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⁺ 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 complexion 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...
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. 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
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.

\[
X_r = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% , \quad (1)
\]
\[
q_e = \left( \frac{C_0 - C_e}{m} \right)V , \quad (2)
\]

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 trilevel 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 materials 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
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 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
OH⁻ in the solution leads to the increase of the negative charge on the adsorbent surface, which promotes the adsorption of Cd²⁺. Therefore, the adsorption mechanism of Cd²⁺ on the pollen@FePO₄ microspheres is related to the electrostatic.

As for Pb²⁺ (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 Pb²⁺ by pollen@FePO₄. The adsorption of Pb²⁺ is mainly related to the complexion, and the optimal pH value is 5.92.

Since there is little difference between the adsorptions of Cd²⁺ 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 Cd²⁺ and Pb²⁺ 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., qₑ) 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 Pb²⁺ is approximately ten times higher than that for Cd²⁺, indicating pollen@FePO₄ prefers adsorbing Pb²⁺ over Cd²⁺.

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 Cd²⁺ and Pb²⁺ by pollen@FePO₄. The adsorption efficiency of Cd²⁺ increases rapidly to 45%
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 given in equation (4) [39–42]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t),$$  \hspace{1cm} (3)

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e}t,$$  \hspace{1cm} (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 $t/q_t$ vs $t$ 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):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2,$$  \hspace{1cm} (5)

$$\frac{t}{q_t} = \frac{1}{(q_e)^2k_2} + \frac{t}{q_e^2},$$  \hspace{1cm} (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):

$$q_t = k_{id}t^{0.5},$$  \hspace{1cm} (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,
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 Cd$^{2+}$ 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 Cd$^{2+}$ 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

| Model                     | Parameters          | pollen@FePO₄ | pollen |
|----------------------------|---------------------|--------------|--------|
|                            | $q_{e,exp}$ (mg·g$^{-1}$) | 2.717        | 2.959  |
|                            | $q_{e,calc}$ (mg·g$^{-1}$) | 2.772        | 3.094  |
|                            | $k_1$ (min$^{-1}$)     | 0.1960       | 0.8490 |
|                            | $R^2$                 | 0.8227       | 0.9643 |
| Pseudo-first order         |                     |              |        |
|                            | $q_{e,calc}$ (mg·g$^{-1}$) | 2.724        | 3.016  |
|                            | $k_2$ (g·mg$^{-1}$·min$^{-1}$) | 3.833        | 0.504  |
|                            | $R^2$                 | 0.9997       | 0.9985 |
| Pseudo-second order        |                     |              |        |
| Intraparticle diffusion    | $k_{id}$ (mg·g$^{-1}$·min$^{-0.5}$) | 0.0729        | 0.2253 |
|                            | $R^2$                 | 0.4384       | 0.5555 |

Figure 9: Adsorption kinetics of Cd$^{2+}$/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$^{-1}$ Cd$^{2+}$ or 200 mg·L$^{-1}$ Pb$^{2+}$; pH 5.92; adsorbent dose 0.3278 g pollen@FePO₄/pollen.
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]:

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

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

where $C_o$ 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 heterogenous 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,
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 mg·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 $R_L$

| Pollen@FePO$_4$ | Pollen |
|-----------------|--------|
| Cd$^{2+}$       | Pb$^{2+}$ | Cd$^{2+}$ | Pb$^{2+}$ |
| q$_m$ (mg·g$^{-1}$) | 4.623 | 61.35 | 4.196 | 38.91 |
| b (L·mg$^{-1}$)   | 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 |

| Pollen@FePO$_4$ | Pollen |
|-----------------|--------|
| Cd$^{2+}$       | Pb$^{2+}$ | Cd$^{2+}$ | Pb$^{2+}$ |
| 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 |
value indicates favorable adsorption. The maximum adsorption capacity of Pb\(^{2+}\) on pollen@FePO\(_4\) 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 Cd\(^{2+}\) and Pb\(^{2+}\) 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@FePO\(_4\). The maximum adsorption capacities for Cd\(^{2+}\) and Pb\(^{2+}\) on pollen are 4.196 and 38.91 mg·g\(^{-1}\), respectively. The modification of pollen with FePO\(_4\) improves its adsorption capacity for Pb\(^{2+}\) significantly.

In addition, Table 3 lists a comparison of the maximum adsorption capacity of pollen@FePO\(_4\) with different adsorbents for Cd\(^{2+}\) and Pb\(^{2+}\) [35, 56–60]. It is found that pollen@FePO\(_4\) 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@FePO\(_4\)) 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@FePO\(_4\) composite material. The sorption of Cd\(^{2+}\) and Pb\(^{2+}\) ions on pollen@FePO\(_4\) corresponds to the pseudo-second-order model and Langmuir isotherm.

The adsorption mechanism involves electrostatic and chemisorption for Cd\(^{2+}\) and mainly complexion for Pb\(^{2+}\). The faster sorption kinetics and higher adsorption capacities of Cd\(^{2+}\) and Pb\(^{2+}\) ions onto pollen@FePO\(_4\) than pollen indicate that it could be a promising material for the removal of heavy metal ions from aqueous solution.

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### Author contributions

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### Conflict of interest

Authors state no conflict of interest.

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