Adsorption of cadmium ions from simulated battery wastewater by polyethylene polyamine-modified activated carbon

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ABSTRACT

The objective of this work was to study the treatment of wastewater containing cadmium ions (Cd\(^{2+}\)). Activated carbon (AC) was modified with potassium hydroxide (KOH) and polyethylene polyamine (PEPA). The structure and morphology of the modified AC was characterized. The effect of pH on adsorption was investigated, and the binary competitive adsorption and the reusability of the modified AC were studied. Subsequently the modified AC was used as an adsorbent for the removal of Cd\(^{2+}\) from wastewater. The adsorption capacity of optimized modified AC was 9.7 times that of unmodified AC. Kinetic adsorption curves were in accordance with pseudo-second-order kinetics, and the isothermal curves were in accordance with the Langmuir equation. The results indicate that the AC has potential in the treatment of the wastewater containing Cd\(^{2+}\) discharged from chemical plants during battery manufacturing.

Key words: activated carbon, adsorption, cadmium ion, heavy metal, modification, polyethylene polyamine

HIGHLIGHTS

- Activated carbon (AC) was modified with potassium hydroxide and polyethylene polyamine (PEPA).
- The adsorption capacity of the AC for Cd\(^{2+}\) is up to 51.4 mg/g.
- The pore size and surface group density of the AC had a good effect on the adsorption.
- The AC can be employed to remove cadmium ions from simulated battery wastewater.

GRAPHICAL ABSTRACT

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INTRODUCTION

With the rapid development of modern society, people’s demand for electronic products is increasing. With the increase in the number of batteries, heavy metal wastewater discharged by chemical plants in the process of battery production increases. Wastewater containing heavy metals is related to the major problems of human health and the living environment. The famous ‘pain disease’ is caused by pollution of the environment by such wastewater containing heavy metals. Cd$^{2+}$ is the main hazardous substance in the wastewater produced by chemical plants in the process of battery manufacturing, a heavy metal that is particularly toxic, ranking third among heavy metals in terms of risk to human health. Cd$^{2+}$ is a highly hazardous, toxic and carcinogenic substance. Cd$^{2+}$ can have harmful effects on organisms even at very low concentrations (Ullah et al. 2019), so it is urgent to remove Cd$^{2+}$ from wastewater.

There are many ways to deal with heavy metal ions such as photocatalytic degradation of heavy metals (Pan et al. 2021), the ion-exchange method (Xu et al. 2021), the sulphide precipitation method (Zeng et al. 2021), membrane filtration (Zhu et al. 2021), phytoremediation (Sharma 2021) and adsorption methods (Ho et al. 2021). However, some of the above pollution-control methods have some problems, such as a slow removal rate of Cd$^{2+}$, a poor removal effect of Cd$^{2+}$ and high resource consumption, so it is necessary to seek cost-effective and innovative solutions to remove Cd$^{2+}$. Among the many methods to remove heavy metals, the adsorption method is widely used for its low cost, safe operation performance and high efficiency.

The adsorption materials of organic polymers include fiber adsorbents, chitosan adsorbents, polyurethane adsorbents, silica gel, etc. The non-polar adsorption materials include zeolite, diatomite, molecular sieve, kaolin, etc. The carbon adsorption materials include biological activated carbon (AC), AC, etc. Among these materials, organic polymer adsorbents are expensive and difficult to produce on a large scale. Inorganic materials have significant adsorption effects on organic substances and general adsorption effects on heavy metals. Carbon materials are commonly used adsorbents. However, because the manufacturing conditions of biological AC are complex and the raw materials are limited, it is not convenient for mass production. In addition, there are strict requirements for acid-base conditions of wastewater and high requirements for carbonization activation (Herbert et al. 2021). Only AC has the advantages of simple production, environmental protection and low price, and is often used for the adsorption of heavy metal wastewater. As one of the most promising adsorbents, AC has attracted increasing attention for its high specific surface area, large pore volume and good thermal stability.

AC is a black porous solid. The main component of AC is carbon, followed by a small amount of hydrogen and oxygen. AC is a substance with an irregular structure. The interlaced part of AC has small pores and low density, providing it with its adsorption function (Duan et al. 2020). Generally, AC has a specific surface area of 500–1,700 m$^2$/g. Activated carbon is an ideal method to treat heavy metal ions from the aspects of operation safety and economic applicability. However, the adsorption method also has some problems, such as poor repeatability and low adsorption efficiency. Previous studies have improved the adsorption capacity of AC, as in the acid modification method, alkali modification method, ozone modification and microwave modification. But using the acid-base modification method, too little acid-base consumption would lead to AC being unable to achieve good modification effects. Conversely, too much acid-base consumption would lead to pore collapse and excessive consumption. Even if the amounts of acid and alkali are appropriate, it is difficult to have significant adsorption effects. Ozone-modified AC is complex and difficult to use because it can be easily reduced to oxygen at room temperature. Microwave-modified AC is not suitable for mass production of adsorbents because of its high equipment investment. To further improve the removal rate of Cd$^{2+}$, this paper explored the potential of modified AC.

