Union of Pure and Applied Chemistry (IUPAC), this isotherm corresponds to materials that have a small mesopore structure, in which unrestricted monolayer–multilayer retention can occur [26]. On the other hand, the pore size distribution of the carbonaceous material prepared by solid-combustion was calculated by the Barrett–Joyner–Halenda (BJH) method based on the N_2 desorption isotherm (inset in Fig. 3). The BJH pore size distribution result shows an average pore radius of 1.21 nm, which accounts for approximately 90% of the pores, indicating that this material presents a homogeneous and narrow pore size distribution. In general, the structural, physical, chemical, and textural characteristics of this material suggest that it can be used as potential adsorbent for cobalt ion adsorption purposes because this carbonaceous material exhibits abundant active sites due to high surface area.

3.2. Co^{2+} adsorption experiments

The experimental kinetic study results of Co^{2+} adsorption on the studied as-prepared material indicated that the Co^{2+} ion adsorption in carbonaceous material increased with increasing time. The adsorption rate was very fast at the beginning of the process due to the higher contact between the adsorbent surface and cobalt ions in aqueous media and then entered a slow phase that reached equilibrium 3 h after contacting the liquid–solid phases. The adsorption of the Co^{2+} ions on the carbonaceous material surface can be attributed to the availability of more than the required number of active sites on the surface of the material, which decreased at a later stage of contact time due to the lack of a sufficient number of adsorption sites to accommodate the cobalt ions available in the solution.

To predict the Co^{2+} ion adsorption kinetic process, different kinetic models were employed to fit the experimental data, including pseudo-first-order [27], pseudo-second-order [28], and intra-particle diffusion kinetic models [29]. As a general procedure, linear regression has been frequently used to determine the best fitting kinetic equations. However, during the last few years, several researchers have demonstrated that



Element	Weigh %	Atomic %
C	84.83	88.95
O	13.25	10.42
K	1.25	0.44
Ca	0.50	0.10
Mg	0.17	0.10

Fig. 2. SEM and EDS analysis of the PSC obtained by the solid-combustion process.

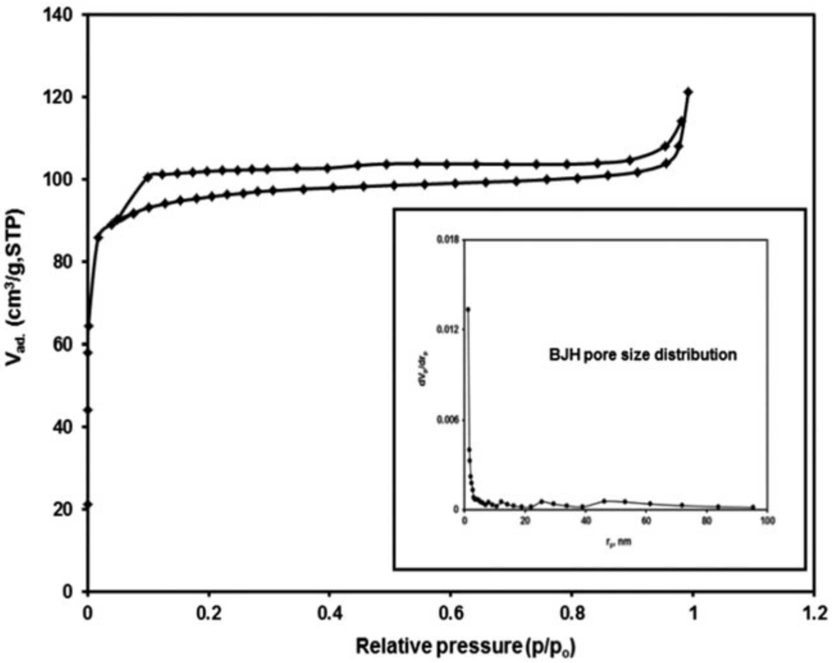


Fig. 3. N_2 adsorption–desorption isotherm and inset BJH study of the PSC obtained by the solid-combustion process.

