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Biosorption of Cd(II) from aqueous solutions using *Crataegus oxyacantha* stone and *Punica granatum* seed

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ABSTRACT

In this research, the biosorption of cadmium from aqueous solution by *Crataegus oxyacantha* (CO) stones and *Punica granatum* (PG) seeds was studied using batch technique. Experiments were conducted on factors, such as initial pH, biosorbent dosage, contact time, and initial concentration of cadmium. The equilibrium adsorption data were modeled according to Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms. It was proven that D–R isotherm with a correlation coefficient of 0.991 was more precise for demonstrating adsorption capacity of CO compared to other two models. The Freundlich equation with R^2 value of 0.996 was used to represent PG adsorption data. By increasing the optimum dosage of PG and CO to 20 g/L, the Cd adsorption was increased to more than 93–95%. Adsorption mechanism was defined by pseudo-first- and pseudo-second-order kinetic models, and it was found that it follows a pseudo-second-order kinetic algorithm. The study showed that the PG and CO can be suitable adsorbents with high absorption capacities for removing Cd(II) from solution.

Keywords: Biosorption; Cadmium; *Crataegus oxyacantha*; *Punica granatum*; Kinetic; Isotherm

1. Introduction

Water pollution is a major environmental problem caused by non-sustainable development of modern society, which may lead to ecological disequilibrium. Heavy metal ions such as copper, cadmium, lead, nickel, and chromium, are often found in industrial wastewater and can cause acute toxicity to both aquatic and terrestrial life. The purification and treatment of toxic effluents, which flow into the environment has been a major concern for numerous scholars [1]. Heavy metals are particularly dangerous because they are not biodegradable and could accumulate in living organisms [2]. Cadmium is toxic to humans and has been widely studied by many researchers. The most important source of Cadmium (II) in the environment is waste effluents. They can be produced as a result of electroplating, smelting, alloy manufacturing, production of pigments and plastic materials as well as batteries, and mining and refining processes [3]. Cd is listed as one of the most toxic metals. It is carcinogenic and can cause mental disturbances, lung insufficiency, bone lesions, anemia, hypertension, Itai–Itai disease, and weight loss [4–6]. The most widely used methods

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for removing heavy metals from wastewater include ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, and adsorption techniques. Most of these methods suffer from some drawbacks, such as high investment and operational cost or problems with disposal of the residual metal sludge. Therefore, they are not suitable for small-scale industries [7]. A promising alternative is biosorption due to its high efficiency and low cost, high adaptability and selectivity in removing a variety of heavy metals, and stable performance in purifying wastewater of low metal concentrations (1–100 mg L^{-1}) [8]. Biosorption is a process that uses inexpensive biomaterials to sequester metals from aqueous solutions. The biomaterials used in this process are known as biosorbents. Biosorption is an attractive and economic methodology and resources used in this method come from agricultural byproducts as well as food and pharmaceutical industries [9]. A wide variety of plant-derived materials such as Olive stones [10], grapefruit peel [11], green coconut shell [12], black gram husk [13], brown marine macro algae [14], *Platanus orientalis* leaves [15], ground pine cone [16], tea waste [17], and baker's yeast [18] are used as biosorbent to remove heavy metals from aqueous solutions. Pomegranate, *Punica granatum* (PG), is an ancient fruit originating in the Middle East and the Orient [19]. Pomegranate fruits are widely consumed both in fresh and processed forms, such as juice, jams, and wine. Pomegranate seeds, a byproduct of the pomegranate juice industry, are an inexpensive resource for biosorption. The *Crataegus oxyacantha* (CO) is a small- to medium-sized tree found mostly in temperate zones, such as North America, Western Asia, India, China, and North Africa. The CO fruits are known as pome, although the seeds and their boney endocarps are termed Pyrenees (stone) that can develop in five years. CO fruit is also used as a medicinal herb in pharmaceutical industry. Therefore, the Pyrenees (stones) are a byproduct of this industry as well. CO fruit is also consumed both in fresh and dried forms [20].

In the current research, the biosorption of cadmium from aqueous solutions by CO stones and PG seeds has been studied. The adsorption capacity of biomass was investigated through batch experiments. The effects of various parameters, such as initial pH of the solution, contact time, adsorbent amount, and Cd(II) concentration were also studied. Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models were used to develop equilibrium isotherms. Kinetic models, such as pseudo-first-order, pseudo-second-order, and Elovich algorithms were used to evaluate the mechanism of adsorption processes.

2. Material and method

2.1. Preparation of adsorbent

PG and CO fruits were collected from Damghan, a city in Semnan Province, Iran. The PG seeds and CO stones were carefully separated and rinsed with distilled water. Cleaned seeds were then dried at room temperature for 72 h. The dried seeds were grinded with Mortar Grinder (RM 200, Retsch Co.) and sieved with a standard sieve # 18 to obtain powder with a particle size of less than 1 mm. The prepared powders of CO stones (PCOS) and PG seeds (PPGS) were kept in polyethylene plastic containers at room temperature.

2.2. Preparing Cd(II) solution

All chemicals used were genuine and of analytical grade. The stock solution of cadmium(II) (100 mg/L) was prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ (E. Merck, Co.) in deionized water. To obtain the desired Cd(II) concentration, the stock solution was diluted with double-deionized water. The pH was adjusted with 0.1 mol/L solutions of either NaOH or HNO_3 and was rated by a digital pH meter (YK-2001CT, Lutron Co.).

