NaOH modification of persimmon powder-formaldehyde resin to enhance Cu$^{2+}$ and Pb$^{2+}$ removal from aqueous solution

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Abstract

An adsorption resin (persimmon powder-formaldehyde resin, PPFR) was developed by immobilizing persimmon powder (extracted from persimmon residual) with formaldehyde in our previous work, and it exhibited outstanding selective adsorption capacity towards Au$^{3+}$ from aqueous solutions and harsh industrial acidic conditions. However, its adsorption behaviour of heavy metal ions was not so good compared with the adsorption of Au$^{3+}$, and it need modification to enhance its adsorption behaviour of heavy metal ions. In this study, a novel adsorbent, named “NPPFR”, was prepared by treating PPFR with NaOH, and its adsorption behaviours of Cu$^{2+}$ and Pb$^{2+}$ from aqueous solutions was investigated. The effects of solution pH, adsorption time, metal ion concentration and coexisting metal ions on adsorption were studied in batch experiments. The adsorption capacity of Cu$^{2+}$ and Pb$^{2+}$ on NPPFR was much higher than that of PPFR, which increased by 323% and 186% at 303 K, respectively. The adsorption of Cu$^{2+}$ and Pb$^{2+}$ onto PPFR and NPPFR was highly affected by pH, and the optimal pH range was 5.0-6.0. Both adsorption kinetics of Cu$^{2+}$ and Pb$^{2+}$ proceeded rapidly and could be well described by pseudo-second-order equation ($R^2 > 0.99$), and the adsorption capacities calculated by the model were close to those determined by experiments. The adsorption isotherms of Cu$^{2+}$ and Pb$^{2+}$ on PPFR and NPPFR could be well described by Langmuir equation ($R^2 > 0.99$), and the maximum Langmuir adsorption capacities for Cu$^{2+}$ and Pb$^{2+}$ removal by NPPFR reached up to 116.28 and 384.62 mg/g (303 K), respectively. Coexisting metal ions (Fe$^{3+}$, Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Mg$^{2+}$ and Ca$^{2+}$) had no obvious influence on the adsorption of Cu$^{2+}$ and Pb$^{2+}$ on PPFR and NPPFR. Moreover, most of metal ions coexisting in solutions could simultaneously removed by NPPFR when the adsorbent dose was 1.0 g/L, while the adsorption of Mg$^{2+}$ and Ca$^{2+}$ on PPFR were not satisfactory at the same adsorbent dose. The results indicate that NPPFR could be employed as an effective low-cost adsorbent for adsorption of heavy metal ions from wastewater.

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1. Introduction

| Nomenclature |
|---------------|
| PT | Persimmon tannin |
| PPFR | Persimmon powder-formaldehyde resin |
| NPPFR | NaOH modified persimmon powder-formaldehyde resin |

China is the origin and main producing country of persimmon (*Diospyros kaki* Thunb.). The total acreage and yield of persimmon were 738,400 ha and 3,386,000 t, respectively, of which China (including ‘Taiwan’) accounted for about 90.13% and about 76.05% in the world (FAO, 2014), respectively. Persimmon is a fruit whose exploitation has a great tradition in China and around 80% of persimmon fruits are utilized for further processing, particularly to produce dried persimmon, which generate large amount of persimmon residual. This material contains abundant persimmon tannin (PT) which consists of a great majority of adjacent hydroxyl groups, which can easily react with metal ions with binding sites for redox$^3$, electrostatic interaction$^4$, ion exchange$^4$, complexation$^5$ and esterification$^6$ reactions. Therefore, it constitutes an interesting alternative to commercial adsorbents, especially due to its low cost and ready availability in large quantities, and its use would contribute to the waste valorisation.