non-linear regression is more appropriate than linear regression to obtain kinetic model parameters [30] because transformations of nonlinear equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of the standard least squares method. In this setting, non-linear optimization provides a mathematically rigorous method for determining model parameter values, which are important for the discussion of experimental results. Therefore, numerous earlier investigations have showed that the non-linear method is a better way to determine the kinetic parameters compared with the linear method [31,32]. Table 1 shows the calculated kinetic parameters obtained from the Co^{2+} ions adsorbed amounts vs. time and their corresponding correlation coefficients (R^2) obtained by a non-linear regression analysis using the Statistica 8.1 computer program. According to the results, it was found that the pseudo-second-order kinetic model provided a better fit to the experimental data, with a level of confidence of 95.0%, representing the kinetic uptake of cobalt ions onto the as-prepared carbonaceous material at the initial Co^{2+} ions concentration studied because it was evident that the R^2 value of 0.981 ± 0.11 was closer to unity (Fig. 4). In this figure, the experimental points are condensed just in the beginning of the curve, as there were used to extrapolate the curves up to much wider time ranges. Hence, the Co^{2+} ion adsorption on this material or for this system can be approximated more appropriately by this kinetic model than by the first-order kinetic model. These results indicate that the rate of covering the adsorption site is proportional to the square of the number of unoccupied and occupied sites. According to literature data, the pseudo-second-order kinetic model includes different adsorption mechanisms, such as surface complexation or ion exchange [33]. Theoretically, this kinetic model is based on the assumption that the rate-controlling step is a chemical adsorption involving valence forces through the sharing or exchange of electrons between the adsorbent and the adsorbate [34].

On the other hand, to determine the intra-particle diffusion effects on Co^{2+} ion adsorption on carbonaceous material, the kinetic experimental results were also tested with the intra-particle diffusion model [35], where the values of q_t were correlated linearly with values of $t^{1/2}$ (Fig. 5), with k_{ip}, which represents the intra-particle diffusion rate constant (mg/g min$^{1/2}$), and C_i, the intercept of stage i, which provides information about the thickness of the boundary layer. The parameter values and the related correlation coefficients obtained from this model are also listed in Table 1. According to Fig. 5, three linear regions were observed, which suggests that the Co^{2+} adsorption process proceeds by external surface adsorption (the initial linear region) completed within the first 20 min (k_{ip1}), intra-particle diffusion or pore diffusion

Table 1
Kinetic parameters evaluated for Co^{2+} ion adsorption onto the PSC prepared by the solid-combustion process

Kinetic models	Parameters	Co^{2+} ion
Pseudo-first order non-linear equation: $q_t = q_e(1 - \exp(-k_1 t))$	k_1 (g/mg min)	0.129 ± 0.012
	q_e (mg/g)	4.093 ± 0.140
	R^2	0.945 ± 0.016
Pseudo-second-order non-linear equation: $q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$	k_2 (g/mg min)	0.053 ± 0.001
	q_e (mg/g)	4.310 ± 0.141
	R^2	0.981 ± 0.110
Intra-particle diffusion model: $q_t = k_{ip} t^{1/2} + C_1$, $0 > t < 20$ min	k_{ip1} (mg/g min$^{1/2}$)	0.836 ± 0.024
	C_1	0.129 ± 0.016
	q_e (mg/g)	3.093 ± 0.013
	R^2	0.959 ± 0.017
$q_t = k_{ip} t^{1/2} + C_2$, $20 > t < 180$ min	k_{ip2} (mg/g min$^{1/2}$)	0.098 ± 0.019
	C_2	3.093 ± 0.011
	q_e (mg/g)	1.318 ± 0.050
	R^2	0.948 ± 0.014
$q_t = k_{ip} t^{1/2} + C_3$, $t > 180$ min	k_{ip3} (mg/g min$^{1/2}$)	−0.002 ± 0.001
	C_3	4.415 ± 0.017
	q_e (mg/g)	0.102 ± 0.008
	R^2	0.868 ± 0.019

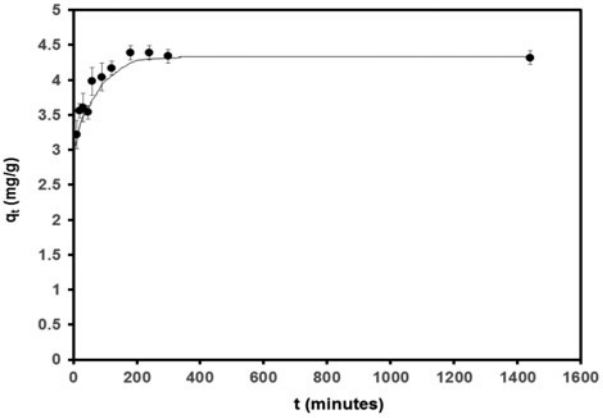


Fig. 4. Pseudo-second-order kinetic obtained by the non-linear method for the Co^{2+} ion adsorption on the as-prepared carbonaceous material.