2.3. Biosorption experiments

To study the adsorptive performance of PCOS and PPGS, sorption experiments were conducted at room temperature ($25 \pm 2^\circ C$). Experiments were carried out by shaking a definite amount of biosorbent with 50 mL of desired concentration of Cd(II) solution for a predetermined time interval at constant speed of 120 RPM in a rotary shaker. After mixing, the mixture was centrifuged. The supernatant solution was decanted and filtered through filter paper (Watmann #42) to measure the concentration of Cd in the filtered solution [21,22] by inductively coupled plasma techniques (ICP—GBC Co.). The effect of initial solution's pH was investigated using 1 g of the adsorbent and 50 mL of the solution with the concentration of 20 mg/L of Cd(II) was mixed for a pH range of 2.0–8.0. Experiments could not be accomplished at a pH value greater than 8.3, because beyond this pH value, Cadmium ions started to precipitate [23,24]. The batch kinetic experiment were carried out at a constant pH of 6.5 with initial concentration of 20 mg/L and adsorbent dose of 1g in 50 mL of solution (20 g/L) for various time intervals (5,10, 15, 30, 45, 60, and 120 min). For the isotherm studies, 1 g of PCOS or PPGS was mixed in 50 mL solution of Cd(II) (0.1, 0.5, 1, 10, 20, 40, 60, 80, and 100 mg/L). Also, at a constant pH of 6.5, the effects of an adsorbent dose of 0.125–2.5 g at

50 mL solution with a concentration of 20 mg/L were analyzed for a period of 45 min. It should be noted that all tests were triplicate to ensure the accuracy and repeatability of the results.

2.4. Data processing

The removal percentage ($R\%$) and uptake capacity (q) were calculated according to the following equations.

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$q = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where V is Cd(II) solution volume (L), m is the dosage of biosorbent (g), and C_0 and C_e (mg/L) are the initial and equilibrium concentrations of the Cd(II) ion in solution, respectively.

3. Results and discussion

3.1. Effect of initial pH of solution

The pH of the solution is one of the most important factors affecting Cd(II) sorption [25,26]. Fig. 1 shows biosorption of Cd(II) by PCOS and PPGS for different pH values. The experiments were conducted using 20 mg/L of initial Cd(II) solution at initial pH values ranging from 2.0 to 8.0. The metal solution was mixed with the biosorbents (20 g/L) for 1 h at 25°C. It was found that removal efficiency increases with an increase in the initial value of pH. If initial pH increases from 2 to 5, the Cd(II) sorption increases rapidly (Fig. 1(a); However, when the pH value stood between 5 and 8, there was no significant increase in Cd sorption (for both the biosorbent). Therefore, pH of 6.5 was selected for the current study. It could be interpreted that in the lower pH, there is a high concentration of H^+ in the reaction system, and the functional groups at the surface of biosorbents are protonated. Therefore, there are electrostatic repulsion between the protonated functional groups and the positively charged Cd(II) [27,28]. Additionally, occupation of the negative ligands of the biosorbents by H^+ and H_3O^+ ions leads to reduction of vacancies for cadmium ions, and consequently causes decrease in cadmium ions biosorption. As the pH increases, the ligands become deprotonated, and the negatively charged ligands attract the positively charged metal ions and binding occurs [29–31]. As seen in Fig. 1(b), the adsorbents showed buffer behavior. When the initial pH is acidic, adding an absorbent to the solution causes the increment of pH to reach to an equilibrium value. It could be due to attraction of H^+ to the surface of adsorbent, which consequently leads to decrease in the pH of the solution. In the other hand, when the initial pH is basic, the adsorbent would preferably attract OH^-, and therefore the pH of the solution declines to reach an equilibrium value.

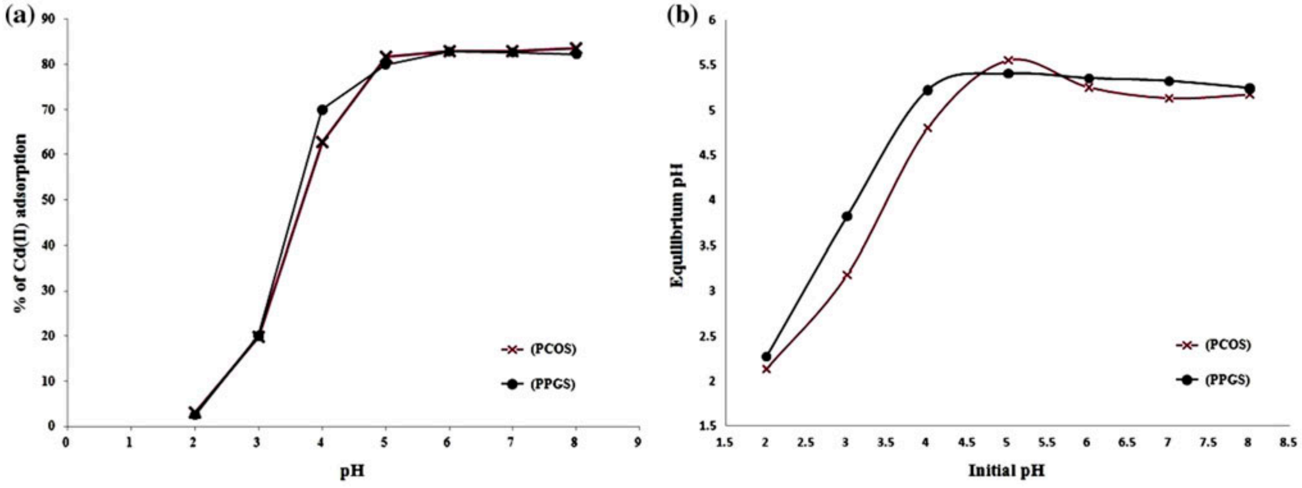

Fig. 1. (a) Effect of the initial pH of the solution on the adsorption of cadmium (contact time = 60 min), (b) The relation between the initial and equilibrium pH (adsorbent dose = 20 g/L, initial concentration of cadmium = 20 mg/L, time of contact time = 60 min).

