Research Article

Using Pomegranate Peel and Date Pit Activated Carbon for the Removal of Cadmium and Lead Ions from Aqueous Solution

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Some agricultural byproducts are useful for solving wastewater pollution problems. These byproducts are of low cost and are effective and ecofriendly. The study aim was to investigate the possibility of using pomegranate peel (PP) and date pit (DP) activated carbon (PPAC and DPAC, respectively) as sorbents to remove Cd(II) and Pb(II) from aqueous solutions. Agricultural wastes of DPs and PPs were subjected to carbonization and chemical activation with H_3PO_4 (60%) and $ZnCl_2$ and used as adsorbents to remove Cd(II) and Pb(II) from their aqueous solutions. The physical characterizations of PPAC and DPAC, including determination of surface area, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Fourier-transform infrared spectroscopy, were performed. The following factors affected adsorption: solution pH, adsorbent dosage, initial metal ion concentration, and contact time. These factors were studied to identify the optimal adsorption conditions. The results showed that the maximum adsorptions of Cd(II) and Pb(II) were achieved at pH ranging from 6 to 6.5, 90 min contact time, and 0.5 g/L for PPAC and 1 g/L for DPAC dosage. Furthermore, the adsorption efficiencies for both Pb(II) and Cd(II) were higher for PPAC than for DPAC. However, the recorded Q_{max} values for PPAC were 68.6 and 53.8 mg/g for Pb(II) and Cd(II) and for DPAC were 34.18 and 32.90 mg/g for Pb(II) and Cd(II), respectively. The Langmuir isotherm model fit the adsorption data better than the Freundlich model. Kinetically, the adsorption reaction followed a pseudo-second-order reaction model, with q_e ranging from 12.0 to 22.37 mg/g and an R^2 value of 0.99.

1. Introduction

The recent notable deterioration of water quality mainly due to urbanization, anthropogenic wastes, increasing population growth, progressive industrialization, and unsafe water resources utilization [1] has led to water resources contaminated with different pollutants (e.g., toxic metal ions, pesticides, agricultural fertilizers). The progressively increasing amounts of different pollutants have caused alarm about water quality [2]. Minimization and control of water pollution problems have become an urgent necessity, and great efforts have been made to develop ecofriendly, low-cost, and effective techniques to remove pollutants from aquatic environments [3]. Several technological processes have been developed by different researchers, including

photo-oxidation [4, 5], advanced oxidation [6, 7], and bioremediation using biomasses [8]. These processes have certain disadvantages, mainly high operational costs and maintenance. In addition, they have some complicated steps and may generate toxic byproducts of their own [9].

Recently, adsorption processes using activated carbon from agricultural wastes, sludge, or other carbonaceous precursors have been used because they are ecofriendly, are of low cost, and enable use of simple procedures. This technique has been used for removing various contaminants from water, including metals and dyes [10–13]. Currently, adsorption reactions are considered the most ecofriendly, low-cost, selective, and efficient treatment technique for removing heavy metals and other organic pollutants from wastewater [14, 15]. This technique involves surface

adsorption in which adsorbate particles are attached and held to the adsorbent surface until reaching equilibrium between free and bound molecules in the carrier liquid or gas [16].

Recently, agricultural wastes are used to produce porous activated carbon (AC), which is considered one of the most popular and widely used adsorbents for the removal of heavy metal ions from wastewater. Various agricultural wastes are found in huge quantities, which provide the advantages for this method such as high availability, low cost, high adsorption efficiency, and high removal capacity [17]. These wastes include orange peel [12], rice husks [18], coconut shells [19], Kiwi, mandarin, and banana peels [20, 21], pomegranate peel modified with zerovalent iron nanoparticles [22], pomegranate peel [23–25], and date pits [26–28]. Some modified natural wastes were used as substrates to remove heavy metals.