Since PT is water-soluble, it should be transformed into water insoluble matrix before use. Formaldehyde is one of the most effective cross-linking agents for condensed tannin$^7$. The A-rings of condensed tannin can react with formaldehyde due to their strong nucleophilicity$^8$, and the probable active-sites are Cs$^9$. In previous works of the authors$^1,2$, persimmon powder-formaldehyde resin (PPFR) was prepared from persimmon residual, and its adsorption behavior towards precious metal ion Au$^{3+}$ from aqueous solutions and harsh industrial acidic conditions was studied. The results demonstrated the potential of this material for the removal of Au$^{3+}$; however, its adsorption behavior of heavy metal ions was not so good compared with the adsorption of Au$^{3+}$, and it need modification to enhance its adsorption behavior of heavy metal ions. So far, the production of bio-sorbent from persimmon by chemical activation with NaOH has not been reported in the literature yet. This paper deals with the preparation of NaOH modified PPFR (NPPFR), along with the detailed investigation of the effect of various parameters including equilibrium pH, contact time, temperature, initial ion concentration and coexisting metal ions on adsorption of Cu$^{2+}$ and Pb$^{2+}$.

2. Experimental

2.1. Materials and chemicals

A sample of dry persimmon residual powder was kindly donated by Huikun Agriculture Product Co. Ltd., Gongcheng, China, which persimmon residual was squeezed and then the generated juice was freeze-dried. The content of PT in the powder was determined to be about 30% with the Folin-Ciocalteu method$^{10}$. Cu$^{2+}$ and Pb$^{2+}$ adsorption experiments were carried out with fresh solutions that were prepared from stock solution of CuSO$_4$·5H$_2$O and Pb(NO$_3$)$_2$, respectively. The pH of solutions was adjusted with diluted HNO$_3$ and/or NaOH solution.

2.2. Preparation of adsorbent

Persimmon powder-formaldehyde resin (PPFR) was prepared according to the method reported previously$^1$. The persimmon powder (30 g) was dissolved in 65 mL of NaOH solution (0.25 mol/L) at room temperature, which was followed by addition of 6 mL of formaldehyde (37 wt%) as a cross-linking reagent. After resination at 353 K for 12 h, the product was filtered, then crushed and grinded into powder and followed by washing successively with
deionized water and 0.05 mol/L HNO₃ solution to remove unreacted substances, and finally rinsed with deionized water. Thus the obtained adsorbent was freeze-dried and stored in a desiccator for further use.

Alkaline modification was performed in a 2 L Pyrex glass reactor with mechanical stirring and temperature control. Solid/liquid ratio was held constant at 1/10 (w/w). PPFR and 0.5 mol/L NaOH were mixed at 298 K and the suspension was continuously stirred for 12 h. Once the time was elapsed, the suspension was vacuum filtered through a Buchner funnel and the solid residue was washed with distilled water until the pH of the filtrate was that of the washing water. The pre-treated PPFR were freeze-dried and then crushed to get power of mesh size 150-250 μm. The dried rigid mess of NaOH modification PPFR is named as NPPFR.

2.3. Batch adsorption studies

The effect of pH, adsorption time and initial concentration towards Cu²⁺ and Pb²⁺ removal on PPFR and NPPFR from aqueous solutions were studied in detail, and all the adsorption experiments were carried out by batch method. For instance, in a typical batch adsorption experiment, 15 mg adsorbent and 50 mL particular solution were mixed in sealed conical flasks and were shaken together at 303 K for 24 h at a speed of 200 r/min. The mixture was separated by filtration and the filtrate was collected for analysis. All the adsorption experiments were replicated three times and the errors were found to be within 5%.

2.4. Instrumentation analyses

Metal ion concentrations in the aqueous solutions were measured by atomic absorption spectrophotometer (AAS, Varian Spectra AA 220) and/or inductively coupled plasma optical emission spectrometer (ICP-OES, optima 2100). The FT-IR spectra of the raw material as well as the adsorbents were recorded by FT-IR spectrophotometer (Thermo 330) using KBr pellet method. The surface area of PPFR and NPPFR was determined using the Btunaure-Emmet-Teller method by autosorb-1 standard physical adsorption analyzer (Quantachrome Autosorb-1 JEDL-6390/LV). The thermal denaturation temperature of PPFR and NPPFR was determined using a differential scanning calorimeter (NETZSCH DSC 204 F1). Zeta potentials of PPFR and NPPFR were measured over the pH range of 2.0-10.0 on a zetasizer (Malvern ZEN 3600).