(the second linear region) for $20 > t < 180$ min (k_{ip2}), and adsorption on the interior surface of the adsorbent (the third region) from 180 min (k_{ip3}), which is the final equilibrium step when intra-particle diffusion starts to slow down due to the extremely low cobalt ions concentrations left in the solutions [36]. From the literature descriptions, a significant property of this kinetic model is that if the intra-particle diffusion is the only rate-limiting step, then the linear plot of q vs. $t^{1/2}$ should pass through the origin. However, if the intercepts of the plots do not equal zero, then it indicates that the intra-particle diffusion is not the sole rate-determining step. Our results show that the intercepts of the plots were not equal to zero. However, the obtained linearity of the plots demonstrated that the intra-particle diffusion played a significant role in Co^{2+} ion adsorption by the PSC adsorbent.

3.3. *Adsorption isotherms for the removal of Co^{2+} ions from PSC*

Classical Langmuir and Freundlich isotherms were used to provide a mathematical description of Co^{2+} ion adsorption on carbonaceous material (PSC), and their respective constants were determined. Those models generally provide insights into the adsorption mechanisms and affinity properties of the adsorbents. The Langmuir isotherm model assumes a monolayer adsorption onto an adsorbent surface at equilibrium containing several energetic identical adsorption sites. The Langmuir model in its non-linear form can be defined as follows:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

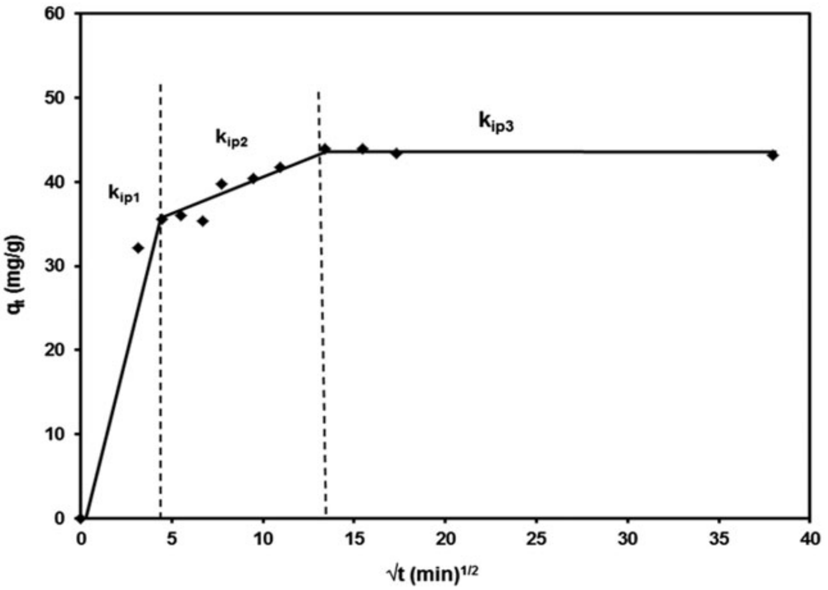


Fig. 5. Intra-particle diffusion kinetic model for Co^{2+} ion adsorption on the PSC obtained by the solid-combustion.

where C_e is the cobalt ion concentration in solution at equilibrium (mg/L), q_e is the amount of cobalt ions adsorbed at equilibrium (mg/g), and K_L and q_{max} are the Langmuir constants related to the adsorption intensity or affinity and the maximum adsorption capacity, respectively. K_L and q_{max} values for all of the studied cobalt concentrations were obtained using non-linear regression analysis by the Statistica 8.1 computer program, with a level of confidence of 95.0% and a correlation coefficient of 0.9693 for the experimental values presented in Table 2.

On the other hand, the Freundlich isotherm model is used for modeling adsorption on heterogeneous surfaces. This isotherm was analyzed using the following non-linear equation:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

where q_e is the amount of adsorbed Co^{2+} ions at equilibrium (mg/g), C_e is the Co^{2+} ion concentration at equilibrium (mg/L), K_F is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent ((mg/g) $(L/mg)^{-1/n}$), and $1/n$ is the adsorption intensity, also reported in Table 2.