Polyethylene polyamine (PEPA) is an excellent polymer that has been widely used in the preparation of anion exchange resin, ion-exchange membranes, and lubricating oil additives (Yuan et al. 2021). In recent years, PEPA has been developed as a new type of material, and has many advantages such as hydrophilicity, environmental friendliness, large adsorption capacity, good selective adsorption and high degree of modifiability. At present, there are many research reports on the adsorption properties of PEPA for metal ions, but the adsorption mechanism for PEPA, its macromolecular characteristics and its interaction with metal ions still remain unclear. While PEPA itself has the disadvantages of difficult recovery and poor stability, the grafting of multifunctional PEPA materials can greatly expand the application of PEPA in the field of environmental metal ion adsorption. Therefore, in this work, PEPA was grafted onto the AC surface and amine groups with adsorption for Cd$^{2+}$ were introduced, which not only improved the adsorption capacity of AC for Cd$^{2+}$, but also...
solved the problems of difficult recovery and poor stability of PEPA (Zhu et al. 2020). Modified AC helps to control Cd\(^{2+}\) pollution, as well as contributes to the diversified development and utilization of AC, and improves the potential economic value. In this study, the adsorption of Cd\(^{2+}\) by modified AC was studied, and the adsorption process was statistically analysed. The main adsorption conditions affecting the adsorption process were studied and the parameters affecting the removal rate of the adsorbent were statistically optimized. The adsorption kinetics curve and isothermal adsorption curve were fitted to explore the influence of PEPA loading on adsorption performance and the influence of pH value on AC, binary competitive adsorption and adsorption–desorption cycle regeneration etc.

**MATERIALS AND METHODS**

**Materials**

Cadmium chloride (CdCl\(_2\)), potassium hydroxide (KOH), potassium hydroxide (NaOH), potassium chloride (KCl), lead chromate (PbCrO\(_4\)), PEPA, and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) were provided by Aladdin Industrial Corporation (Shanghai, China). Hydrochloric acid (HCl) and absolute ethanol (C\(_2\)H\(_6\)O\(_2\)) were provided by Sinopharm Chemical Reagent Co., Ltd. AC was provided by Ningxia Bertley Co., Ltd (Yinchuan). All reagents were of analytical purity.

Here, 0.1 g of AC was added to 200 mL deionized water, which was then kept in a constant-temperature vibration incubator at 300 r/min for 3 h at room temperature. After this process the AC was washed, and filtered using a Brinell funnel and dried at 80 °C for 12 h. The AC was added to 2 mol/L KOH and put it into a constant-temperature oscillation chamber for oscillation. AC was given an electric charge and then washed repeatedly with deionized water to neutral pH, filtered and dried. This completed the preparation, which was named AC-0. PEPA of the amounts of 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g were added into 50 mL anhydrous ethanol solution, and placed in a numerical control ultrasonic cleaning machine for 30 minutes at 25 °C and 40% power. Then, grafting was carried out by shaking for 5 h at the speed of 300 r/min in a constant temperature shaking box. After grafting of AC-0, the PEPA floating on the AC-0 surface was washed off, and the prepared modified AC was dried. The grafted PEPA with different amounts of AC were named AC-0.5, AC-1.0, AC-1.5, AC-2.0 and AC-2.5. In this work, the optimum loading amount of PEPA, adsorption equilibrium time, the effects of different initial concentrations on AC adsorption, and the effects of solution pH were studied in solution.

**Characterization of the ACs**

The N\(_2\) adsorption–desorption isotherm and pore size distribution of the adsorbent were measured using a N\(_2\) adsorption–desorption instrument (Tri Star 3020, −196 °C, scanning range 400–4,000 cm\(^{-1}\)), and the specific surface area and pore structure of AC were determined by the specific surface area and pore size analyser according to the N\(_2\) adsorption principle. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area of AC, the method was used to calculate the micropore volume of AC, and the Barrett–Joyner–Halenda (BJH) equation was used to calculate the pore size of AC. The surface functional groups of the adsorbent were determined using a Fourier transform infrared spectrometer (FTIR, Prestige-21, 400–4,000 cm\(^{-1}\)). The crystal structure of the adsorbent were determined by X-ray diffraction (XRD, XRD-6100, 200 Ma, 40 kV, \(\lambda = 0.151418\) nm, \(2\theta = 55–60^\circ\)). The surface morphology of the adsorbent was determined by scanning electron microscope (SEM, Hitachi, Japan). Nanoparticle size and a zeta potential analyser (Malvern Zetasizer Nano ZS90, pH = 7) were used to measure the potential of the sample. An inductively coupled plasma emission spectrometer (ICP, ICP-7000, 228.802 nm) was used for residual concentration analysis. The standard curve was established before analysis.