3.2. Effect of contact time

The biosorption of Cd(II) by PPGS and PCOS was a rapid process and occurred in two phases. The effect of contact time on the biosorption of Cd(II) from aqueous solution is shown in Fig. 2. During the initial stage, the sorption rate increased quickly for 15 min, then the increase in Cd(II) sorption began to slow down and stabilized as it reached equilibrium. Fig. 2 also shows a sinusoidal shape after 45 min, which might be due to the desorption process. The initial fast phase occurs due to large surface area of the biosorbent being available for the adsorption of the Cd(II). The subsequent slow phase occurs due to quick exhaustion of the adsorption sites. Biosorption of the Cd(II) seems to follow a two-phase sorption mechanism [32,33]. In this study, for both the biosorbents (PPGS and PCOS), the optimum contact time was selected as 15 min for further experiments.

3.3. Effect of adsorbent dose

Effect of adsorbents (PPGS and PCOS) dosage on Cd(II) adsorption was investigated by changing the sorbent dose from 2.5 to 50 g/L with an initial metal concentration of 20 mg/L at a pH value of 6.5 for a contact time of 15 min (for both the biosorbents). Fig. 3 shows that the increase in removal efficiency and the adsorption capacity (mg/g) are proportional to the increase in adsorbent doses (PCOS and PPGS). As shown in Fig. 3, removal of Cd(II) increases with increase in the dosage of adsorbent from 2.5 to 50 g/L. The effect of dose increase was not significant beyond 20 g/L. When the dosage of PPGS and PCOS reached 20 g/L or more, the Cd sorption reached over 93–95%, respectively, and reached a steady state as the adsorbent dosage increased. This suggests that the maximum biosorption is attained when a certain biosorbent dosage is reached. Therefore, the quantity of ions remains constant even with further increase in the surface area of the biosorbent, which in turn increases the number of binding sites. However, at high sorbent dosages, the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, resulting in low metal uptake [34–36]. The optimum biosorbents dosage (for both the biosorbents) is selected as 20 g/L and is used for further experiments.

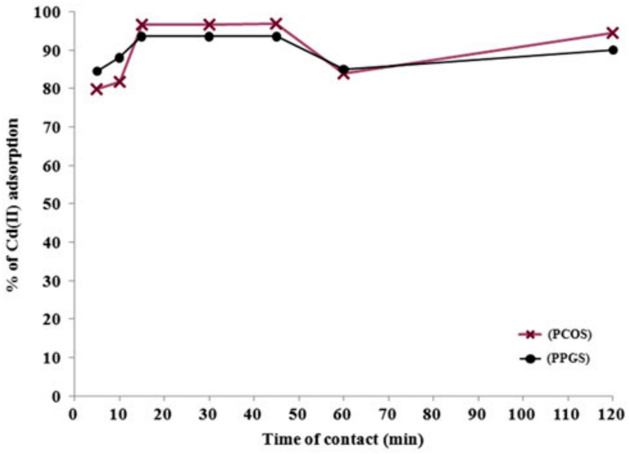

Fig. 2. Effect of contact time on the adsorption of cadmium at a pH of 6.5 (adsorbent dose = 20 g/L, initial concentration of cadmium = 20 mg/L, pH = 6.5).

3.4. Effect of initial concentration of cadmium

The Cd(II) adsorption is significantly influenced by the initial concentration of Cd(II) in aqueous solutions. The initial concentration of cadmium ions ranged from 0.1 to 100 mg/L, while the quantity of the adsorbent was maintained at 20 g/L at an initial pH value of 6.5. Fig. 4 shows the effect of initial Cd(II) concentration on the removal of Cd(II) and the adsorption capacity of two biosorbents. When PPGS was used, the Cd(II) removal decreased from 98 to 85% and the adsorption capacity increased from 0.005 to 4.25 mg/g with an increase in the initial Cd(II) concentration from 0.1 to 100 mg/L. Also, for the PCOS, the Cd(II) removal decreased from 99 to 70% and the adsorption capacity increased from 0.005 to 3.5 mg/g. In comparison with PPGS, this lower adsorption capacity can be explained as a result of insufficient binding sites. In other words, the saturation of binding sites can decrease the removal efficiency at higher concentrations [37–39].

3.5. Adsorption isotherm studies

Biosorption isotherm describes the relationship between the mass of the adsorbed components per the mass of biosorbent in solute phase. Equilibrium parameters provide important information for future efficient design of adsorption. In the present study, the Langmuir [40,41], Freundlich [42], and Dubinin and Radushkevich [43,44] isotherm models were tested and developed using the measured experimental data.

