Research Article

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Removal of cadmium and lead from aqueous solutions using iron phosphate-modified pollen microspheres as adsorbents

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Abstract: Iron phosphate-modified pollen microspheres (pollen@FePO₄) were prepared and applied as sorbents for the removal of heavy metals (Cd²⁺ and Pb²⁺) from the aqueous solution. Batch sorption studies were conducted to investigate the effects of solution pH, contact time, sorbent dosage, and metal concentration on the adsorption process. The sorption of Cd²⁺ and Pb²⁺ ions on pollen@FePO₄ corresponds to the pseudo-second-order model and Langmuir isotherm, which is similar to the unmodified pollen. At pH 5.92, pollen@FePO₄ offers maximum adsorption capacities of 4.623 and 61.35 mg·g⁻¹ for Cd²⁺ and Pb²⁺, respectively. The faster sorption kinetics and higher adsorption capacities of Cd²⁺ and Pb²⁺ ions onto pollen@FePO₄ than pollen indicates that it might be a promising material for the removal of heavy metal ions in aqueous solutions. The possible adsorption mechanism involves electrostatic and chemisorption for Cd²⁺ and mainly complexation for Pb²⁺.

Keywords: iron phosphate, pollen, heavy metals, adsorption, kinetic, isotherm

1 Introduction

Nowadays, human activities have caused serious environmental pollution, and water pollution is one of the most important problems worldwide. The main sources of heavy metal pollutants are mining, metallurgy, machinery

manufacturing, electroplating, chemical industry, pesticide, paint, fuel, etc. Heavy metals are not biodegradable and have become an ecotoxicological hazard with increasing significance because they are harmful to human physiology and other biological systems when they exceed tolerance levels [1]. Cadmium and lead are toxic heavy metals [2]. Cadmium may result in renal damages, emphysema, elevated blood pressure, cardiovascular disorders, and skeletal malformations in the living organism even at little concentrations [3,4]. Lead can cause damage to the central nervous system, kidney, liver, reproductive system, basic cellular processes, and brain functions at a concentration of >7.0 µg·L⁻¹ according to the World Health Organization [5].

The various techniques for heavy metal removal from aqueous solutions have been widely investigated, including chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation–flocculation, and flotation techniques [6]. Adsorption is one of the most preferred methods among these techniques because it has many advantages, such as high efficiency, easy handling, and low cost [7,8]. The selection of adsorbents is an important research topic in the application of adsorption techniques. In this regard, various adsorbents have been studied for the wastewater treatment, including conventional materials (e.g., active carbon, silica gel) and non-conventional adsorbents (e.g., biosorbents, nanomaterials) [9–15]. Interest in biosorption for the removal of heavy metals is growing because of its excellent efficiency, minimization of secondary waste, and low cost of biosorbent materials [16]. Pollen grains are naturally occurring substances from plants and are the physiological containers that produce the male gametes of seed plants [17], which contain high contents of glucose, fructose, and sucrose [18]. They have been applied for the preparation of novel materials [19–22], as novel adsorbents for protein chromatography and removal of organic pollutants [23,24] and heavy metals [25,26], and solid-phase extraction of 16 plant growth regulators and trans-resveratrol [27,28].

In our previous study, iron phosphate has been applied for the adsorption and solid-phase extraction of

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some heavy metals and has shown good adsorption properties due to its unique structural characteristics [29–31]. The latest review on iron phosphates can be seen in the literature [32]. Considering that the modified plant materials are found to exhibit better adsorption ability toward heavy metals in comparison with bare plant adsorbents [33], it is quite possible that the iron phosphate-modified pollen grains might perform well for the adsorption and removal of heavy metals. The prepared composite might have not only the advantages of biosorption but also better adsorption performance.

On the basis of the aforementioned ideas, the iron phosphate-modified pollen microspheres (pollen@FePO₄) were prepared, and its ability to adsorb Cd(II) and Pb(II) ions from aqueous solutions was investigated. Environmental parameters affecting the sorption process such as solution pH, contact time, sorbent dosage, and metal concentration were studied. The adsorption kinetics, isotherm, and probable mechanism were also explored.

2 Experimental

2.1 Instrumentation

The particle size and Zeta potential of the material were measured by a Nano Zetasizer (Nano ZS90, Malvern, England). The surface morphology of the material was observed under a BX51 fluorescence microscope (Olympus, Japan). Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet iS5 Fourier Transform Infrared Spectrometer (Thermo Fisher, USA) with attenuated total reflectance (ATR) module. The quantification of cadmium and lead was facilitated by a TAS-990 atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co., LTD, China). A ZD-810 shaker (Shanghai Jinghong Experimental Equipment Co., Ltd, China) was used for facilitating the adsorption of metal ions. A TDL-80-2B centrifuge (Shanghai Anting Scientific Instrument Factory, China) was employed for the centrifugation of solutions. The pH values were measured with a PHS-3E pH meter (Shanghai INESA Scientific Instrument CO., LTD, China).

2.2 Reagents and solutions

Reagents used in this study were at least of analytical reagent grade unless otherwise specified, including CdCl₂·2.5H₂O,

Pb(NO₃)₂, FeCl₃·6H₂O, Na₂HPO₄·12H₂O, CH₃COONa·3H₂O, 95% ethanol, nitric acid, and sodium hydroxide. The stock solution of cadmium (1,000 mg·L⁻¹) was prepared by dissolving 2.0315 g of CdCl₂·2.5H₂O in deionized (DI) water and diluted to 1,000 mL. The stock solution of lead (1,000 mg·L⁻¹) was prepared by dissolving 1.5985 g of Pb(NO₃)₂ in DI water and diluted to 1,000 mL. The prepared stock solutions were stored at 4°C for future use. Working standards of different concentrations were obtained by step-wise dilution of the stock solutions. DI water of 18 MΩ·cm was used throughout. The pH value of the solutions was adjusted with diluted NaOH and/or HNO₃ (0.1 mol·L⁻¹). Rape bee pollen, purchased from the market, was pretreated before use. It was thoroughly washed alternately with 95% ethanol and DI water by ultrasonic dispersion method and dried at room temperature.