In this study, pomegranate peels (PPs) and date pits (DPs) were used because they are the most locally available precursors in Saudi Arabia for the preparation of AC materials. PP is a byproduct of tanneries and pomegranate juice industries [29]. Additionally, DPs are common commercial agricultural wastes in the palm food industry [30]. Hence, DPs and PPs are suitable for AC preparation because of their good natural structure, renewable sources, low cost, and low ash content [31]. Therefore, AC from PPs (PPAC) and DPs (DPAC), which are characterized by large surface area, high micropore volume, and extremely high adsorption efficiency, potentially can be used to prepare efficient sorbents for the removal of pollutants from water. Therefore, the prepared PPAC and DPAC adsorbents are considered excellent novel adsorbents because of their low cost and highly effective substrates. However, the hydrothermal chemical activation processing modified the adsorbents' characteristics that made them have great abilities to remove toxic metals (Cu(II) and Ni(II)) and Pb(II) in a single-step process from aqueous solutions due to their high surface area, enlarged pore size, and existence of several different functional groups onto their surfaces.

The study aim was to investigate the possibility of using PPAC and DPAC as sorbents to remove Cd(II) and Pb(II) from aqueous solutions. Some factors that affect the adsorption process, such as solution pH, sorbent dose, duration time, and initial metal concentrations, were studied. Furthermore, different kinetic and isotherm models for Pb(II) and Cd(II) adsorption were investigated.

2. Materials and Methods

2.1. Chemicals and Reagents. Lead nitrate, cadmium nitrate, sodium hydroxide, and hydrochloric acid used in this study were of analytical grade and purchased from Sigma (Germany). Cd(II) and Pb(II) stock solutions of 1000 mg/L were prepared by dissolving Pb(NO₃)₂ and Cd(NO₃)₂ in deionized water. For each experiment, serial dilutions were prepared using deionized water to obtain the required concentrations. The pH of each solution was adjusted using 0.1N HCl or 1N NaOH to the required experimental value.

2.2. Activated Carbon (AC) Preparation. Date pit (DP) and pomegranate peel (PP) wastes were collected from local markets in Riyadh City, Saudi Arabia. In the laboratory, the DPs and PPs were washed well with hot deionized water and dried in an open-air oven (Genlab–Mino 50) at 105°C for 24 hr. After reaching constant weight, the DPs and PPs were crushed and ground in a mill to a fine powder and then sieved through progressively finer sieves to yield a final particle size of <120 μm. AC from DPs (DPAC) and PPs (PPAC) was prepared by soaking dry fine particles of DPs and PPs with H₃PO₄ (60%) and ZnCl₂ (50 wt%) at a ratio 1 : 1 by volume for 24 hr to chemically activate them. Then, the mixtures were dried in an oven at 105°C. Finally, carbonization was performed in a muffle furnace (Nabertherm L5) at 500°C for 60–70 min in the absence of air.

2.3. Characterizations. The surface area (S_{BET}) of the prepared AC was estimated by using the Brunauer–Emmett–Teller method (S_{BET}) using a Coulter SA3100 instrument with outgas for 15 min at 150°C. A scanning electron microscope (model: JEM-2100-JEOL; Tokyo, Japan) was used for scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) measurements. Fourier-transform infrared spectroscopy (FTIR) analysis was performed to identify the different principal functional groups using a spectrometer (6700 FTIR; Nicolet, America).

2.4. Batch Adsorption Study. A series of serial standard solutions was prepared by dissolving Pb(NO₃)₂ and Cd(NO₃)₂ salts in deionized water. The effect of solution pH, contact time, initial metals' concentrations, and sorbent dosage was investigated as important factors that could affect the adsorption process. A 100 ml aliquot of the metal ions mixture was used for each experiment under fixed conditions. All experiments were performed at room temperature between 22 and 25°C and a fixed shaking speed of 250 rpm. Then, samples were centrifuged at 10,000 rpm for 10 min, the solution was withdrawn, and the concentrations of Pb(II) and Cd(II) were measured by using inductively coupled plasma–atomic emission spectroscopy (ICP–AES; Agilent 5800). The metal adsorption capacity (q_e , mg/g) and removal efficiency (R%) are calculated as follows:

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

$$R\% = \frac{(C_0 - C_e) \times 100}{C_e},$$

where q_e is the equilibrium metal concentration; C_0 and C_e are the initial and final metal ion concentrations in solution (mg/L), respectively; V is the volume of metal ions in solution (L); and M is the sorbent mass (g).