3.5.1. Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of uniform adsorption sites without migration of adsorbed

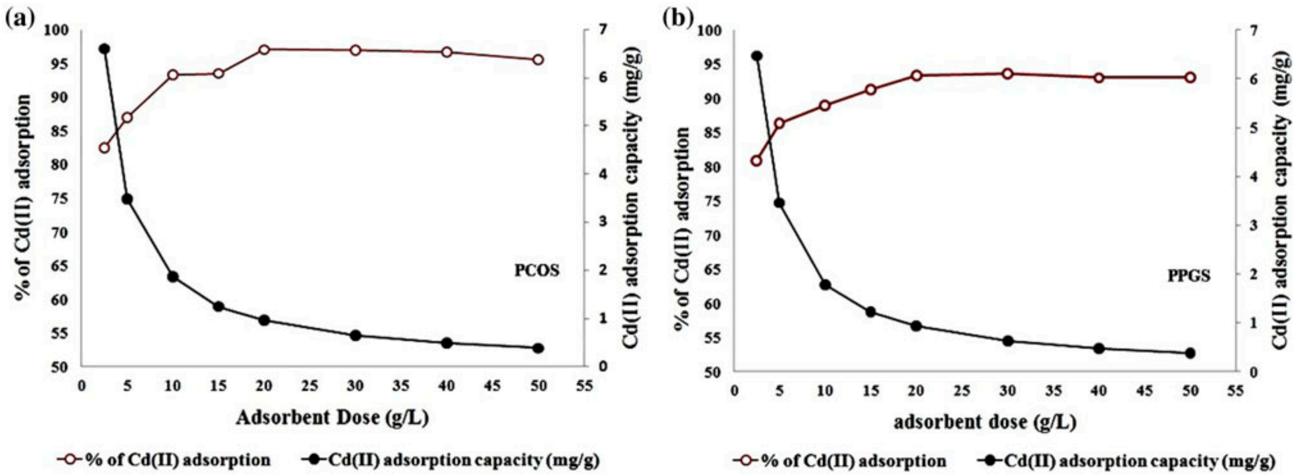

Fig. 3. Effect of adsorbent dose on the adsorption of cadmium with an adsorbent dose of (a) PCOS and (b) PPGS, range = 2.5–50 g/L, (contact time of 15 min, initial concentration of cadmium = 20 mg/L, pH = 6.5).

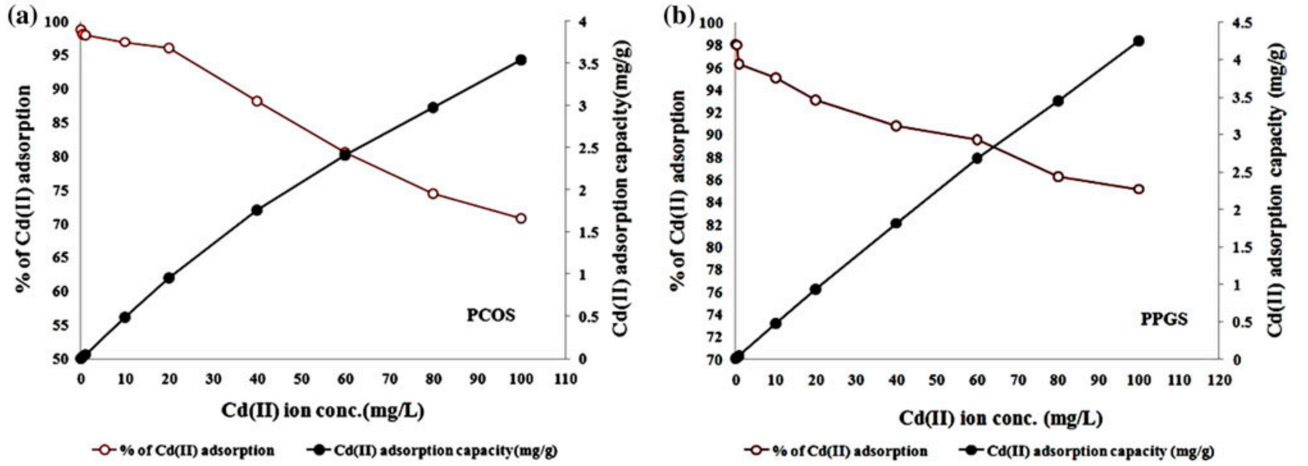

Fig. 4. Effect of initial metal ion concentration on the adsorption of cadmium by (a) PCOS and (b) PPGS (adsorbent dose = 2.5–50 g/L, pH = 6.5, time of contact = 15 min).

molecules to the surface. The Langmuir model for single-solute sorption is represented as:

$$q_e = \frac{q_{\max} \times b \times C_e}{1 + bC_e} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the quantity of cadmium adsorbed per gram of the adsorbent at equilibrium (mg/g), $q_{\max}$ is the monolayer sorption capacity of the sorbent (mg/g), and b is the Langmuir sorption constant (L/mg) relating the free energy of sorption and a high value is a sign of a higher dependency. A dimensionless constant, commonly known as separation factor (R_L), has been also defined by Webber and Chakkravorti, as [45]:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where b (L/mg) refers to the Langmuir constant and C_0 (mg/L) denotes the initial concentration of the adsorbate. The value of R_L lies between 0 and 1 for the favorable adsorption, while $R_L > 1$ represents unfavorable adsorption; $R_L = 1$ shows a linear adsorption, and $R_L = 0$, shows an irreversible adsorption [46,47].