3. Results and Discussion

3.1. Characterization of the adsorbent

Characterization of crude persimmon powder and the both adsorption materials was investigated by FTIR spectra, the results of which are shown in Fig. 1. In the spectrum of persimmon powder, the peaks at 3383 cm⁻¹ and 1345 cm⁻¹ are attributed to O–H stretching vibration and O–H bending, the weak peak at 1695 cm⁻¹ and the sharp peak at 1614 cm⁻¹ are attributed to C=O stretching vibrations of ester and ketone groups, and the peaks at 1236 cm⁻¹ is attributed to C=C–O stretching. The peaks at the region of 920-740 cm⁻¹ can be attributed to the deformation vibrations at C–H bond in the phenolic rings. In the spectrum of PPFR, intensity of O–H stretching vibrations was slightly decreased, inferring that cross-linking has taken place through the condensation reaction of phenolic hydroxyl groups, and the peaks at 1236 cm⁻¹ is attributed to C=C–O stretching. The peaks at the region of 920-740 cm⁻¹ can be attributed to the deformation vibrations at C–H bond in the phenolic rings. In the spectrum of PPFR, intensity of O–H stretching vibrations was slightly decreased, inferring that cross-linking has taken place through the condensation reaction of phenolic hydroxyl groups, and the peaks at 1701 cm⁻¹, 1612 cm⁻¹ and 1221 cm⁻¹ due to C=O stretching and C=C–O stretching vibrations were broadened probably due to partial oxidation of phenolic hydroxyl groups to quinone groups. The intensity of 920-740 cm⁻¹ was decreased, inferring that PT was highly cross-linked with formaldehyde. After NaOH modification, the C=O peak of ester groups at 1701 cm⁻¹ was shifted to 1705 cm⁻¹, and the intensity of the peak was slightly decreased, the C=O peak of ketone groups at 1612 cm⁻¹ was shifted to 1621 cm⁻¹, and the intensity of the peak increased, the results inferring that part of ester groups have become to ketone groups. The intensity of 920-740 cm⁻¹ was decreased again, inferring that PT was further cross-linked. However, spectra comparison demonstrated that the main functional groups found in PPFR remained practically unchanged after the alkaline modification.

The zeta potentials of PPFR and NPPFR at the pH range of 2.0-10.0 were measured and the results are shown in Appendix Fig. 1. The isoelectric point of PPFR occurs at pH 2.21, inferring that the surface would be negative
charged above this pH value due to the ionization of the functional groups such as adjacent hydroxyl groups. It can be seen that the zeta potentials of PPFR became more negative as pH increases within the pH range of 2.21-5.0. However, it was found that the zeta potentials of NPPFR were not changed much at the pH range of 2.0-10.0. The bulk density was decreased while thermal denaturation temperature and BET specific surface area were increased after NaOH modification (as shown in Table1), inferring that NaOH altered the surface morphological features of PPFR which made it to be more porosity and stability.

Fig. 1 FT-IR spectrum of persimmon powder, PPFR and NPPFR.
3.2. Effect of pH

Cu$^{2+}$ and Pb$^{2+}$ adsorption from aqueous solutions by PPFR and NPPFR was highly affected by solution pH. As shown in Fig. 2, the adsorption capacity was increased with the increase of pH value in the range of 2.0-5.0, and the optimal pH range was 5.0-6.0. As pH increases, the PPFR surface becomes more and more negatively charged within the pH range 2.21-5.0 which is presented in Appendix Fig. 1. The PPFR becoming more negative led to higher adsorption capacity of Cu$^{2+}$ and Pb$^{2+}$, inferring that the attraction of cationic charged Cu$^{2+}$ and Pb$^{2+}$ species onto the PPFR particles is favourable via electrostatic interaction. In addition, it was interesting to find that the pH of the solution was decreased rapidly with adsorption of Cu$^{2+}$ and Pb$^{2+}$. The phenomena that the pH was decreased with adsorption of Cu$^{2+}$ and Pb$^{2+}$ could be attributed to the hydrogen ions that were released from phenolic hydroxyl groups of PT during the adsorption process. However, the adsorption mechanism of Cu$^{2+}$ and Pb$^{2+}$ on NPPFR is not very clear, and further research is needed.