3. Results and Discussion

3.1. Characterization. SEM is useful for describing the porous heterogeneity and surface morphological structures of the adsorbents. Figures 1(a) and 1(b) show the SEM

FIGURE 1: Scanning electron microscopy (SEM) images: (a) DPAC sorbent and (b) PPAC sorbent.

micrographs for DPAC and PPAC at different magnifications. The SEM micrographs showed that both sorbents had amorphous irregular surface structures. A smoother texture, a more porous surface, and a lower particle size were observed for PPAC than for DPAC, which have been shown to be associated with the compositional nature of the initial precursor and lignin content [32]. However, pomegranate peel contains a higher level of lignin than date pits, and therefore, the morphological structures of PPAC and DPAC are different after carbonization and activation [33, 34]. EDX spectroscopy was performed to determine the elemental composition of DPAC and PPAC (Figures 2(a) and 2(b)). The EDX spectra showed the presence of two major peaks of oxygen and carbon with abundance percentages of 52.48% and 25.43% in the DPAC adsorbent, respectively, while the corresponding abundance ratio were 52.2% and 24.2% in the PPAC adsorbent. In general, the high percentages of oxygen and carbon are closely related to the nature of the PPs and DPs used [35]. Additionally, some minor peaks were detected in the PPAC adsorbent, which belong to Mg (5.1%), Si (3.1%), and K (3%). A slightly higher difference was observed in the minor peaks that detected in DPAC than PPAC, and the minor peaks are Si (5.5%), Mg (4.2%), K (2.1%), and S (1.1%).

FTIR spectroscopy was used to identify and characterize different functional groups present on the surface of the PPAC and DPAC sorbents. Table 1 and Figure 3 show the different function groups existing on the surface of the two sorbents. Before the adsorption process, a narrow band at 3950 cm^{-1} was observed on the surface of PPAC that attributed to the -OH stretching of water molecules; this band was shifted after adsorption to 3949 cm^{-1} , indicating the interaction between metal ions adsorbed onto the active sites. A broad band at $3600\text{--}3150\text{ cm}^{-1}$ was attributed to the carboxylic acid -OH stretching in lignin and cellulose [36], asymmetric stretching O=C=O of the CO_2 group appeared at 2370 cm^{-1} . A carboxyl peak was observed at 1650 cm^{-1} , and a band at 565 cm^{-1} was attributed to out-of-plane C-H vibrations [37, 38]. After the adsorption process, all these bands were significantly shifted to other wave numbers, indicating successful binding of metal ions with different

function groups onto the surface of PPAC (Table 1). However, five peaks were observed for DPAC before adsorption at 3460 , 2935 , 1750 , 1470 , and 1025 cm^{-1} and were attributed to carboxylic acid -OH stretching, C-H symmetric vibrations, nonionic carboxyl groups (COOH), C-H bending in cellulose, and C-O stretching in the alcoholic hydroxyl group, respectively [39]. These bands are significantly shifting to 3451 , 2927 , 1741 , 1461 , and 1022 cm^{-1} after adsorption of metal ions (Table 1). FTIR spectroscopy indicated the presence of oxygen-containing functional groups (e.g., -OH , -COOH , -O=C=O , and -C-O) onto the surface of PPAC and DPAC adsorbents, and this indicates that the main mechanism of metal ions adsorption is the typical oxidation process due to the presence of functional groups containing oxygen, leading to enhancing the adsorption of heavy metals [40].

Determination of the specific surface area is most important for showing the capacity of adsorption onto an AC sorbent. Table 2 and Figure 4 show the calculated values of S_{BET} for DPAC and PPAC. Compared with DPAC ($278.18\text{ m}^2/\text{g}$), PPAC has a higher S_{BET} ($350.22\text{ m}^2/\text{g}$). These S_{BET} values were less than those obtained by Abedi et al. [41] who reported $887\text{ m}^2/\text{g}$ for the surface area of AC from PP modified by iron and by Manel et al. [42] who recorded $1354\text{ m}^2/\text{g}$ for PP activated thermally at 800°C . The maximum S_{BET} for date seeds was previously found to be $860\text{ m}^2/\text{g}$ after thermal activation at 800°C [43].

3.2. Batch Biosorption Experiments

3.2.1. Effect of pH. The adsorption process was greatly affected by the pH values of aqueous solutions of metal ions since it not only controls active sites dissociation on the sorbent surface but also governs the ionization degree and metals speciation in the solution [41]. To study the effect of pH values on the adsorption efficiency of DPAC and PPAC, a pH range of 2.5–7 was selected to show the removal capacity of Cd(II) and Pb(II) onto both adsorbents' surface at a 100 mg/L metal concentration for a 90-min contact time and 0.5 g/L PPAC and 1 g/L DPAC adsorbent doses (Figure 5).