**Adsorption studies**

The kinetic adsorption equation was used to design the adsorption experiment, 0.1 g of AC-1.5 was added in 0.1 g/L of 200 mL Cd\(^{2+}\) for adsorption (Zhang et al. 2021). Then, the residual concentration of supernatant was measured every interval. The equilibrium adsorption capacity equation is as follows, where \(Q = (C_0 - C_e)V/m\), in which \(C_0\) is the initial concentration, \(C_e\) is the equilibrium concentration, \(V\) is the Cd\(^{2+}\) volume and \(m\) is the AC-1.5 quantity. The pseudo-first-order kinetic equation is \(ln(Qe - Q) = lnQe - k_1t\), where \(Qe\) is the adsorption capacity at equilibrium, \(Q_1\) is the adsorption capacity at time \(t\) and \(k_1\) is the rate constant of the first order reaction. The pseudo-second-order kinetic equation is \(t/Q_t = t/Q_e + 1/(k_2Q_e^2)\), where \(Q_e\) is the adsorption capacity at equilibrium, \(Q_t\) is the adsorption capacity at time \(t\) and \(k_2\) is the rate constant of pseudo-second-order reaction.
For the isotherm study, different initial concentrations of the Cd²⁺ solution (0.01–0.1 g/L) were studied. The Langmuir equation is

\[ \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{(K_L \cdot Q_m)} \]

in which \( C_e \) is the concentration of residual metal ions in adsorption equilibrium system, \( Q_e \) is the adsorption capacity at equilibrium, \( Q_m \) is the maximum adsorption capacity and \( K_L \) is the Langmuir adsorption equilibrium constant. The Freundlich equation is

\[ \ln Q_e = \ln K_F + \left( \frac{1}{n} \right) \ln C_e \]

in which \( Q_e \) is the adsorption capacity at equilibrium, \( 1/n \) is the heterogeneous factor and \( K_F \) is the Freundlich adsorption equilibrium constant (Sahu et al. 2021).

**RESULTS AND DISCUSSION**

**Characterization of the ACs**

The main factors affecting the adsorption capacity of adsorbent include the specific surface area (\( S_{BET} \), m²/g) of adsorbent, the density of surface adsorption sites, the characteristics of pores and surface adsorption sites (Dao et al. 2020). All the modified ACs were characterized by N₂ adsorption and desorption. Figure 1 shows the adsorption and desorption isotherms and pore size distribution. The effects of \( S_{BET} \), total pore volume (\( V_g \), cm³/g), micropore volume (\( V_{g_{micro}} \), cm³/g) and average pore size (\( D_{pore} \), nm) of AC on the adsorption capacity of the adsorbent were studied. Figure 1(a) shows that the N₂ adsorption and desorption isotherms of all the modified ACs belong to type IV isotherms. Under the low-pressure section of \( P/P_0 = 0–0.4 \), the gentle inflection point represents the formation of single-layer dispersion, and the middle region with small slope represents the formation of multilayer dispersion. Hysteresis loop was closed at \( P_0 = 0.4 \), indicating the existence of mesoporous structure in the sample. In the region of \( P/P_0 = 0.4–0.8 \), there was obvious H₄-type hysteresis loop representing the capillary condensation in the mesoporous. The pore size distribution curve of Figure 1(b) indicates that the pore size of the all modified ACs were mainly distributed between 10–30 nm, and the pore size distribution was narrow, which indicated that the prepared samples were mesoporous adsorbents. Table 1 shows the detailed changes of \( S_{BET} \), \( D_{pore} \), \( V_g \) and \( V_{g_{micro}} \) of all AC. After KOH treatment, the \( S_{BET} \) of the AC changed from 1,188.09 m²/g to 1,441.46 m²/g, and the \( V_g \) changed from 0.284 cm³/g to 0.341 cm³/g, this proved the success of pore modification of AC. With the increased amount of grafted PEPA, the \( S_{BET} \) of modified AC and the \( V_g \) decreased. After grafting AC-0, its \( S_{BET} \) ranged from 1,441.46 m²/g to 724.98 m²/g and \( V_g \) ranged from 0.341 cm³/g to 0.203 cm³/g, this is because PEPA occupied a certain space inside the modified AC after grafting, and bonded to the surface of AC and blocked some pores. The decrease of \( S_{BET} \) and partial pore blockage also indirectly proved that PEPA was successfully grafted (Ma et al. 2021). However, excessive PEPA filled the pores and affected the adsorption capacity of the adsorbent.