2.3 Preparation of pollen@FePO₄

20 g of pretreated rape pollen and 100 mL of the aqueous solution of 0.04 mol·L⁻¹ FeCl₃ were added into a round-bottom flask. The mixture was stirred by a magnetic stirrer for ca. 3 h at room temperature to get a well-dispersed suspension. 0.04 mol Na₂HPO₄·12H₂O and 0.04 mol CH₃COONa·3H₂O were dissolved in 100 mL of DI water, which was then added dropwise into the suspension under stirring. The resulting mixture was continuously stirred for 24 h. Then, the mixture was transferred into a beaker, washed with DI water and ethanol, and collected by centrifugation. The received iron phosphate-modified pollen microspheres, denoted as pollen@FePO₄, were then suspended in DI water, diluted to 250 mL in a volumetric flask, and stored at 4°C for future use. The preparation process of pollen@FePO₄ is shown in Figure 1.

2.4 Sorption studies of heavy metal ions on pollen@FePO₄

Batch mode experiments were used to investigate the adsorption of heavy metal ions on the adsorbents, as shown in Figure 1. A mixture of pollen@FePO₄ microspheres and an aqueous solution of Cd²⁺ or Pb²⁺ at certain pH in a conical flask was shaken by a shaker at room temperature. Then, the suspension was centrifuged, and the supernatant was decanted to allow the determination of the residual amounts of the heavy metal ions in the

Figure 1: Preparation of pollen@FePO₄ and sorption of heavy metals on pollen@FePO₄.

solution after adsorption. The adsorption efficiency and the adsorption capacity of the heavy metal ions on pollen@FePO₄ microspheres were obtained by calculating according to equations (1) and (2) as follows.

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

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

where X_r (%) is the adsorption efficiency of adsorbate on the adsorbent, q_e (mg·g⁻¹) is the equilibrium adsorption, C_0 and C_e (mg·L⁻¹) are the concentration of adsorbate at initial and equilibrium state, respectively, V (L) is the solution volume, and m (g) is the weight of adsorbent applied.

The investigation of several important affecting factors of adsorption, including the dosage of adsorbent, initial pH value of the solution, adsorption time, and initial concentration of heavy metal ions in solution, was conducted similarly as aforementioned procedures.

The comparison study with pretreated rape pollen was performed according to the aforementioned steps.

3 Results and discussions

3.1 Characterization studies

The morphologies of pollen and pollen@FePO₄ are shown in Figure 2. It can be observed that the pollen consists of uniform spherical particles (Figure 2a), and no obvious changes of the particle appearance are found after the modification by iron phosphate (Figure 2b), which indicates that the pollen is stable in the process of preparing pollen@FePO₄. However, some broken spheres exist among the modified pollen particles. Due to the trilayer construction of the pollen wall, the coating on the surface of pollen spheres is made up of two different kinds of layers [24]. The outer layer of FePO₄ precipitate on the network structure might collapse in the subsequent cleaning and centrifugation process, and thus some broken pieces appear. The average diameter of pollen spheres measured by the Nano Zetasizer is 3,940 nm and that of pollen@FePO₄ is 5,168 nm. The particle size of pollen@FePO₄ increases obviously, which further illustrates the coating of iron phosphate on the pollen surface.

The FTIR spectra of pollen and pollen@FePO₄ are shown in Figure 3. In the case of pollen (Figure 3a), the peak at ~3,281 cm⁻¹ is ascribed to the stretching vibration of the hydroxyl group. The characteristic peaks (~2,923, ~2,852, ~1,454 cm⁻¹, etc.) corresponding to organic matters may be attributed to the absorption bands of cellulose and hemicellulose in pollen. The peak at ~1,737 cm⁻¹ corresponds to the amide group of protein. For the prepared pollen@FePO₄ (Figure 3b), the peaks at ~2,923, ~2,852, ~1,454, and ~1,737 cm⁻¹ are weakened obviously. In addition, a new peak that appeared at 1,002 cm⁻¹ can be assigned to P–O stretching vibration, which indicates the existence of the PO₄ group [34]. The aforementioned

Figure 2: Microscope images (×100) and size distribution of pollen (a) and pollen@FePO₄ (b).

Figure 3: ATR-FTIR spectra of pollen (a) and pollen@FePO₄ (b).

information demonstrates that an iron phosphate coating is formed on the surface of the pollen grains.

Zeta potentials of pollen and pollen@FePO₄ within pH 2–7 are shown in Figure 4. As shown in Figure 4a, the isoelectric point (IEP) of pollen is approximately pH 4.7, and the IEP of pollen@FePO₄ (Figure 4b) changes to approximately pH 5.0. Since the material surface is positively charged at pH < pI and negatively charged at pH > pI, the pI change of the material reflects that there might be some changes on its surface. The above results indicate the coating of iron phosphate on the pollen grains.

3.2 Selection of experimental parameters

3.2.1 Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Cd²⁺ by pollen@FePO₄ microspheres is shown in Figure 5. The adsorption of Cd²⁺ increases rapidly from 11.75 to 45.75% with the increase of pollen@FePO₄ from 0.08195 to 0.3278 g due to the increase of active adsorption sites on the adsorbent. Thereafter, with the increase of adsorbent dose, the increase of cadmium adsorption slows down

Figure 4: Zeta potentials of pollen (a) and pollen@FePO₄ (b).

Figure 5: Effect of adsorbent dose on (a) the adsorption efficiency and (b) the equilibrium adsorption of Cd²⁺ on pollen@FePO₄ microspheres. Sample: 50 mL, 40 mg·L⁻¹ Cd²⁺, pH 5.92; contact time 60 min.

and the equilibrium adsorption capacity decreases sharply. Considering the adsorption performance and actual cost, 0.3278 g of pollen@FePO₄ microspheres are taken as the optimum amount for the following experiments. The same dosage is used for the comparison tests with the pollen adsorbent.