![Fig. 2 Effect of initial pH on the adsorption of Cu$^{2+}$ and Pb$^{2+}$ on PPFR and NPPFR. (Initial conc. =30 mg/L (Cu$^{2+}$) and 60 mg/L (Pb$^{2+}$); pH=2.0-6.0; adsorbent dose= 0.3 g/L; temperature= 303 K; shaking speed= 200 r/min; shaking time= 24 h)](image)

3.3. Adsorption kinetics

The adsorption kinetics of Cu$^{2+}$ and Pb$^{2+}$ on PPFR and NPPFR is presented in Fig. 3. It can be observed that the adsorption rate is very fast and the adsorption equilibrium could be achieved within 30 min at 303 K, 313 K and 323 K, respectively. Both the adsorption of Cu$^{2+}$ and Pb$^{2+}$ was fast due to little micropore at the outer surface of PPFR and NPPFR, which suggested that the adsorption of Cu$^{2+}$ and Pb$^{2+}$ should take place at the outer surface of Cu$^{2+}$ and Pb$^{2+}$, and thus the intraparticle diffusion resistance could be neglected. The adsorption capacity of Cu$^{2+}$ and Pb$^{2+}$ on NPPFR was much higher than that of PPFR, which increased by 323% and 186% at 303 K, respectively.

| Physical properties               | PPFR | NPPFR |
|-----------------------------------|------|-------|
| Thermal denaturation temperature (K) | 367.6| 411.7 |
| The bulk density (g/cm)           | 0.81 | 0.55  |
| BET specific surface area (m²/g)  | 0.23 | 0.47  |
Fig. 3 Adsorption kinetics of Cu\(^{2+}\) and Pb\(^{2+}\) on PPFR and NPPFR. [Initial conc. = 30 mg/L (Cu\(^{2+}\)) and 80 mg/L (Pb\(^{2+}\)); pH=5.0; adsorbent dose= 0.3 g/L; temperature= 303 K, 313 K and 323 K, respectively; shaking speed= 200 r/min; shaking time= 5-480 min]

Table 2 The adsorption kinetics model parameters of Cu\(^{2+}\) and Pb\(^{2+}\) on PPFR and NPPFR.

| Metal ions | T (K) | Exp\(·q_e\) (mg/g) | Pseudo second-order rate model | Pseudo first-order rate model | Intraparticle diffusion model |
|------------|-------|---------------------|-------------------------------|-----------------------------|-----------------------------|
|            |       |                     | \(k_2\) (g/mg·min) | Calk\(·q_e\) (mg/g) | Error % | \(R^2\) | \(k_1\) (min\(^{-1}\)) | \(R^2\) | \(K_id\) (mg/g·min\(^{0.5}\)) | \(R^2\) |
| Cu\(^{2+}\)-PPFR | 303   | 21.40               | 0.0250 | 21.32 | 0.37 | 0.9999 | 0.0223 | 0.8240 | 0.5930 | 0.8232 |
|            | 313   | 22.10               | 0.0180 | 22.37 | -1.22 | 0.9990 | 0.0327 | 0.8828 | 0.5162 | 0.9126 |
|            | 323   | 22.19               | 0.0252 | 22.17 | 0.09 | 0.9992 | 0.0322 | 0.7865 | 0.4160 | 0.7863 |
| Cu\(^{2+}\)-NPPFR | 303   | 90.53               | -0.0212 | 86.96 | 3.94 | 0.9999 | 0.0472 | 0.9896 | 0.4962 | 0.3971 |
|            | 313   | 88.99               | -0.0353 | 87.18 | 2.03 | 0.9998 | 0.0441 | 0.9019 | 0.2835 | 0.2503 |
|            | 323   | 89.25               | 0.0104 | 89.29 | -0.04 | 1.0000 | 0.0623 | 0.4069 | 0.4962 | 0.3971 |
| Pb\(^{2+}\)-PPFR | 303   | 92.70               | 0.0015 | 91.74 | 1.04 | 0.9913 | 0.0184 | 0.8237 | 2.9374 | 0.8433 |
|            | 313   | 92.48               | 0.0015 | 94.34 | -2.01 | 0.9989 | 0.0170 | 0.8994 | 3.5717 | 0.8509 |
|            | 323   | 97.55               | 0.0034 | 93.46 | 4.19 | 0.9978 | 0.0009 | 0.7694 | 1.8056 | 0.7541 |
| Pb\(^{2+}\)-NPPFR | 303   | 265.17              | 0.0057 | 265.25 | -0.03 | 1.0000 | 0.0265 | 0.5947 | 1.2805 | 0.2640 |
|            | 313   | 263.83              | 0.0133 | 263.85 | -0.01 | 1.0000 | 0.0329 | 0.6352 | 0.8402 | 0.2678 |
|            | 323   | 264.64              | 0.0154 | 263.85 | 0.30 | 1.0000 | 0.020 | 0.3953 | 0.7919 | 0.2352 |