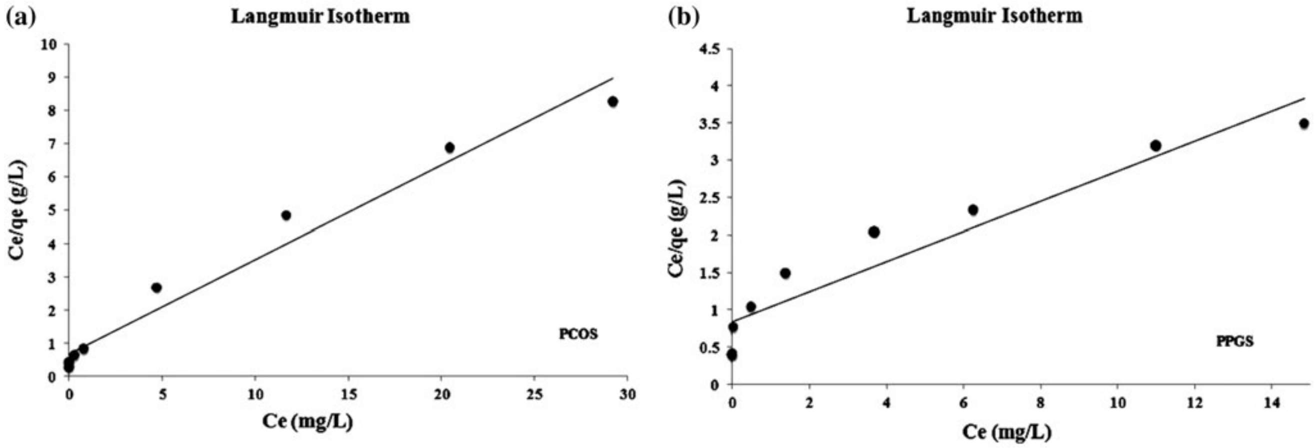

Fig. 5. Langmuir isotherm model: Cd(II) adsorption by (a) PCOS and (b) PPGS.

The isotherm experimental data were linearized using the Langmuir equation, which is shown in Fig. 5.

The dimensionless constant R_L ranged from 0.04 to 0.976 for PPGS and from 0.023 to 0.96 for PCOS. Therefore, both the biosorbants were classified as favorable. Table 1 shows data representing slope and intercept for linear Langmuir model. The data was used to calculate q_m (mg/g) and b (L/mg). The correlation coefficient (R^2) for both the biosorbents was greater than 0.97, which shows an efficient adsorption process. The maximum adsorption capacity was estimated at 5–3.53 mg/g for PPGS and PCOS, respectively. A comparison between the adsorption capacities of PPGS and PCOS and the capacity of other adsorbents is shown in Table 2. Variations in the adsorption capacity are most likely due to different properties of each adsorbent such as structure, functional groups, and surface area [45].

3.5.2. Freundlich isotherm

The Freundlich isotherm proposes a monolayer sorption pattern with a heterogeneous energetic distribution of active sites, accompanied by interaction among adsorbed molecules [48]. The Freundlich isotherm model can be expressed as:

$$q_e = k_f \times C_e^{\frac{1}{n}} \tag{5}$$

where k_f and n are the constants incorporating all factors affecting the adsorption process such as adsorption capacity and adsorption intensity. The linear form of Freundlich isotherm is shown as:

$$\ln\left(q_e\right) = \ln\left(k_f\right) + \frac{1}{n}\ln\left(C_e\right) \tag{6}$$

Table 1
Adsorption isotherm constants as described by PCOS and PPGS

	PCOS			PPGS		
Model	Langmuir	Freundlich	D–R	Langmuir	Freundlich	D–R
Slope	0.284	0.650	−0.0004	0.202	0.753	−0.0004
Intercept	0.679	−0.553	0.928	0.837	−0.430	0.946
R^2	0.972	0.972	0.991	0.913	0.996	0.972
Parameters	b = 0.418 (L/mg)	k_f = 0.575 ((mg/g)/(mg/L)^n)	k_{DR} = 0.0004 (mol^2/J^2)	b = 0.241 (L/mg)	k_f = 0.650 ((mg/g)/(mg/L)^n)	k_{DR} = 0.0004 (mol^2/J^2)
	q_{max} = 3.530 (mg/g)	n = 1.540	q_{max} = 2.530 (mg/g)	q_{max} = 5.0 (mg/g)	n = 1.330	q_{max} = 2.576 (mg/g)
	R_L = 0.023–0.96	–	E = 0.353 (kJ/mol)	R_L = 0.04–0.976	–	E = 0.353 (kJ/mol)

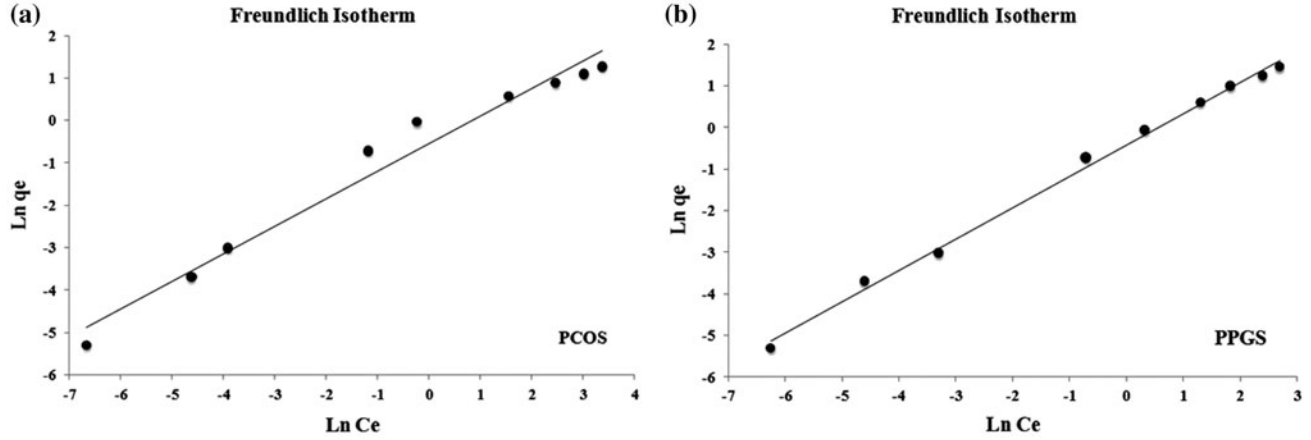

Fig. 6. Freundlich isotherm model: Cd(II) adsorption by (a) PCOS and (b) PPGS.