3.2.2 Effect of pH

Solution pH is one important parameter in the adsorption of Cd²⁺ and Pb²⁺ ions from aqueous solutions using pollen@FePO₄ microspheres as sorbents. The effect of pH on the adsorption efficiency is determined in the pH ranging from 3 to 8 with the initial heavy metal concentration of 40 mg·L⁻¹ (Cd²⁺) or 200 mg·L⁻¹ (Pb²⁺), as illustrated in Figure 6.

As can be seen from the black curve in Figure 6, when the pH value increases from 3.01 to 4.02, the adsorption of Cd²⁺ on the pollen@FePO₄ microspheres is not improved significantly, whereas a rapid increase to 44.2 is observed by increasing the pH value to 5.03, and then the variation of the adsorption is not obvious when further increasing to pH 8. The maximum adsorption of Cd²⁺ appears at pH 7.01. The effect of pH might be explained considering the surface charge and the active adsorption sites on the adsorbent. At low pH values, H⁺ might combine with the adsorption sites of active groups on the surface of the microspheres, which not only occupies the active sites but also increases the positive charge density of the surface sites, and thus, electrostatic repulsion between Cd²⁺ and the surface of the adsorbent prohibits the adsorption of heavy metal ions. With the increase of pH value, the increased concentration of

Figure 6: Adsorption efficiency of Cd^{2+} or Pb^{2+} onto pollen@FePO₄ microspheres as a function of pH. Sample: 50 mL, 40 mg·L⁻¹ Cd^{2+} or 200 mg·L⁻¹ Pb^{2+} ; adsorbent dosage 0.3278 g; contact time 60 min.

OH^- in the solution leads to the increase of the negative charge on the adsorbent surface, which promotes the adsorption of Cd^{2+} . Therefore, the adsorption mechanism of Cd^{2+} on the pollen@FePO₄ microspheres is related to the electrostatic.

As for Pb^{2+} (the red curve in Figure 6), its adsorption on pollen@FePO₄ adsorbents remains at approximately 99% when regulating the pH value of the solution within the range of 3–8. This illustrates that there is no obvious effect of solution pH on the retention of Pb^{2+} by pollen@FePO₄. The adsorption of Pb^{2+} is mainly related to the complexation, and the optimal pH value is 5.92.

Since there is little difference between the adsorptions of Cd^{2+} at the optimal pH 7.01 and that at pH 5.92 (DI water), the samples are prepared with DI water in the follow-up experiments, and the pH value of the solutions is 5.92.

3.2.3 Effect of initial metal ion concentration

The initial metal ion concentration of metal ions in the solution always plays an important role in the adsorption

of heavy metal ions by pollen@FePO₄ microspheres. The effect of the initial concentration of Cd^{2+} and Pb^{2+} ions on the adsorption performance was studied in aqueous solutions at room temperature by varying the initial metal ion concentrations while keeping all other parameters constant. As shown in Figure 7, the equilibrium adsorption of metal ions increases, while the adsorption efficiency decreases with the increase of initial concentrations. Since the higher initial metal ion concentration provides a greater driving force by a higher concentration gradient pressure to overcome the mass transfer resistance between the solution and solid phases, the collision frequency between metal ions and the adsorbent surface increases [35,36]. This is the main reason for the higher amount of metal ions adsorbed (i.e., q_e) with a higher initial metal ion concentration. Conversely, the adsorption sites might generally adsorb the available metal ions more quickly at low concentrations. With the increase of concentration, intraparticle diffusion gradually becomes dominant, and the adsorption efficiency of metal ions shows a trend of gradual decrease due to a lack of sufficient surface area to accommodate much more metal ions [37]. Therefore, the adsorption efficiency of metal ions by pollen@FePO₄ can be improved by diluting the solution when treating the actual samples with a high concentration of metal ions. In addition, the adsorption capacity of pollen@FePO₄ for Pb^{2+} is approximately ten times higher than that for Cd^{2+} , indicating pollen@FePO₄ prefers adsorbing Pb^{2+} over Cd^{2+} .

3.2.4 Effect of contact time

To further understand the adsorption process, it is important to investigate the contact time required to complete the adsorption. Figure 8 shows the effect of contact time on the sorption of Cd^{2+} and Pb^{2+} by pollen@FePO₄. The adsorption efficiency of Cd^{2+} increases rapidly to 45%

Figure 7: Effect of initial metal ion concentration on (a) the adsorption efficiency and (b) the equilibrium adsorption of Cd^{2+} or Pb^{2+} on pollen@FePO₄ microspheres. Sample: 50 mL, pH 5.92; adsorbent dose 0.3278 g; contact time 60 min.

Figure 8: Effect of contact time on the adsorption efficiency of Cd²⁺ or Pb²⁺ on pollen@FePO₄ microspheres. Sample: 50 mL, 40 mg·L⁻¹ Cd²⁺ or 200 mg·L⁻¹ Pb²⁺, pH 5.92; adsorbent dose 0.3278 g.

with contact time of 5 min. No appreciable changes in terms of adsorption efficiency are observed within 5–30 min. The rapid adsorption of Cd²⁺ at the beginning might be due to the initial bare surface of the adsorbent, which provides a large number of active sites for the adsorption. With the increase of contact time, the Cd²⁺ concentration of the solution gradually decreases; meanwhile, the active sites of the adsorbent gradually saturates, which leads to the increase in the mass transfer resistance between the solid and the solution. Thus, the adsorption rate gradually decreased until it reaches equilibrium.

Similarly, the adsorption efficiency of Pb²⁺ increases rapidly to 99% with a contact time of 5 min. Further increasing the contact time has a negligible effect on the adsorption of Pb²⁺, indicating that the adsorption equilibrium can be reached within 30 min.