Error% = \(\frac{\text{Exp}\cdot q_e - \text{Calk}\cdot q_e}{\text{Exp}\cdot q_e} \times 100\).

The adsorption kinetic data were further analyzed using the pseudo-first-order rate model\(^{12}\), the pseudo-second-order rate model\(^{13}\) and the intraparticle diffusion model\(^{14}\), which are expressed as Eqs. (1), (2) and (3), respectively:

\[ \log(q_e - q_t) = \log q_e - \frac{k_t t}{2.303} \]  

\[ \frac{t}{q_t} = \frac{1}{(q_e)^2 k_2} + \frac{t}{q_e} \]
\[ q_t = k_{id} t^{0.5} \]  \hspace{1cm} (3)

Where \( q_e \) and \( q_t \) are the amounts of Cu\(^{2+}\) or Pb\(^{2+}\) adsorbed (mg/g) at equilibrium and at time \( t \) (min), respectively, \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg·min) are the rate constant of pseudo-first-order and pseudo-second-order adsorption process, respectively, \( k_{id} \) (mg/g·min\(^{0.5}\)) is the intraparticle diffusion rate constant.

The adsorption kinetics parameters are given in Table 2, from which, it can be concluded that pseudo-second-order equation provides the better correlation coefficient (\( R^2 > 0.99 \)) and agreement between calculated \( q_e \) values and the experimental data (Error% < ± 5%), whereas the pseudo-first-order model and the intraparticle diffusion model do not give a good fit to the experimental data for the adsorption of Cu\(^{2+}\) and Pb\(^{2+}\) with poor correlation coefficient. This suggests the chemical adsorption is the rate limiting step for the adsorption process.

### 3.4. Adsorption isotherms

Fig. 4 presents the adsorption isotherms of Cu\(^{2+}\) and Pb\(^{2+}\) onto the PPFR and NPPFR at initial pH 5.0 and \( T = 303 \) K. The adsorption capacity was positively correlated to the initial solution concentration. The adsorption isothermal data were further analyzed by the Langmuir isotherm model\(^{15}\) and Freundlich isotherm model\(^{16}\), which are expressed as Eqs. (4) and (5), respectively:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}
\]  \hspace{1cm} (4)

\[
\ln q_e = \ln k_F + \frac{1}{n} \ln C_e
\]  \hspace{1cm} (5)