The Freundlich constants, k_f and n can be estimated by plotting the $\ln(q_e)$ vs. $\ln(C_e)$ as shown in Table 1. The Freundlich isotherm is shown in Fig. 6. The value of n is related to the distribution of bonded ions on the sorbent surface, which may represent beneficial adsorption if it is between 1 and 10. If the values of n are close to 1, it shows that the heterogeneity of the sorbent surface has little importance, while the value gets closer to 10, the heterogeneity becomes more important [29,49]. As shown in Table 1, the value of n for the biosorbents used was found to be greater than 1 that is 1.330 and 1.540 for PPGS and PCOS, respectively. These values indicate the favorable adsorption of Cd(II) by both the biosorbents as well as low importance of heterogeneity of the solid surface on the sorption process. The correlation coefficients (R^2) for PPGS and PCOS stood at 0.996–0.972, respectively.

3.5.3. D–R isotherm

To assess the nature of biosorption process and see whether it is physical or chemical, D–R isotherm was utilized. The D–R isotherm can be expressed as:

$$q_e = q_m \exp(-k_{\mathrm{DR}}\varepsilon^2) \tag{7}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

where q_m (mg/g) is the maximum biosorption capacity, k_{DR} ($\mathrm{mol}^2/\mathrm{J}^2$) is the constant expressing the adsorption energy, ε is the Polanyi potential, T (K) is the absolute temperature, and R [J/(mol K)] is the gas constant. The linear form of D–R isotherm is shown as:

$$\ln(q_e) = \ln(q_m) - k_{\mathrm{DR}} \times \varepsilon^2 \tag{9}$$

The mean biosorption energy (E, kJ/mol) is obtained from the following equation:

$$E = \frac{1}{\sqrt{2k_{\mathrm{DR}}}} \tag{10}$$

The mean biosorption energy, E, is the free energy, which causes transference of 1 mol of solute from solution phase by the surface of the adsorbent. The E value can be used to assess the sorption properties (Eq. (10)). If the E value is between 8 and 16 kJ/mol, a chemical reaction is dominant, and if $E < 8$ kJ/mol, a physical adsorption is dominant [50,51].

The D–R isotherm constants, k_{DR} and q_m, are estimated on the basis of the slope and the intercept of the plot between $\ln(q_e)$ and ε^2 (Fig. 7). The constants, q_m and k_{DR}, and the correlation coefficient (R^2) for both the biosorbents are shown in Table 1. The mean biosorption energy was calculated at 0.35 kJ/mol for both the biosorbents. The results showed that the biosorption process of Cd(II) by PPGS and PCOS is mainly performed by physical adsorption process.

3.5.4. Final remarks on isotherm study

The biosorption isotherm is important in wastewater treatment facilities to estimate biosorption capacity of the adsorbent. For PCOS, the correlation coefficient is high in D–R model ($R^2 = 0.99$) compared with Freundlich and Langmuir models ($R^2 = 0.97$). It indicates that D–R model is more suitable for describing

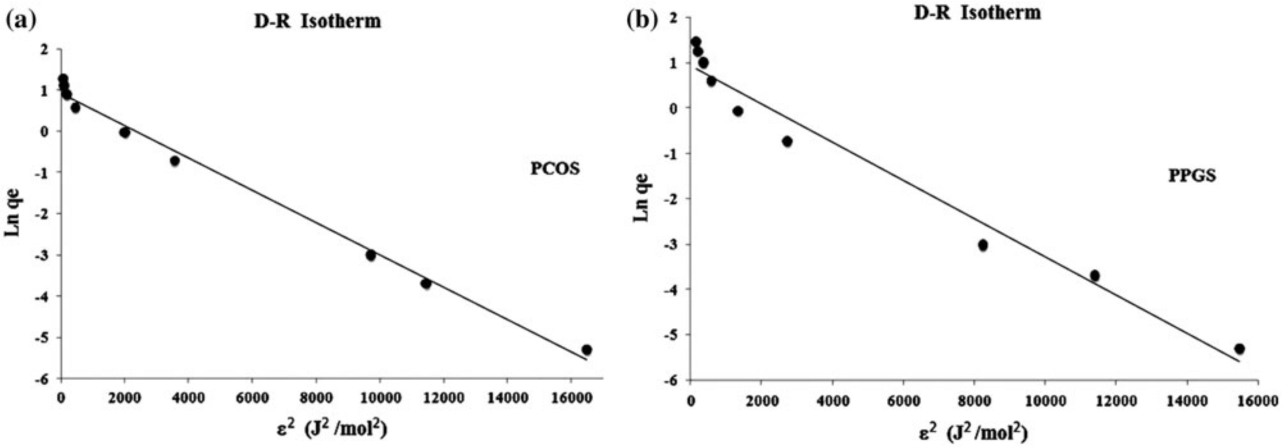

Fig. 7. D–R isotherm adsorption model: Cd(II) by (a) PCOS and (b) PPGS.

the biosorption equilibrium. For PPGS, the Freundlich model has a higher correlation coefficient ($R^2 = 0.99$) compared with Langmuir ($R^2 = 0.91$) and D–R ($R^2 = 0.97$). It indicates that Freundlich model is more suitable for describing the biosorption equilibrium. Finding the biosorption isotherm is helpful for the design of a fixed-bed adsorption column that is needed to assess the amount of cadmium accumulated on the solid surface. The latter is required to obtain the liquid phase concentration of Cd at the column height in any given time. The shape of the breakthrough curve is also identified by the adsorption isotherm. This shape is the main parameter in designing the fixed-bed adsorption columns [52].