Compared with cadmium, although pollen@FePO₄ can adsorb more lead ions, it takes a little longer to get equilibrium. Since the surface active sites of the adsorbent might show different properties in adsorbing different ions and Pb²⁺ ions with the larger ionic radius need to overcome a greater space resistance to adsorb on the surface of pollen@FePO₄ microspheres, the adsorption equilibrium time is longer. Nevertheless, the contact time of 60 min is sufficient for subsequent experiments. The possible errors that might be caused by the contact time were considered in the determination of this parameter.

3.3 Adsorption kinetic study

It is essential to study the kinetics of the adsorption process because it provides much important information for

designing batch adsorption systems, e.g., the adsorption rate, the performance of adsorbent, and the rate-limiting step in the sorption process. The kinetics of the adsorption data in this article are investigated using three kinetic models, pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model. The consistency between the experimental data and the predicted values of models is expressed by the correlation coefficient (R^2).

The pseudo-first-order model proposed by Lagergren [38] is generally described by equation (3), which can be transformed to the form as given in equation (4) [39–42]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (3)$$

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t}, \quad (4)$$

where q_e and q_t (mg·g⁻¹) are the adsorption at equilibrium and at time t , respectively, and k_1 (min⁻¹) is the rate constant of pseudo-first-order sorption. The straight-line plots of $1/q_t$ vs $1/t$ of equation (4) (Figure 9a) are used to determine the values of k_1 , R^2 , and $q_{e,calc}$ (Table 1).

The pseudo-second-order model is expressed by Ho and McKay [43] as equation (5). Its linearized form may be represented by equation (6):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{(q_e)^2 k_2} + \frac{t}{q_e}, \quad (6)$$

where k_2 (g·mg⁻¹·min⁻¹) is the rate constant of pseudo-second-order sorption. The plot of t/q_t vs t of equation (6) should give a linear relationship, from which the values of k_2 , R^2 , and $q_{e,calc}$ can be determined, as presented in Figure 9b and Table 1. The pseudo-second-order model could represent the experimental condition that the adsorbent material is abundant with active sites [44].

The internal diffusion models assume that the diffusion of adsorbate within the adsorbent is the slowest step. The diffusion of adsorbate in the liquid film around the adsorbent and the adsorption onto the active sites are instantaneous [45]. One of the most used internal diffusion models, deduced by Weber and Morris [46], Uoginté *et al.* [47], and Badawy *et al.* [48], describes the intraparticle diffusion process, as presented in equation (7):

$$q_t = k_{id} t^{0.5}, \quad (7)$$

where k_{id} (mg·g⁻¹·min^{-0.5}) is the intraparticle diffusion coefficient. The plot of q_t vs $t^{0.5}$ of equation (7) is used to determine the values of k_{id} and R^2 (Figure 9c, Table 1). If the plot is a straight line and passes through the origin,

Figure 9: Adsorption kinetics of $\text{Cd}^{2+}/\text{Pb}^{2+}$ on pollen@FePO₄/pollen microspheres: (a) pseudo-first order, (b) pseudo-second order, and (c) intraparticle diffusion model. Sample: 50 mL, 40 mg·L⁻¹ Cd²⁺ or 200 mg·L⁻¹ Pb²⁺, pH 5.92; adsorbent dose 0.3278 g pollen@FePO₄/pollen.

the intraparticle diffusion might be the sole rate-limiting factor for the adsorption [45,49]. Otherwise, the adsorption might be controlled by multiple factors.

As for the adsorption of heavy metal ions on pollen@FePO₄, the kinetic parameters listed in Table 1 show that the correlation coefficient R^2 value of Cd²⁺ obtained using the pseudo-second-order model (0.9997) is much higher than those obtained using the pseudo-first-order model (0.8227) and the intraparticle diffusion model (0.4384). The calculated q_e value derived from the

pseudo-second-order model (2.742 mg·g⁻¹) shows good agreement with the experimental q_e value (2.717 mg·g⁻¹). These results indicate that the adsorption kinetic of Cd²⁺ onto pollen@FePO₄ follows the pseudo-second-order model and support the assumption behind the model that the adsorption is related to chemisorption [37]. The pollen@FePO₄ microspheres are abundant with active sites, including rich groups uncovered on the pollen grains like hydroxyl group and amide group, and the iron phosphate coating on the pollen surface, which

Table 1: Kinetic parameters for the adsorption of Cd²⁺/Pb²⁺ on pollen@FePO₄/pollen

Model	Parameters	pollen@FePO ₄		pollen	
		Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺
Pseudo-first order	$q_{e,\text{exp}}$ (mg·g ⁻¹)	2.717	30.506	2.959	25.461
	$q_{e,\text{calc}}$ (mg·g ⁻¹)	2.772	30.581	3.094	25.381
	k_1 (min ⁻¹)	0.1960	0.0398	0.8490	0.6700
	R^2	0.8227	0.8836	0.9643	0.9433
Pseudo-second order	$q_{e,\text{calc}}$ (mg·g ⁻¹)	2.742	30.581	3.016	26.385
	k_2 (g·mg ⁻¹ ·min ⁻¹)	3.833	0.891	0.504	0.0422
	R^2	0.9997	1.000	0.9985	0.9996
Intraparticle diffusion	k_{id} (mg·g ⁻¹ ·min ^{-0.5})	0.0729	0.1984	0.2253	2.0756
	R^2	0.4384	0.5811	0.5555	0.7612

provide a good chance for the chemisorption of metal ions on the pollen@FePO₄ microspheres. Hence, the Cd²⁺ adsorption on the pollen@FePO₄ microspheres involves not only electrostatic but also chemisorption.

Table 1 also suggests that the correlation coefficient R^2 value of Pb²⁺ obtained using the pseudo-second-order model (1.000) is higher than those obtained using the pseudo-first-order model (0.8836) and the intraparticle diffusion model (0.5811). The calculated q_e value derived from the pseudo-second-order model (30.581 mg·g⁻¹) agrees well with the experimental q_e value (30.506 mg·g⁻¹). These findings indicate that the adsorption kinetic of Pb²⁺ onto pollen@FePO₄ favors a pseudo-second-order process and further confirm that the sorption mechanism might be mainly attributed to the complexation.