FIGURE 2: EDX spectra: (a) DPAC adsorbent and (b) PPAC adsorbent.

TABLE 1: The main functional groups detected on the surfaces of DPAC and PPAC.

Frequency (cm^{-1})		DPAC	PPAC
Before adsorption	After adsorption	Band function groups	Function groups
3956	3949	*	–OH stretching
3600–3150	3590–3142	*	Carboxylic acid –OH stretch
3460–3350	3451–3339	Carboxylic acid –OH stretch	*
2935	2927	C–H vibrations	*
2369	2391	*	O=C=O asymmetric stretch (CO_2)
1750	1741	Carboxylic COOH stretching	*
1654	1659	*	Carboxylic COOH stretching
1470–1269	1461–1260	C–H bending	*
1025	1022	C–O stretching of alcoholic OH	*
565	561	*	C–H vibration

*Not available.

TABLE 2: The specific surface areas, radii, and pore volumes obtained for DPAC and PPAC.

Sorbent	S_{BET} (m^2g^{-1})	r (nm)	V_p^{total} (cm^3g^{-1})
DPAC	278.185	53.94	0.485
PPAC	350.22	31.17	0.383

FIGURE 4: N₂ sorption-desorption isotherms of prepared nanocomposites.

FIGURE 5: Effect of pH on the adsorption efficiencies of Pb(II) and Cd(II) on the surfaces of DPAC and PPAC (metal concentration = 100 mg/L, contact time = 90 min, dose of DPAC = 1 g/L, and dose of PPAC = 0.5 g/L).

We observed an obvious increase in removal efficiency by gradually increasing pH values. The maximum removal ratio for Pb(II) was 91.1% for PPAC and 88.8% for DPAC at pH 6. The maximum removal ratio for Cd(II) was 92.5% for PPAC and 87.3% for DPAC at pH 6.5 (Figure 5). A remarkable lowering in removal efficiency was observed at very low pH values (1–3) because of the high protonation process, which causes the formation of protonated hydrous oxides besides generating the positive charges that accumulate on the adsorbent surface layer, leading to electrostatic repulsion between positive metal ions and the positively charged adsorbent surface as shown in the following equations:

With increasing pH, the hydrous oxides were deprotonated in addition to the decrease of the positive charges, so the sorption sites become available and the adsorption of

metal ions increases [44, 45], and at very high pH values (>8), the metal ions precipitated (Figure 6).

Analysis of variance (ANOVA) revealed an insignificant difference in the removal efficiencies between the two adsorbents ($r = 0.08$ at $P > 0.11$).

3.2.2. Effect of Contact Time. The effect of contact time on the adsorption of Pb(II) and Cd(II) onto the surfaces of DPAC and PPAC was studied over the range of 15–150 min (Figure 7). The adsorption rates notably increased in the beginning of the reaction during the first 30–45 min because of the high availability of active sites on the adsorbents' surfaces. But then the reaction slowed down until reaching equilibrium after 90 min, with a maximum adsorption capacity of 91.1% and 91.2% for Pb(II) and 91.1% and 91.3% for

FIGURE 6: Effect of pH on the adsorption of Cd(II) and Pb(II) onto PPAC and DPAC at different pH values.

FIGURE 7: Effect of contact time on the adsorption of Pb(II) and Cd(II) onto the surfaces of DPAC and PPAC (pH = 6, metal concentration = 100 mg/L, DPAC dose = 1 g/L, and PPAC dose = 0.5 g/L).

Cd(II) on the surfaces of DPAC and PPAC, respectively. ANOVA showed no significant difference in the removal efficiencies between the adsorbents ($r = 0.15$, $P > 0.20$), but there was a significant difference in time intervals ($r = 0.82$, $P < 0.05$) between the adsorbents.

Our recent data were consistent with the Hilal et al. [46] data showing 75 min as the optimum duration for the adsorption of Cd(II) and Cu(II) onto the surface of DPAC. In addition, Salmani et al. [44] found that the optimum equilibrium time was 90 min for the adsorption of Pb(II) onto modified PPAC (Table 3).