Table 2
Summarized non-linear isotherm constants for the Co^{2+} ion adsorption onto the PSC prepared by the solid-combustion process

Non-linear isotherm models	Data
Langmuir	$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$ $q_e = \frac{q_{max}K_LC_e}{1+K_LC_e}$
K_L	0.0299 L/mg
q_{max}	4.1516 mg/g
R^2	0.9693
Freundlich	$q_e = K_FC_e^{\frac{1}{n}}$ $q_e = K_FC_e^{\frac{1}{n}}$
K_F	0.3461 mg/g $(mg/L)^{1/n}$
$1/n$	0.3909
R^2	0.9102

Table 2 shows that the fitted Langmuir isotherm adsorption affinity is larger than that of the Freundlich model, in accordance with the obtained correlation coefficients (R^2) values. From the Langmuir isotherm, the Langmuir constant (K_L) can be used to predict whether an adsorption system is favorable or unfavorable. The favorable adsorption nature can be expressed in terms of a dimensionless constant called the equilibrium parameter (R_L), defined by the following Eq. (4):

$$R_L = 1/(1 + K_L C_o) \tag{4}$$

where R_L is the Langmuir constant and C_o is the initial cobalt concentration. From the experimental data, R_L showed values between 0.8699 and 0.2506 over all of the initial cobalt ions concentrations over the studied range (5–100 mg/L), with K_L equal to 0.0299, indicating that the adsorption isotherm type was favorable ($0 < R_L < 1$) [37]. Therefore, it can be concluded that the experimental data for the carbonaceous material and Co^{2+} ions was correctly adjusted to the simplest

Langmuir isotherm model over the entire concentration of cobalt studied (Fig. 6), assuming the formation of a complete monolayer of cobalt ions on the homogeneous surface of carbonaceous adsorbent material (PSC) and a finite number of identical sites.

3.4. Effect of pH on Co^{2+} adsorption behavior

The pH effect on the Co^{2+} adsorption behavior onto the as-prepared material (PSC) was examined in the pH range 2–10 at room temperature. It is clear from Fig. 7 that the adsorption capacity of the adsorbent gradually increases as the equilibrium pH increases. A plausible explanation for this behavior is the chemical speciation of cobalt in solution over the considered solution pH range. The cobalt pH behavior in aqueous solution is well documented [38] in the computer program Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA) [39], which provides information about the distribution of chemical species as a function of pH. According to the cobalt chemical species distribution diagram for a 50 mg/L concentration (Fig. 8), the bivalent cobalt species Co^{2+} is the only one that appears in the pH range from 1 to 8. At a pH higher than 8, a neutral species was found, which corresponds to cobalt(II) hydroxide $Co(OH)_2$ in molecular solution. Under our experimental conditions, the pH value of the equilibrium solution after Co^{2+} retention was 5.5; therefore, Co^{2+} species dominated, accounting for 100% of Co, which means that the cationic Co^{2+} species should be adsorbed on the charged surface of the carbonaceous material. Then, as the pH increased and surface functional groups were activated, Co^{2+} adsorption increased in accordance with a pH increase from pH 2 to 8. According to Fig. 8, the maximum Co^{2+} ion adsorption occurred after pH 4 until pH 8, exhibiting a similar trend to the pH effect. In this work, pH 5.5 was taken as the natural pH value for carrying out the adsorption studies. However, the increased adsorption at higher pH values (>8) may be attributed to the formation of a hydroxide complex of cobalt ions or to a possible precipitation phenomenon that may occur due to the presence of abundant $Co(OH)_2$ chemical species at these pH values. To understand this effect, we must consider the following: the pH effect of the Co^{2+} adsorption on the PSC surface can also be explained on the basis of the zero point of charge (pH_{ZPC}). It is well known that surfaces are negatively charged above their pH_{ZPC} favoring the Co^{2+} adsorption due to electrostatic attraction. The obtained experimental pH_{ZPC} of the studied carbon material was 5.0. As the pH increases, the number of positively charged sites decreases, favoring Co^{2+} adsorption. Therefore, in the present study, the optimal cobalt adsorption onto a carbonaceous material occurs when the pH solution is slightly alkaline.

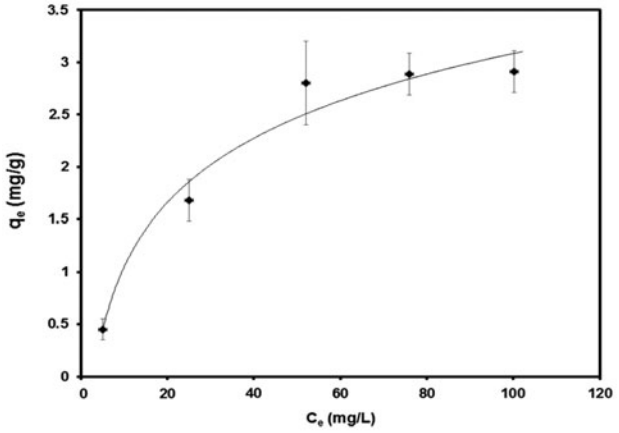


Fig. 6. Langmuir isotherm obtained by the non-linear method for Co^{2+} ion adsorption on the as-prepared carbonaceous material.