The parameter k_2 is the second-order equilibrium rate constant. It can be observed from Table 1 that the value of k_2 for Cd²⁺ (3.833) is higher than that of Pb²⁺ (0.891). This result is consistent with the longer time needed to reach adsorption equilibrium for Pb²⁺ compared with that needed for Cd²⁺.

Figure 9 also displays the comparison of the adsorption kinetics of heavy metals onto pollen@FePO₄ with that on pollen. The comparison study shows that the adsorption kinetics of Cd²⁺ and Pb²⁺ onto the pollen microspheres favor the pseudo-second-order model, which is similar to the adsorption kinetics of pollen@FePO₄. However, the values of k_2 (0.504 for Cd²⁺ and 0.0422 for Pb²⁺) are lower than those on pollen@FePO₄, which illustrates that the Cd²⁺ and Pb²⁺ sorption on the pollen@FePO₄ appears to reach the equilibrium state faster than that on pollen. The q_e values of Cd²⁺ on the two adsorbent materials are equivalent, yet the value of Pb²⁺ on pollen@FePO₄ is higher than that on pollen. These results illustrate that the modification of iron phosphate improves the adsorption performance of heavy metal ions on the pollen microspheres.

3.4 Adsorption isotherm study

The adsorption isotherm is generally applied to study the interaction between the adsorbate and the adsorbent, which can help to understand the adsorption mechanism. Experiments were carried out by mixing 50 mL of metal solution of varying concentrations (10–100 mg·L⁻¹ for Cd and 20–400 mg·L⁻¹ for Pb) with adsorbent at pH 5.92 at room temperature. The equilibrium data were analyzed by two adsorption isotherms: Langmuir and Freundlich.

The Langmuir isotherm model assumes that the surface of the adsorbent is homogeneous, all sites on the surface have equal affinity for the adsorbate, and there is no interaction between adsorbates [50]. This model can be expressed in the linearized form (equation (8)) as follows [51]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}, \quad (8)$$

$$R_L = \frac{1}{1 + bC_0}, \quad (9)$$

where C_0 and C_e (mg·L⁻¹) are the concentrations of adsorbate at initial and equilibrium state, respectively, q_e (mg·g⁻¹) is the equilibrium adsorption, q_m (mg·g⁻¹) represents the maximum adsorption capacity, and b (L·mg⁻¹) is the binding energy constant. The values of q_m and b can be calculated from the slope and intercept of the plot of C_e/q_e vs C_e , respectively. R_L is used to express the essential features of Langmuir isotherm in terms of a dimensionless constant separation factor [52]. The value of R_L indicates the nature of the adsorption process as follows: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 1$).

The Freundlich isotherm model [53] can be expressed by an empirical equation describing adsorption onto a heterogeneous surface with the linearized form (equation (10)) as follows:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e, \quad (10)$$

where k_F and n are Freundlich constants, which indicate the adsorption capacity and adsorption intensity, respectively. The plot of $\ln q_e$ vs $\ln C_e$ should be a straight line with a slope of $1/n$ and an intercept of $\ln k_F$. The value of $1/n$ between 0 and 1 implies the chemisorption process, whereas a value above 1 is indicative of cooperative adsorption [54]. The Freundlich isotherm model does not estimate surface saturation and predicts infinite surface coverage; thus, the exponential distribution of active sites must be considered [55].

The Langmuir and Freundlich isotherm plots of heavy metal ions on pollen@FePO₄ microspheres are shown in Figures 10 and 11, respectively. The calculated results of the Langmuir and Freundlich isotherm constants are presented in Table 2. The values of correlation coefficients R^2 of Langmuir (0.9908) and Freundlich (0.9974) for Cd²⁺ are found to be both greater than 0.99, yet the value obtained from Freundlich is slightly higher. These results indicate that both isotherm models can explain the adsorption behavior of Cd²⁺ on pollen@FePO₄. However,

Figure 10: Langmuir isotherm plots of $\text{Cd}^{2+}/\text{Pb}^{2+}$ on $\text{pollen@FePO}_4/\text{pollen}$ microspheres. Sample: 50 mL, initial pH 5.92; adsorbent dose 0.3278 g $\text{pollen@FePO}_4/\text{pollen}$; contact time 60 min.

the Freundlich model seems to be more suitable than the Langmuir. The possible reason is as follows: some broken pieces appear in the preparation of pollen@FePO_4 (Figure 2b), which leads to a slight inhomogeneity of the adsorption system. The adsorption behavior of Cd^{2+} onto pollen@FePO_4 might better fit the Langmuir model if the broken pieces in the adsorbent could be removed clearly. The maximum adsorption capacity (q_m value) of Cd^{2+} on pollen@FePO_4 derived from the Langmuir isotherm is

$4.623 \text{ mg}\cdot\text{g}^{-1}$. In addition, the R_L value (0.5886) reveals the adsorption of Cd^{2+} by pollen@FePO_4 is favorable. The $1/n$ value obtained from the Freundlich (0.4188) between 0 and 1 suggests a high affinity between Cd^{2+} and pollen@FePO_4 via a chemisorption process.

It can be seen from Table 2 that the Pb^{2+} adsorption behavior onto pollen@FePO_4 fits the Langmuir model better due to its higher R^2 value (0.9309) compared with that from the Freundlich isotherm (0.9101), which indicates that the adsorption of Pb^{2+} by pollen@FePO_4 occurs via monolayer adsorption. Meanwhile, the R_L

Figure 11: Freundlich isotherm plots of $\text{Cd}^{2+}/\text{Pb}^{2+}$ on $\text{pollen@FePO}_4/\text{pollen}$ microspheres. Sample: 50 mL, initial pH 5.92; adsorbent dose 0.3278 g $\text{pollen@FePO}_4/\text{pollen}$; contact time 60 min.