3.2.3. Effect of Dose. To detect the optimum amount of adsorbent required for the maximum adsorption efficiency, the adsorbent dose was investigated by varying the quantities of both adsorbents from 0.1 to 1 g/L at pH 6, initial metal ion concentration of 100 mg/L, and a 90 min contact time (Figure 8). The results showed a gradual increase in adsorption efficiency by increasing the adsorbent mass because

of the great availability of active exchange sites onto the adsorbents' surfaces. The removal capacity reached a maximum of 92.3% for both Pb(II) and Cd(II) at 0.5 g/L of PPAC and remained steady. The removal capacity reached a maximum of 91% for Pb(II) and Cd(II) at 1 g/L of DPAC. ANOVA showed a slightly significant difference in adsorption efficiency between DPAC and PPAC ($r = 0.41$, $P < 0.05$). Moghadam et al. [43] and Salmani et al. [44] found that 1 g/L was the optimum dose of PPAC for the maximum removal of Fe(II) and Pb(II) from their aqueous solution. Al-Balushi et al. [47] reported an optimum dose of 1 g/L for DPAC to reach the maximum removal efficiency for methylene blue dye from aqueous solutions.

3.2.4. Effect of Initial Metal Concentration. The effect of initial Pb(II) and Cd(II) concentrations on the efficiency of adsorption was investigated over a concentration range from 10 to 100 mg/L (Figure 9). The results showed increasing removal rates with increasing Pb(II) and Cd(II)

TABLE 3: Comparison of the parameters affecting the maximum adsorption efficiencies of different metal ions using different agricultural precursors between the two AC adsorbents.

Adsorbent	Elements	pH	Dose (g/L)	Time (min)	q_e (mg/g)	Kinetics	Ref.
Orange peel	Cu(II)	5.8	0.5	120	25.8	Pseudo 2 nd order	[12]
Raw date pits	Hg(II)	5	4	90	38.5–52.6	Pseudo 2 nd order	[48]
Pomegranate peel	Pb(II)	6–6.5	1	60	22.5–27.5	Pseudo 2 nd order	[43]
Date pits	Cd(II)	5.8	1	75	7.4–33.44	Pseudo 2 nd order	[46]
Pomegranate peel	Pb(II)	6.5	1	80	18.52	Pseudo 1 st order	[44]
<i>Phragmites australis</i>	Cd(II)	6	0.5	30	5.8–7.8	*	[49]
Plum stone	Pb(II)	5.5	0.5	90	48.3–80.6	Pseudo 2 nd order	[50]
Banana peel	Cd(II)	3	30	20	5.7	*	[51]
Modified orange peel	Cu(II)	5	2	180	28.9	*	[52]
Pomelo peel	Cu(II)	4	5	60	34.84	*	[53]
Mango peel	Ni(II)	4–6	2	80	28.21	*	[54]
Date pits	Pb(II)	6–6.5	1	90	53.8–68.6	Pseudo 2 nd order	Recent data
Pomegranate peel	Cd(II)	6–6.5	0.5				

*Not available.

FIGURE 8: Effect of adsorbent dose on the adsorption of Pb(II) and Cd(II) (pH=6, metal concentration = 100 mg/L, and contact time = 90 min).

FIGURE 9: Effect of initial metal concentration on the adsorption of Pb(II) and Cd(II) (pH = 6, contact time = 90 min, dose of DPAC = 1 g/L, and dose of PPAC = 0.5 g/L).

concentrations. The maximum removal efficiencies of Pb(II) and Cd(II) were 93.9% and 94.4% for DPAC and 93.1% and 92.3% for PPAC at 100 mg/L metal ion concentrations, respectively. Slight variations in the removal efficiency were observed for both adsorbents.

4. Adsorption Equilibrium Isotherms

The equilibrium between the adsorbent (solid phase) and adsorbate (liquid phase) was described by using adsorption isotherm models. The reaction system reached equilibrium when a balance between the concentrations of the adsorbate and adsorbent was achieved. The calculated constants of an adsorption isotherm measured the surface properties' affinities of the DPAC and PPAC adsorbents for Pb(II) and Cd(II) ions. The Langmuir and Freundlich isotherm models were used to illustrate the adsorption process.

4.1. Langmuir Isotherm Model. The isotherm models of Langmuir postulate that adsorption occurred as a homogeneous monomolecular layer onto the adsorbent's surface.