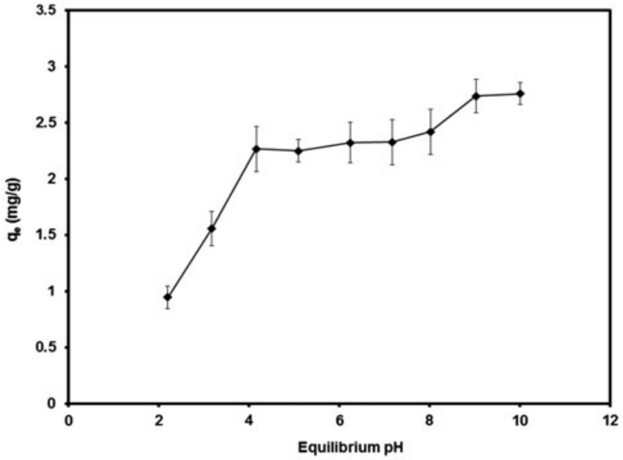


Fig. 7. pH effect of Co^{2+} ion adsorption on the carbonaceous adsorbent.

3.5. Thermodynamic parameters

The thermodynamic parameters related to Co^{2+} ion adsorption on the as-prepared material (PSC) over the temperature range (293–323 K) were calculated by using the following equations:

$$\log K_d = -\Delta H^\circ/2.303\,RT + \Delta S^\circ/2.303\,R \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

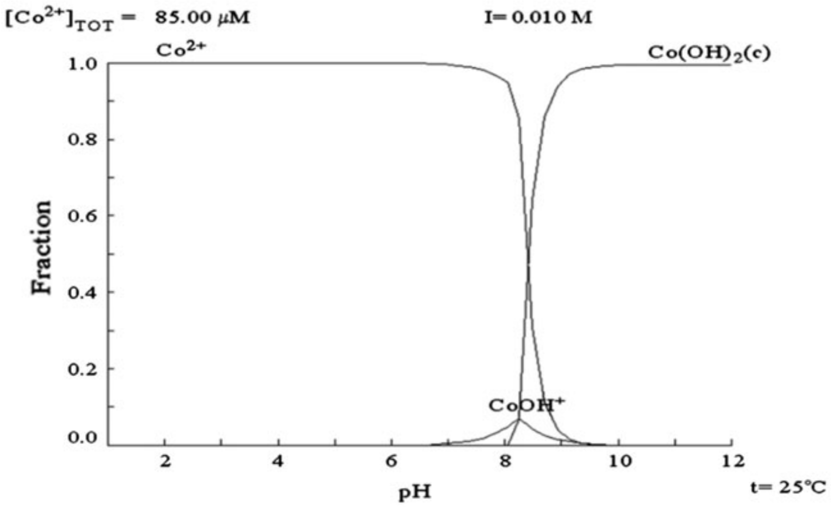


Fig. 8. Speciation diagram for Co(II) ions in aqueous solution.

$$K_d = C_a/C_e \tag{7}$$

where ΔH°, ΔS°, ΔG° are the enthalpy change, entropy change, and Gibbs free energy change, respectively, and T, R, and K_d correspond to the absolute temperature in degrees Kelvin, ideal gas constant (8.314×10^3 kJ mol/K), and dimensionless distribution coefficient [Co^{2+} ion concentration adsorbed (C_a)/Co^{2+} ion concentration in solution at equilibrium (C_e)], respectively. The ΔH°, ΔS° values were obtained from the slope and intercept of the linear Van't Hoff plot of $\log K_d$ vs. $1/T$, as shown in Fig. 9, and the evaluated values are summarized in Table 3. The thermodynamic analysis revealed that the Co^{2+} ion adsorption process on the (PSC) adsorbent was endothermic in nature due to the positive ΔH° value. The magnitude of ΔH° may also be used to distinguish between physisorption (2–20 kJ/mol) and chemisorption (80–20 kJ/mol) mechanisms. The values between 20 and 80 kJ/mol, as in the present work, 57.228 kJ/mol cannot clarify what type of adsorption (physical or chemical) is occurring, since both types of adsorption may be present [40]. However, the study of chemisorption kinetic pseudo-second-order model shows clearly that in the present work, the adsorption of Co^{2+} on PSC is a chemisorption process. For ΔG° and ΔS°, the obtained values indicate that the Co^{2+} adsorption on the carbonaceous material surface can occur under ordinary conditions and can reflect a more energetically favorable adsorption, with increased randomness. Therefore, based on the signs and magnitudes of the obtained thermodynamic parameter values in the present study, we can establish that the cobalt ion adsorption occurs via chemical adsorption through a thermodynamically spontaneous and endothermic process.