Table 2: Adsorption isotherm constants and correlation coefficients

	Pollen@FePO ₄		Pollen	
	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺
Langmuir				
$q_m \text{ (mg}\cdot\text{g}^{-1}\text{)}$	4.623	61.35	4.196	38.91
$b \text{ (L}\cdot\text{mg}^{-1}\text{)}$	0.0699	1.045	0.129	0.104
R_L	0.5886	0.0457	0.4367	0.3247
R^2	0.9908	0.9309	0.9986	0.9872
Freundlich				
k_F	0.673	23.380	0.922	5.643
$1/n$	0.4188	0.2584	0.3475	0.4081
R^2	0.9974	0.9101	0.9527	0.9087

Table 3: Comparison of adsorption capacities of various adsorbents for metal ions

Sorbents	Sorption capacity (mg·g ⁻¹)		References
	Cd	Pb	
Brewed tea waste	1.197	2.468	[56]
Modified ZSCs	5.38	9.06	[57]
Processed walnut shell	11.6	32	[58]
Natural walnut shell	—	9.912	[59]
Meranti sawdust	—	34.246	[35]
DAC-TETA	4.59	—	[60]
Pollen@FePO ₄ /pollen	4.623/4.196	61.35/38.91	This work

value indicates favorable adsorption. The maximum adsorption capacity of Pb²⁺ on pollen@FePO₄ derived from the Langmuir isotherm is 61.35 mg·g⁻¹.

The comparison study shows that the adsorption of heavy metal ions on the pollen microspheres is correlated better with the Langmuir equation, as indicated in Table 2, suggesting the monolayer adsorption of Cd²⁺ and Pb²⁺ on the pollen surface. The R_L values remain within 0–1 consistent with the requirement for a favorable adsorption process. These results are similar to the adsorption behavior of heavy metal ions by pollen@FePO₄. The maximum adsorption capacities for Cd²⁺ and Pb²⁺ on pollen are 4.196 and 38.91 mg·g⁻¹, respectively. The modification of pollen with FePO₄ improves its adsorption capacity for Pb²⁺ significantly.

In addition, Table 3 lists a comparison of the maximum adsorption capacity of pollen@FePO₄ with different adsorbents for Cd²⁺ and Pb²⁺ [35,56–60]. It is found that pollen@FePO₄ shows better than or at least comparable over other adsorbents for its heavy metal ion adsorption performance. This indicates that it could be a potential material for the removal of heavy metal ions from water bodies.

4 Conclusion

Iron phosphate-modified pollen microspheres (pollen@FePO₄) were prepared by a simple and environmentally friendly method. Then, a fast efficient procedure was proposed for the removal of heavy metals through adsorption by the pollen@FePO₄ composite material. The sorption of Cd²⁺ and Pb²⁺ ions on pollen@FePO₄ corresponds to the pseudo-second-order model and Langmuir isotherm.

The adsorption mechanism involves electrostatic and chemisorption for Cd²⁺ and mainly complexation for Pb²⁺. The faster sorption kinetics and higher adsorption capacities of Cd²⁺ and Pb²⁺ ions onto pollen@FePO₄ than pollen indicate that it could be a promising material for the removal of heavy metal ions from aqueous solution.

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References

- [1] Shaker, M. A. Thermodynamic profile of some heavy metal ions adsorption onto biomaterial surfaces. *American Journal of Applied Sciences*, Vol. 4, 2007, pp. 605–612.
- [2] Friberg, L., G. F. Nordberg, and V. B. Vouk. *Handbook on the toxicology of metals*, Elsevier/Biomedical Press, North-Holland/Amsterdam, 1979.
- [3] Godt, J., F. Scheidig, C. Grosse-Siestrup, V. Esche, P. Brandenburg, A. Reich, et al. The toxicity of cadmium and resulting hazards for human health. *Journal of occupational medicine and toxicology (London, England)*, Vol. 1, 2006, pp. 1–6.
- [4] Nelke, K., M. Mulak, K. Łuczak, W. Pawlak, J. Nienartowicz, D. Szumny, et al. Occurrence and exposure to lead and cadmium and their environmental influence on eyesight. *Polish Journal of Environmental Study*, Vol. 24, 2015, pp. 1491–1496.
- [5] Singh, S., K. C. Barick, and D. Bahadur. Functional oxide nanomaterials and nanocomposites for the removal of heavy metals and dyes. *Nanomaterials and Nanotechnology*, Vol. 3, 2013, id. 15.
- [6] Fu, F. L. and Q. Wang. Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, Vol. 92, 2011, pp. 407–418.
- [7] Hur, J., J. Shin, J. Yoo, and Y. S. Seo. Competitive adsorption of metals onto magnetic graphene oxide: comparison with other carbonaceous adsorbents. *The Scientific World Journal*, Vol. 2015, 2015, id. 836287.