The Langmuir model is expressed by Langmuir equation as follows [55]:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bq_{\max}} \cdot \frac{1}{c_e}, \quad (4)$$

where $q_{\max}$ (mg·g⁻¹) is the maximum uptake of sorbate, q_e is the equilibrium concentration of sorbate (mg·g⁻¹), c_e (mg·L⁻¹) is the metal concentration at equilibrium, and b (L·mg⁻¹) is the Langmuir constant.

The calculated equilibrium constants for the Pb(II) and Cd(II) adsorptions onto the surface of the two adsorbents showed good fits to the Langmuir isotherm model with $R^2 > 0.95$ (Table 4, Figure 10), so homogeneous monolayer adsorptions of Pb(II) and Cd(II) appeared to best explain this adsorption process. Furthermore, the adsorption efficiencies for both Pb(II) and Cd(II) were higher ($q_{\max} = 68.6$ and 53.8 mg/g for Pb(II) and Cd(II)) for PPAC than for DPAC ($q_{\max} = 34.18$ and 32.90 mg/g for Pb(II) and Cd(II)). The Langmuir dimensionless separation constant (R_L) that defines the affinity sorbate-sorbent affinity is an important feature of the adsorption isotherm. R_L is expressed in equation (5) [56].

$$R_L = \frac{1}{1 + bC_i}, \quad (5)$$

where C_i is the initial metal ion concentration (mg/L) and b is the Langmuir constant. R_L describes the type of Langmuir isotherm: irreversible if $R_L = 0$, linear if $R_L = 1$, unfavorable if $R_L > 1$, or favorable if $0 < R_L < 1$ [57]. R_L values for Pb(II) and Cd(II) adsorption onto the surface of PPAC and DPAC were found in the range of $0 < R_L < 1$, so a favorable adsorption was achieved (Table 4).

4.2. Freundlich Isotherm Model. The Freundlich isotherm model assumed that a heterogeneous adsorption took place on the adsorbent surface by the adsorbate molecules, so this

model could be applied to both monolayer and multilayer adsorption. The Freundlich isotherm model is described by equations (6) and (7) [58].

$$q_e = K_f C_e^{1/n}, \quad (6)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (7)$$

where q_e is the amount of metal adsorbed by the adsorbent (mg/g), C_e is the equilibrium adsorbate concentration in mg/L, K_f is the adsorbent capacity, and n is the adsorption intensity determined from the linear plot.

Figure 11 shows the linear relationship between $\log q_e$ and $\log C_e$ at constant temperature. The Freundlich constants (K_f , n , and R^2) for both adsorbents are presented in Table 4. It is clear that the adsorption process does not follow the Freundlich model because the R^2 values are lower than those corresponding to those for the Langmuir model (Table 4). The Freundlich intensity parameter ($1/n$) is a function of the strength of adsorption [59], and the values of n were < 1 , which indicated that the adsorption of both metal ions was a chemical adsorption process [60].

5. Kinetics Studies

Kinetic adsorption is one of the most important parameters used to evaluate the adsorption process efficiency in addition to the transferring behavior of adsorbed molecules onto the adsorbents' surfaces [61]. Thus, pseudo-first-order and pseudo-second-order models were applied to investigate the kinetics of adsorption of Pb(II) and Cd(II) onto the surfaces of DPAC and PPAC.

5.1. Pseudo-First-Order Model. This model assumed that metal ions uptake is directly proportional to the difference between saturation levels and is expressed by the Lagergren [62] equation as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{0.203} t, \quad (8)$$

where q_t is the concentration of adsorbed metal ions (mg/g) at time t , q_e is the amount of adsorbed metal ions (mg/g) at equilibrium, and k_1 (min⁻¹) is the pseudo-first-order reaction constant.

5.2. Pseudo-Second-Order Model. This model supposes that chemical adsorption occurred since chemical bonds were formed between the adsorbent surface and adsorbate [63]. The pseudo-second-order model is expressed in equation (9) as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (9)$$

where q_t is the concentration of adsorbed metal ions (mg/g) at time t , q_e is the amount of adsorbed metal ions (mg/g) at equilibrium, and k_2 (mg/g·min⁻¹) is the pseudo-second-order reaction constant.

TABLE 4: Constants of Langmuir and Freundlich isotherms for Pb(II) and Cd(II) adsorption by DPAC and PPAC adsorbents.