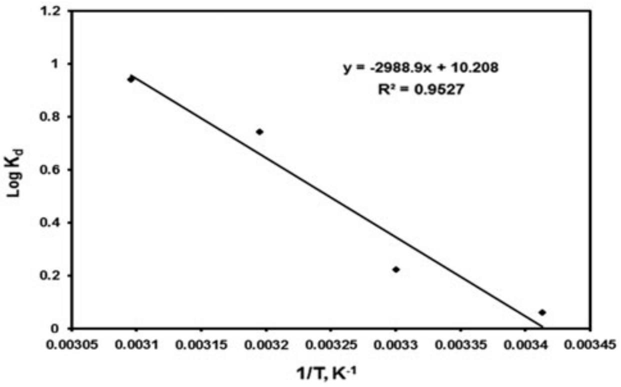


Fig. 9. Linear plot of $\log K_d$ vs. $1/T$ for the prepared carbonaceous adsorbent.

Table 3
Thermodynamic parameters at 20°C for the Co^{2+} ion adsorption on the PSC prepared from the solid-combustion process

ΔH° (kJ/mol)	ΔS° (kJ/K mol)	ΔG° (kJ/mol)
57.228	0.196	−0.334

The comparison of the Co^{2+} ion adsorption capacity (q_e) with other high-quality studied adsorbents reported in the specialized literature is summarized in Table 4. These reported results are varied, with some values lower, others similar to, and still others higher

Table 4
Maximum Co^{2+} ion adsorption capacities (q_{max}) by Langmuir isotherm on the PSC prepared by the solid-combustion process and other adsorbents

Adsorbent	Adsorption capacity, q_{max} (mg/g)	Refs.
Activated carbon from hazelnut shells	13.88 at 303 K and pH 6	[41]
Coir pith	12.82	[42]
Hectorite particles	2.650	[43]
Kaolinite	0.919	[44]
Lemon peel adsorbent	22.0 at 300 K and pH 4.3, dosage 2,000 mg/L	[45]
Natural Bahhah clay	3.44	[46]
Natural Khiber clay	4.66	[46]
Natural Tabbuk clay	3.94	[46]
Spent coffee	5.37 at 293 K and pH 6, dosage 10 mg/L	[47]
Plum stones carbon	4.23	Present study

than the values obtained for cobalt ions with carbonaceous material. However, it is difficult to compare all of these results because the nature of the adsorption process will mainly depend on different physicochemical characteristics of both the solution and the soil. Indeed, the efficiency of cobalt ion adsorption on adsorbents is highly dependent on the studied initial metal-ion concentration, and in many cases, these adsorbents are chemically treated. Therefore, in the present study, a carbon obtained from waste plum stones prepared by a solid-combustion process can be applied to the control of water pollution, as suggested by the obtained results, which show the feasibility of this carbonaceous material as an alternative low-cost adsorbent to efficiently remove cobalt ions from aqueous solution.

4. Conclusions

A PSC prepared by solid combustion was obtained with important features, such as a higher porosity and large surface area, associated with an improved ability to remove cobalt ions from aqueous solutions. The experimental results showed that the Co^{2+} ion adsorption process can be mathematically modeled using the pseudo-second-order kinetic model, with intra-particle diffusion as one of the rate determining steps and with a better adjustment to the Langmuir isotherm model. Optimum equilibrium time was 160 min, and optimal cobalt adsorption onto a carbonaceous material occurs when the pH solution is slightly alkaline; a maximum cobalt adsorption capacity of 4.23 mg/L was obtained. The thermodynamic analyses indicate that the Co^{2+} ion adsorption process was endothermic, feasible, and spontaneous, with an increased randomness in nature. This process is favorably regulated by an increase in temperature. The results obtained in these studies demonstrated that (PSC) may be useful in the removal of cobalt ion pollutants in water, with goods results.

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