- [8] Sengupta, S. and R. Mondal. A novel gel-based approach to wastewater treatment—unique one-shot solution to potentially toxic metal and dye removal problems. *Journal of Materials Chemistry A: Materials for Energy and Sustainability*, Vol. 2, 2014, pp. 16373–16377.
- [9] Crini, G., E. Lichtfouse, L. D. Wilson, and N. Morin-Crini. Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters*, Vol. 17, 2019, pp. 195–213.
- [10] Wadhawan, S., A. Jain, J. Nayyar, and S. K. Mehta. Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. *Journal of Water Process Engineering*, Vol. 33, 2020, id. 101038.
- [11] Qin, H., T. Hu, Y. Zhai, N. Lu, and J. Aliyeva. The improved methods of heavy metals removal by biosorbents: A review. *Environmental Pollution*, Vol. 258, 2020, id. 113777.
- [12] Tang, Z., Z. Qiu, S. Lu, and X. Shi. Functionalized layered double hydroxide applied to heavy metal ions absorption: A review. *Nanotechnology Reviews*, Vol. 9, 2020, pp. 800–819.
- [13] Lin, Y., J. Xu, B. S. Sudhakar, J. Gu, and R. Hong. Preparation of spherical aminopropyl-functionalized MCM-41 and its application in removal of Pb(II) ion from aqueous solution. *Nanotechnology Reviews*, Vol. 8, 2019, pp. 275–284.
- [14] Sadegh, H. Development of graphene oxide from graphite: A review on synthesis, characterization and its application in wastewater treatment. *Reviews on Advanced Materials Science*, Vol. 49, 2017, pp. 38–43.
- [15] Li, Z., B. Yu, H. Cong, H. Yuan, and Q. Peng. Recent development and application of solid phase extraction materials. *Reviews on Advanced Materials Science*, Vol. 49, 2017, pp. 87–111.
- [16] Vankar, P. S., R. Sarswat, A. K. Dwivedi, and R. S. Sahu. An assessment and characterization for biosorption efficiency of natural dye waste. *Journal of Cleaner Production*, Vol. 60, 2013, pp. 65–70.
- [17] Lu, Q., J. H. Wu, Q. W. Yu, and Y. Q. Feng. Using pollen grains as novel hydrophilic solid-phase extraction sorbents for the simultaneous determination of 16 plant growth regulators. *Journal of Chromatography A*, Vol. 1367, 2014, pp. 39–47.
- [18] Qian, W. L., Z. Khan, D. G. Watson, and J. Fearnley. Analysis of sugars in bee pollen and propolis by ligand exchange chromatography in combination with pulsed amperometric detection and mass spectrometry. *Journal of Food Composition and Analysis*, Vol. 21, 2008, pp. 78–83.
- [19] Hall, S. R., H. Bolger, and S. Mann. Morphosynthesis of complex inorganic forms using pollen grain templates. *Chemical Communications*, 2003, Vol. 22, pp. 2784–2785.
- [20] Wang, Y., Z. Liu, B. Han, Y. Huang, and G. Yang. Carbon microspheres with supported silver nanoparticles prepared from pollen grains. *Langmuir*, Vol. 21, 2005, pp. 10846–10849.
- [21] Hall, S. R., V. M. Swinerd, F. N. Newby, A. M. Collins, and S. Mann. Fabrication of porous titania (Brookite) microparticles with complex morphology by sol-gel replication of pollen grains. *Chemistry of Materials*, Vol. 18, 2006, pp. 598–600.
- [22] Cao, F. and D. X. Li. Biotemplate synthesis of monodispersed iron phosphate hollow microspheres. *Bioinspiration & Biomimetics*, Vol. 5, 2010, id. 016005.
- [23] Erzengin, M., N. Ünü, and M. Odabaşı. A novel adsorbent for protein chromatography: Supermacroporous monolithic cryogel embedded with Cu²⁺-attached sporopollenin particles. *Journal of Chromatography A*, Vol. 1218, 2011, pp. 484–490.
- [24] Thio, B. J., K. K. Clark, and A. A. Keller. Magnetic pollen grains as sorbents for facile removal of organic pollutants in aqueous media. *Journal of Hazardous Materials*, Vol. 194, 2011, pp. 53–61.
- [25] Sargin, I., M. Kaya, G. Arslan, T. Baran, and T. Ceter. Preparation and characterisation of biodegradable pollen-chitosan microcapsules and its application in heavy metal removal. *Bioresource Technology*, Vol. 177, 2015, pp. 1–7.
- [26] Chiappe, C., M. J. Rodriguez-Douton, M. C. Mozzati, D. Prete, A. Griesi, L. Guazzelli, et al. Fe-functionalized paramagnetic sporopollenin from pollen grains: one-pot synthesis using ionic liquids. *Scientific Reports*, Vol. 10, 2020, id. 12005.
- [27] Lu, Q., J. H. Wu, Q. W. Yu, and Y. Q. Feng. Using pollen grains as novel hydrophilic solid-phase extraction sorbents for the simultaneous determination of 16 plant growth regulators. *Journal of Chromatography A*, Vol. 1367, 2014, pp. 39–47.
- [28] Lu, Q., Q. Zhao, Q. W. Yu, and Y. Q. Feng. Use of Pollen Solid-Phase Extraction for the Determination of trans-Resveratrol in Peanut Oils. *Journal of Agricultural and Food Chemistry*, Vol. 63, 2015, pp. 4771–4776.
- [29] Zhang, X. X., S. S. Tang, M. L. Chen, and J. H. Wang. Iron phosphate as a novel sorbent for selective adsorption of chromium(III) and chromium speciation with detection by ETAAS. *Journal of Analytical Atomic Spectrometry*, Vol. 27, 2012, pp. 466–472.
- [30] Bai, W. K., Z. H. Wu, E. Shen, J. Z. Zhang, and B. Hu. Improvement on the selectivity and sorption capacity of cadmium by iron loaded carbon nanotubes with detection by electrothermal atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry*, Vol. 27, 2012, pp. 1680–1687.
- [31] Zhang, X., C. Sun, L. Zhang, H. Liu, B. Cao, L. Liu, et al. Adsorption studies of cadmium onto magnetic Fe₃O₄@FePO₄ and its preconcentration with detection by electrothermal atomic absorption spectrometry. *Talanta*, Vol. 181, 2018, pp. 352–358.
- [32] Zhang, X., L. Zhang, H. Liu, B. Cao, L. Liu, and W. Gong. Structure, morphology, size and application of iron phosphate. *Reviews on Advanced Materials Science*, Vol. 59, 2020, pp. 538–552.
- [33] Kumar, U. and M. Bandyopadhyay. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology*, Vol. 97, 2006, pp. 104–109.
- [34] Zaghib, K. and C. M. Julien. Structure and electrochemistry of FePO₄·2H₂O hydrate. *Journal of Power Sources*, Vol. 142, 2005, pp. 279–284.
- [35] Rafatullah, M., O. Sulaiman, R. Hashim, and A. Ahmad. Adsorption of copper(II), chromium(III), nickel(II) and lead(II) ions from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials*, Vol. 170, 2009, pp. 969–977.
- [36] Sun, X., H. Huang, Y. Zhu, Y. Du, L. Yao, X. Jiang, and et al. Adsorption of Pb²⁺ and Cd²⁺ onto *Spirulina platensis* harvested by polyacrylamide in single and binary solution systems. *Colloid. Surface. A*, Vol. 583, 2019, id. 123926.
- [37] King, P., N. Rakesh, S. Beenalahari, Y. Prasanna Kumar, and V. S. Prasad. Removal of lead from aqueous solution using *Syzygium cumini* L.: Equilibrium and kinetic studies. *Journal of Hazardous Materials*, Vol. 142, 2007, pp. 340–347.