Where \( C_e \) is the equilibrium concentration of Cu\(^{2+}\) or Pb\(^{2+}\) (mg/L), \( q_e \) is the amount of Cu\(^{2+}\) or Pb\(^{2+}\) adsorbed at equilibrium (mg/g), \( q_m \) is the monolayer adsorption capacity (mg/g) and \( b \) is the Langmuir constant related to the energy of adsorption (L/mg), \( k_F \) is the Freundlich constant related to the adsorption capacity, and \( n^{-1} \) is the heterogeneity factor. The Langmuir and Freundlich isotherm model parameters are listed in Table 3. From the correlation coefficients of Cu\(^{2+}\) and Pb\(^{2+}\), it can be concluded that Cu\(^{2+}\) and Pb\(^{2+}\) adsorption on PPFR and NPPFR can be well described by Langmuir model (\( R^2 > 0.99 \)). The maximum Langmuir adsorption capacities (\( q_m \)) for Cu\(^{2+}\) and Pb\(^{2+}\) adsorbed by NPPFR are calculated as 116.28 mg/g and 384.62 mg/g at 303 K, respectively, which was much higher than that of PPFR.

![Fig. 4 Adsorption isotherms of Cu\(^{2+}\) and Pb\(^{2+}\) on PPFR and NPPFR. (Initial conc. =30-110 mg/L (Cu\(^{2+}\)) and 100-300 mg/L (Pb\(^{2+}\)); pH=5.0; adsorbent dose= 0.3 g/L; temperature= 303 K; shaking speed= 200 r/min; shaking time= 24 h)](image-url)
### Table 3 The Langmuir and Freundlich isotherm parameters of Cu²⁺ and Pb²⁺ on PPFR and NPPFR.

| Metal ions | Adsorbents | Langmuir | Freundlich |
|------------|------------|----------|-------------|
|            |            | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ | $k_F$ | $n$ | $R^2$ |
| Cu²⁺       | PPFR       | 63.69    | 0.0666 | 0.9918   | 7.33 | 1.8975 | 0.9841 |
|            | NPPFR      | 116.28   | 0.0901 | 0.9995   | 47.77 | 5.8275 | 0.9677 |
| Pb²⁺       | PPFR       | 125.00   | 0.0674 | 0.9966   | 30.11 | 3.3501 | 0.9688 |
|            | NPPFR      | 384.62   | 0.0359 | 0.9991   | 164.45 | 7.5930 | 0.9777 |

### 3.5. Effect of coexisting metal ions

Table 4 Effect of coexisting metal ions on the adsorption of PPFR and NPPFR to Cu²⁺ and Pb²⁺. [Initial conc. =0.1 mmol/L; pH=5.0; adsorbent dose= 0.5, 1.0 g/L; temperature= 303 K; shaking speed= 200 r/min; shaking time= 24 h]

| Adsorbent dose (g/L) | Metal ions | Concentration before adsorption (mg/L) | Concentration after adsorption (mg/L) | Removal extent (%) |
|----------------------|------------|----------------------------------------|---------------------------------------|--------------------|
|                      |            | PPFR | NPPFR | PPFR | NPPFR | PPFR | NPPFR |
| 1.0                  | Ca²⁺       | 4.02 | 4.01 | 0.28 | 0.25 | 93.03 |
|                      | Cd²⁺       | 11.26 | 5.95 | 0   | 47.16 | 100 |
|                      | Cu²⁺       | 6.36 | 0   | 0   | 100 | 100 |
|                      | Fe³⁺       | 5.60 | 0   | 0   | 100 | 100 |
|                      | Mg²⁺       | 2.44 | 2.23 | 0.09 | 8.61 | 96.43 |
|                      | Mn²⁺       | 5.50 | 3.36 | 0   | 38.91 | 100 |
|                      | Pb²⁺       | 20.82 | 0   | 0   | 100 | 100 |
|                      | Zn²⁺       | 6.55 | 3.85 | 0   | 41.22 | 100 |
| 0.5                  | Ca²⁺       | 4.02 | 4.02 | 2.87 | 0   | 28.61 |
|                      | Cd²⁺       | 11.26 | 7.97 | 0.61 | 29.22 | 94.58 |
|                      | Cu²⁺       | 6.36 | 1.12 | 0   | 82.39 | 100 |
|                      | Fe³⁺       | 5.60 | 0   | 0   | 100 | 100 |
|                      | Mg²⁺       | 2.44 | 2.27 | 1.75 | 6.97 | 28.28 |
|                      | Mn²⁺       | 5.50 | 4.01 | 1.63 | 27.09 | 70.36 |
|                      | Pb²⁺       | 20.82 | 1.33 | 0   | 93.61 | 100 |
|                      | Zn²⁺       | 6.55 | 4.87 | 1.20 | 25.65 | 81.68 |