3.6. Adsorption kinetic studies

The process of Cd(II) removal from an aqueous phase by any adsorbent can be explained using kinetic models. These models show the rate-controlling mechanism of the adsorption process. The kinetic parameters are also useful in predicting the adsorption rate which could be used as important data for design and modeling of the fixed-bed adsorption process. The kinetic models, such as Lagergren's pseudo-first order [53], McKay and Ho's pseudo-second order [54], and Chein and Clayton's Elovich equation [55], were utilized to assess the biosorption kinetics of Cd(II) in the present research.

3.6.1. Pseudo-first-order kinetic model

The pseudo-first-order model of adsorption was proposed by Lagergren, [54,56]. It describes a rate of adsorption that is proportional to the number of unoccupied binding sites in the biosorbent. The model works efficiently in cases where the biosorption process occurs quickly. The pseudo-first-order model for prediction of biosorption is not suitable when the adsorption process is too long [54,56]. The linear form of the pseudo-first-order model is represented as:

$$\log\,(q_e + q_t) = -\frac{k_1}{2.303}t + \log\,(q_e) \tag{11}$$

where q_e and q_t (mg/g) are, respectively, the adsorption capacities at equilibrium phase and at time t, and k_1 (per min) represents the rate constant of pseudo-first-order sorption. The values of k_1 and the calculated $q_{e,\text{cal}}$, which were estimated by plotting log ($q_e - q_t$) vs. t, are shown in Table 3.

3.6.2. Pseudo-second-order kinetic model

The pseudo-second-order model described by Lagergren [53] is represented as:

$$\frac{dq_t}{dt} = k_2 \times (q_e - q_t)^2 \tag{12}$$

Or

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{13}$$

where q_e and q_t (mg/g) represent the adsorption equilibrium and capacity at time t, respectively, and k_2 (g/(mg.min)) is the rate constant of pseudo-second-order sorption model. The plot of t/q_t vs. t as shown in Fig. 8 can provide a linear relationship from which the coefficients q_e and k_2 can be calculated. The pseudo

Table 2
Comparison of different adsorbents used for the removal of Cd(II) from aqueous solution

No	Adsorbent	q_m (mg/g)	References	No	Adsorbent	q_m (mg/g)	References
1	Moringa olifera	1.06	[57]	9	Almond shell	7.0	[65]
2	Spruce wood	2	[58]	10	Olive stone	7.33	[66]
3	Rice husk ash	3.02	[59]	11	Bamboo charcoal	12.08	[67]
4	Raw corn stalk	3.39	[60]	12	Papaya wood	17.22	[68]
5	Activated carbon	3.4	[61]	13	Sugar beet pulp	46.1	[69]
6	Aspergillus niger	4.0	[62]	14	Red mud	106.04	[70]
7	Coconut copra meal	4.99	[63]	15	CO stone	3.53	This study
8	Walnut tree sawdust	5.76	[64]	16	PG seed	5	This study

Table 3
Parameters of kinetic isotherm models described for the adsorption of Cd(II) by PCOS and PPGS

	PCOP			PPGS		
Model	Pseudo-first order	Pseudo-second order	Elovich	Pseudo-first order	Pseudo-second order	Elovich
Slope	−0.1145	0.9982	0.0868	−0.0811	1.054	0.0428
Intercept	−0.158	1.366	0.6625	−0.85	0.576	0.7874
R^2	0.841	0.998	0.753	0.876	0.999	0.8044
Parameters	$q_e = 0.695$ (L/mg)	$q_e = 1.002$ (L/mg)	$\alpha = 179.2$ (g/mg min)	$q_e = 0.14$ (L/mg)	$q_e = 0.95$ (L/mg)	$\alpha = 4179145$ (g/mg min)
	$K_1 = 0.264$ (min^{-1})	$K_2 = 0.729$ (g/mg min)	$\beta = 11.52$ (g/mg)	$K_1 = 0.187$ (min^{-1})	$K_2 = 1.93$ (g/mg min)	$\beta = 23.36$ (g/mg)
	Experimental $q_e = 0.97$ (L/mg)			Experimental $q_e = 0.94$ (L/mg)		

constants and the corresponding correlation coefficient (R^2) are shown in Table 3. The calculated q_e values are highly correlated with the experimental values when R^2 is more than 0.99 for both the biosorbents.

3.6.3. Elovich kinetic model

Elovich model is a rate equation based on the adsorption capacity commonly expressed as Eq. (14):

$$\frac{dq_t}{dt} = \alpha \cdot e^{-\beta q_t} \tag{14}$$

where α (mg/mg.min) is the initial adsorption rate and β (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. Eq. (14) is simplified by assuming $\alpha{\cdot}\beta > t$, and also by assuming the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, as given by Eq. (15):

$$q_t = \frac{1}{\beta}\ \ln\ (\alpha \cdot \beta) + \frac{1}{\beta}\ \ln\ (t) \tag{15}$$

The values of initial adsorption rate (α) and desorption constant (β) were determined by plotting q vs. ln(t), which is shown in Fig. 9. Parameters of Elovich model are shown in Table 3. The correlation coefficient of PCOS and PPGS are 0.753–0.804, respectively.