- [38] Lagergren, S. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, Vol. 24, 1898, pp. 1–39.
- [39] KaiFeng, W., P. Na, T. Changqing, and W. Kairong. Study on adsorption of Cr(VI) in water by typical agricultural wastes. *Technology of Water Treatment*, Vol. 36, 2010, pp. 58–62.
- [40] Gopalapillai, Y., B. Hale, and B. Vigneault. Study on arsenic adsorption performance by sulfhydryl silane modified oxidation graphite. *Environmental Chemistry*, Vol. 32, 2013, pp. 810–818.
- [41] Sun, H., Y.-F. Jiang, L.-P. Shi, Z.-F. Mu, and H.-Y. Zhan. Adsorption and influential factors of carbofuran on the loess soil by adding biochar prepared at different temperatures. *Acta Science Circumstances*, Vol. 36, 2016, pp. 1015–1020.
- [42] Oulaid, O. and J. Zhang. Study on the adsorption and influential factors of sodium pentachlorophenol on the loess soil in Northwestern China. *Journal of Safety Environment*, Vol. 14, 2014, pp. 229–234.
- [43] Ho, Y. S. and G. McKay. Pseudo-second order model for sorption processes. *Process Biochemistry*, Vol. 34, 1999, pp. 451–465.
- [44] Guo, X. and J. L. Wang. A general kinetic model for adsorption: Theoretical analysis and modeling. *Journal of Molecular Liquids*, Vol. 288, 2019, id. 111100.
- [45] Wang, J. L. and X. Guo. Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, Vol. 390, 2020, id. 122156.
- [46] Weber, W. J. and J. C. Morris. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division: American Society of Civil Engineers*, Vol. 89, 1963, pp. 31–60.
- [47] Uogintė, I., G. Lujanienė, and K. Mažeika. Study of Cu(II), Co(II), Ni(II) and Pb(II) removal from aqueous solutions using magnetic Prussian blue nano-sorbent. *Journal of Hazardous Materials*, Vol. 369, 2019, pp. 226–235.
- [48] Badawy, N. A., A. A. El-Bayaa, and E. Abd AlKhalik. Vermiculite as an exchanger for copper(II) and Cr(III) ions, kinetic studies. *Ionics*, Vol. 16, 2010, pp. 733–739.
- [49] McKay, G. The removal of colour from effluent using various adsorbents - III. Silica: Rate processes. *Water Research*, Vol. 14, 1980, pp. 15–20.
- [50] Peng, W., H. Li, Y. Liu, and S. Song. Comparison of Pb(II) adsorption onto graphene oxide prepared from natural graphites: Diagramming the Pb(II) adsorption sites - ScienceDirect. *Applied Surface Science*, Vol. 364, 2016, pp. 620–627.
- [51] Langmuir, I. The adsorption gasses on plane surface of glass, mica and platinum. *Journal of the American Chemical Society*, Vol. 40, 1916, pp. 1361–1368.
- [52] Hall, K. R., L. C. Eagleton, A. Acrivos, and T. Vermeulen. Pore and solid diffusion kinetics in fixed bed adsorption under constant-pattern condition. *Industrial and Engineering Chemistry, Fundamentals*, Vol. 5, 1966, pp. 212–223.
- [53] Freundlich, H. M. F. Over the adsorption in solution. *Journal of Physical Chemistry*, Vol. 57, 1906, pp. 385–470.
- [54] Foo, K. Y. and B. H. Hameed. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, Vol. 156, 2010, pp. 2–10.
- [55] Ferreira, L. S., M. S. Rodrigues, J. de Carvalho, A. Lodi, E. Finocchio, P. Perego, et al. Adsorption of Ni²⁺, Zn²⁺ and Pb²⁺ onto dry biomass of *Arthrospira* (*Spirulina*) *platensis* and *Chlorella vulgaris*. I. Single metal systems. *Chemical Engineering Journal*, Vol. 173, 2011, pp. 326–333.
- [56] Çelebi, H., G. Gök, and O. Gök. Adsorption capability of brewed tea waste in waters containing toxic lead(II), cadmium(II), nickel(II), and zinc(II) heavy metal ions. *Scientific Reports-UK*, Vol. 10, 2020, id. 17570.
- [57] Assirey, E. A., S. M. Sirry, H. A. Burkani, and M. A. Ibrahim. Modified *Ziziphus spina-christi* stones as green route for the removal of heavy metals. *Scientific Reports-UK*, Vol. 10, 2020, id. 20557.
- [58] Almasi, A., M. Omid, M. Khodadadian, R. Khamutian, and M. B. Gholivand. Lead(II) and cadmium(II) removal from aqueous solution using processed walnut shell: kinetic and equilibrium study. *Toxicological & Environmental Chemistry*, Vol. 94, 2012, pp. 660–671.
- [59] Celebi, H. and O. Gok. Evaluation of lead adsorption kinetics and isotherms from aqueous solution using natural walnut shell. *International Journal of Environmental Research*, Vol. 11, 2017, pp. 83–90.
- [60] de Oliveira, F. M., B. F. Somera, M. Z. Corazza, M. J. Yabe, M. G. Segatelli, E. S. Ribeiro, et al. Cellulose microfiber functionalized with *N,N'*-bis (2-aminoethyl)-1,2-ethanediamine as a solid sorbent for the fast preconcentration of Cd(II) in flow system analysis. *Talanta*, Vol. 85, 2011, pp. 2417–2424.