	Langmuir								Freundlich					
	PPAC				DPAC				PPAC			DPAC		
	b	$q_{\max}$	R_L	R^2	b	$q_{\max}$	R_L	R^2	K_f	n	R^2	K_f	n	R^2
Pb(II)	0.01	68.60	0.50	0.95	0.01	34.18	0.45	0.98	1.08	0.54	0.82	1.13	0.55	0.91
Cd(II)	0.01	53.80	0.42	0.97	0.01	32.90	0.55	0.98	1.06	0.53	0.97	1.22	0.54	0.90

FIGURE 10: Langmuir isotherm plot for adsorption of Pb(II) and Cd(II) ions by the DPAC and PPAC adsorbents.

FIGURE 11: Freundlich isotherm plot for adsorption of Pb(II) and Cd(II) ions by the DPAC and PPAC adsorbents.

The linear plots and kinetic constants of the pseudo-first- and pseudo-second-order reactions are presented in Table 5 and Figures 12 and 13. Notably, all kinetics constants were higher for the pseudo-second-order reaction than for the pseudo-first-order reaction, and the recorded q_e ranged from 12.0 to 22.37 mg/g, with $R^2=0.99$. Therefore, the Pb(II) and Cd(II) adsorption processes followed the pseudo-second-order kinetic model. Our findings are concordant with those obtained by Al-Qahtani et al. [64] who reported that the pseudo-second-order model reflected the adsorption of Ni(II),

Pb(II), and Cu(II) onto the surface of some extremophilic cyanobacterial mats. In addition, several studies proved that the pseudo-second-order kinetic model fit the data well for the adsorption processes of Pb(II), Cd(II), and Hg onto the surfaces of different adsorbents [27, 35, 41, 65].

The proposed adsorption mechanism onto the PPAC and DPAC is demonstrated in Figure 14. Many research studies have reported that the dominant mechanism is ion exchange in the sorption of heavy metals by natural materials.

TABLE 5: Pseudo-first-order and pseudo-second-order reaction constants for adsorption of Pb(II) and Cd(II) onto the surface of PPAC and DPAC adsorbents.

	Pseudo-first-order reaction						Pseudo-second-order reaction					
	PPAC			DPAC			PPAC			DPAC		
	q_e	K_1	R^2	q_e	K_1	R^2	q_e	K_2	R^2	q_e	K_2	R^2
Pb(II)	6.24	0.029	0.46	12.88	0.035	0.87	20.28	0.003	0.99	13.21	0.001	0.91
Cd(II)	13.15	0.033	0.67	8.50	0.038	0.59	22.37	0.002	0.97	12.00	0.002	0.94

FIGURE 12: Pseudo-first-order reaction plots for Pb(II) and Cd(II) adsorption onto DPAC and PPAC.

FIGURE 13: Pseudo-second-order reaction plots for Pb(II) and Cd(II) adsorption onto DPAC and PPAC.

FIGURE 14: Schematic diagram illustrating the proposed mechanisms for heavy metals' adsorption onto DPAC and PPAC.

6. Conclusion

Removal of different inorganic or organic pollutants by adsorption onto the surface of agricultural wastes has the advantages such as low cost, high efficiency and selectivity, environmental savings, and minimal levels of toxicity. Raw PPs and DPs were used as primary precursors for carbonization and chemical activation with H_3PO_4 (60%) and ZnCl_2 for use as biosorbents (adsorbents) to remove Cd(II) and Pb(II) from their aqueous solutions. Factors found to affect the adsorption process were solution pH, contact time, initial metal ion concentrations, adsorbent quantity, pH (with maximum removal capacities of Cd(II) and Pb(II) achieved at pH values from 6 to 6.5), and a contact time of 90 min for each adsorbent. The results showed that adsorption efficiency was higher for PPAC than for DPAC. The recorded Pb(II) and Cd(II) q_{max} values were 68.6 and 53.8 mg/g for PPAC and 34.18 and 32.90 mg/g for DPAC, respectively. The adsorption process data fit the Langmuir isotherm model better than the Freundlich model. Kinetically, the adsorption reaction followed a pseudo-second-order reaction model, with q_e ranging from 12.0 to 22.37 mg/g and $R^2 = 0.99$.

Data Availability

All data are available within the manuscript.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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