The effect of coexisting metal ions on the adsorption of PPFR and NPPFR to Cu²⁺ and Pb²⁺ are summarized in Table 4. It can be seen that the decrease of Cu²⁺ and Pb²⁺ adsorption capacity was not remarkable and the removal extent of Cu²⁺ and Pb²⁺ also increased with the increase of the adsorbent dose, indicating that coexisting metal ions had no obvious influence on the adsorption of PPFR and NPPFR to Cu²⁺ and Pb²⁺. Moreover, NPPFR showed strong adsorption abilities to the coexisting metal ions such as Fe³⁺, Cd²⁺, Zn²⁺, Mn²⁺, Mg²⁺ and Ca²⁺. In fact, most of the metal ions coexisting in solutions were simultaneously removed on NPPFR when the adsorbent dose was 1.0 g/L, however, the adsorption of Mg²⁺ and Ca²⁺ on PPFR were not satisfactory at the same adsorbent dose. The possible explanation for this phenomenon could be that the adsorption capacity of NPPFR was large enough for adsorbing Cu²⁺, Pb²⁺ and other metal ions. Similar experimental results were also reported by other researchers. These experimental results indicate that NPPFR can simultaneously remove Cu²⁺, Pb²⁺ and many other metal ions from aqueous solutions.

The order of removal for PPFR and NPPFR was Fe³⁺ > Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Mn²⁺ > Mg²⁺ > Ca²⁺, which
differs from the affinity order. PPFR and NPPFR showed higher adsorption capacity for Pb\(^{2+}\) compared to Cu\(^{2+}\) which is in accordance to their respective ionic radii. Cu\(^{2+}\) ions have smaller ionic radius, thus, Cu\(^{2+}\) ions have larger degree of hydration and surrounded by more water molecules to form a water layer or hydration shell. This in turn hindered the interaction between the Cu\(^{2+}\) ions and the adsorbent surface due to weaker ionic attraction force.

4. Conclusions

The adsorption capacity of Cu\(^{2+}\) and Pb\(^{2+}\) on NPPFR was much higher than that of PPFR. The solution pH had great effect on the adsorption of Cu\(^{2+}\) and Pb\(^{2+}\) by PPFR and NPPFR, and the optimal pH range was 5.0-6.0. The pseudo-second-order rate model could be used to satisfactorily describe the adsorption kinetics of Cu\(^{2+}\) and Pb\(^{2+}\) on PPFR and NPPFR (R\(^2\) > 0.99), and the adsorption capacities calculated by the model were close to those determined by experiments. The adsorption isotherms of Cu\(^{2+}\) and Pb\(^{2+}\) on PPFR and NPPFR could be well described by Langmuir equation (R\(^2\)>0.99), and the equilibrium adsorption capacities of Cu\(^{2+}\) and Pb\(^{2+}\) at 303 K calculated by Langmuir equation were much higher than that of PPFR. Coexisting metal ions (Fe\(^{3+}\), Pb\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\), Mn\(^{2+}\), Mg\(^{2+}\) and Ca\(^{2+}\)) had no obvious influence on the adsorption of Cu\(^{2+}\) and Pb\(^{2+}\) on PPFR and NPPFR. Moreover, most of metal ions coexisting in solutions could simultaneously removed by NPPFR when the adsorbent dose was 1.0 g/L, while the adsorption of Mg\(^{2+}\) and Ca\(^{2+}\) on PPFR were not satisfactory at the same adsorbent dose. The results suggested that NPPFR can be used as an active bio-sorbent for the removal of heavy metal ions from aqueous environment.

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Appendix A. Fig. 1 Zeta potentials of PPFR and NPPFR.

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