3.6.4. Final remarks on kinetic studies

Pseudo-first-order, pseudo-second-order, and Elovich kinetic models were utilized to simulate the Cd(II) sorption behavior. As is shown in Table 3, a pseudo-second-order model with higher correlation coefficient ($R^2 = 0.99$) is more suitable for the simulation of the Cd(II) sorption process. In addition, the theoretical equilibrium capacity (q_e) deduced from the pseudo-second-order equation (1.002 mg/g for PCOS and 0.95 mg/g for PPGS as shown in Table 3) was closer to the experimental values (0.97 mg/g for PCOS and 0.94 mg/g for PPGS as shown in Table 3). These findings are of importance, when it comes to the design of a fixed-bed adsorption column to determine the equilibrium capacity of adsorbent at various fluid phase concentrations [52].

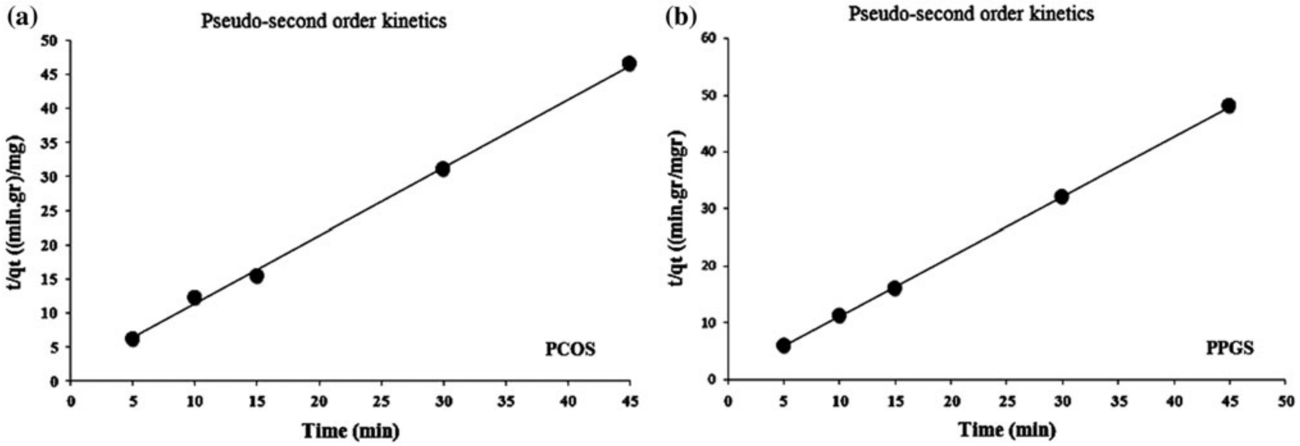

Fig. 8. Pseudo-second-order plot for Cd(II) adsorption onto (a) PCOS and (b) PPGS.

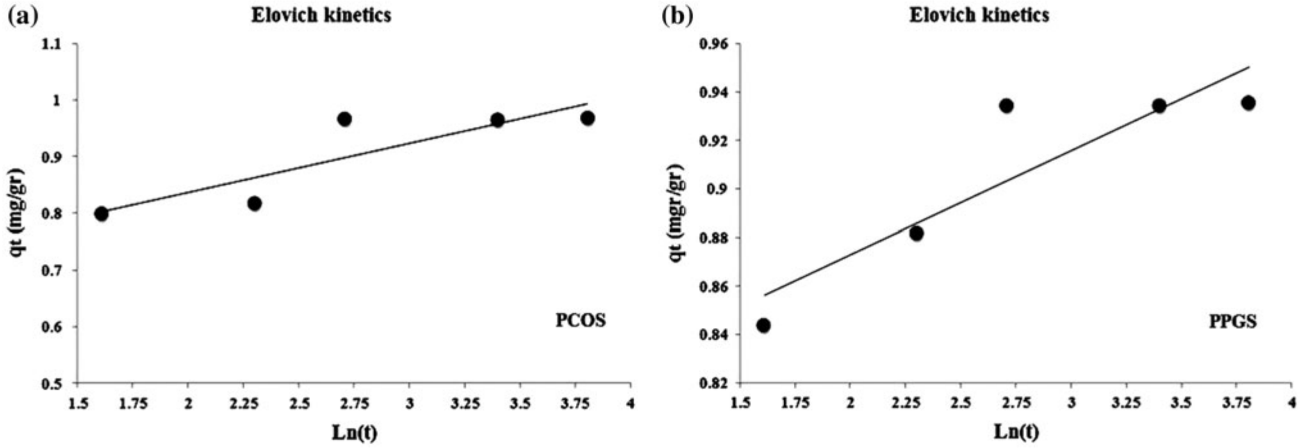

Fig. 9. Elovich kinetic model plot for Cd(II) adsorption by (a) PCOS and (b) PPGS.

4. Conclusion

The feasibility of the use of PCOS and PPGS for biosorption of Cd from an aqueous solution was investigated. With a wide pH range, short biosorption equilibrium time, and acceptable biosorption capacity, both PCOS and PPGS may prove to be efficient, low-cost and environment-friendly biosorbent for cadmium bioremediation. Both the adsorbents had buffer properties and the optimum pH was found to be 6.5. The best isotherm models with higher correlation coefficient ($R^2 = 0.99$) were Freundlich for PPGS and D–R model for PCOS. Since the values of n for both the sorbents in Freundlich isotherm were close to unity, the heterogeneity of their surface has a little importance on the amount of sorption. The biosorption process for both the biosorbents followed the pseudo-second-order kinetic model with R^2 value of 0.99, which was more efficient when compared with pseudo-first-order and Elovich models. The free energy of sorption was found to be less than 8 kJ/mol, which is an indication of physical adsorption for both the sorbents.

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