Figure 2 shows the infrared transmission spectra of each AC. All the samples showed typical infrared spectra that resembled original AC, indicating that modified AC still maintained its basic structure. All samples usually showed significant absorbance at approximately 1,487–1,538 cm⁻¹, which was classified as carboxylic acid (–C=O). With the increase in PEPA concentration, the absorbance at 1,515–1,556 cm⁻¹, 1,625 cm⁻¹ and 3,424 cm⁻¹ was increased, and was classified as the N-H band. With the increase of PEPA load, the absorbance of AC increased because it contained a large amount of amino groups. The increase in absorbance indicated that PEPA interacted with carboxyl groups on the AC surface, and PEPA was successfully loaded. The modified amino functional groups were helpful to adsorb Cd²⁺ and improved the adsorption efficiency of the adsorbent. The tensile vibration of 3,742–3,831 cm⁻¹ was due to the presence of surface hydroxyl and chemisorbed water (Saleh et al. 2018). Many hydrophilic amine groups could be introduced via PEPA, which was very
conducive to the adsorption of Cd$^{2+}$. The infrared transmission spectra of AC-1.5 and AC-1.5-adsorbed calcium ion summarized that the infrared spectrum peak of AC-1.5-adsorbed calcium ion was weakened relative to the N-H peak of AC-1.5, which indicated that AC-1.5 successfully adsorbed Cd$^{2+}$.

Figure 3 shows the crystal structure of each AC characterized by XRD. In $2\theta = 24.38^\circ$, $2\theta = 36.37^\circ$ and $2\theta = 43.37^\circ$, there were some obvious adsorption peaks, which indicated that the main component of the sample was graphite-like carbon nitride (Jang & Park 2012). With the increase of PEPA loading, the XRD diffraction peak intensity of the corresponding modified AC increased and moved to the high angle direction, which indicated that the graphene layer spacing decreased and the crystallinity of the corresponding adsorbent graphite increased. The results showed that although the $S_{BET}$, $D_{pore}$
Vg and Vg_{micro} and other parameters of AC changed after the PEPA regulation, the structure still maintained an amorphous stacking state, and that there was no typical crystal material generation, and the internal structure and crystal morphology of AC did not change.

**Adsorption capacity**

Table 2 summarizes some modified AC made by predecessors. The adsorption capacity of polyethylene imine-modified AC for cadmium ions reached 45 mg/g, the adsorption capacity of grafted polyglucosamine polymer on the surface of AC reached 35 mg/g, and the adsorption capacity of AC prepared from hazelnut shell activated by phosphoric acid reached 19 mg/g. It could be seen that simple acid-base modification or graft modification of AC could not achieve a good adsorption capacity. Table 3 shows the adsorption capacity of Cd\(^{2+}\) on all AC; 0.1 g/L of 200 mL Cd\(^{2+}\) sample solution adsorbed 0.1 g all AC. The adsorption capacity of AC was 5.31 mg/g. After modification, the adsorption capacity of AC-1.5 was as high as 51.4 mg/g. In the process of grafting PEPA, it could be found that the amount of grafting PEPA was directly proportional to the adsorption amount. However, excessive PEPA could block the pore size of AC, resulting in pore collapse; this further weakened the adsorption performance of AC. AC-1.5 was the highest adsorption capacity, therefore, it was selected as the research object in the follow-up test.

The adsorption site of unit mass AC-1.5 was determined. When the initial concentration of sample waste liquid was constant, the adsorption capacity increased over a certain time, and then reached equilibrium; 0.1 g/L of 200 mL Cd\(^{2+}\) sample solution was adsorbed with 0.1 g AC-1.5. Figure 4 shows that the adsorption capacity increased with time at 5–180 min, and the adsorption capacity was balanced at 180 min. However, the capacity slightly desorbed at 180–240 min. Therefore, 180 min was the equilibrium time chosen.

The adsorption site of AC-1.5 per unit mass was certain. When the initial concentration of sample waste liquid was small, the adsorption capacity of AC-1.5 increased with the increase of initial concentration. When the initial concentration reached a certain amount, the adsorption site reached the saturation state and the adsorption capacity reached the saturation value at the same time; 200 mL Cd\(^{2+}\) sample solution was adsorbed with 0.1 g AC-1.5. Figure 5 shows that the adsorption capacity of AC-1.5 increased at the initial concentration of 0.01–0.09 g/L, while the AC-1.5 was gradually balanced at the initial concentration of 0.1–0.14 g/L. Therefore, the initial concentration of 0.1 g/L was selected as the subsequent test condition.

The pH value of the Cd\(^{2+}\) sample solution was one of the important factors that affected the adsorption. The pH value of the sample solution affected the existing form of metal ions in the solution, the chemical state of active groups on AC and the charge distribution on the surface of adsorbent (Lu et al. 2021). To avoid the formation of cadmium hydroxide precipitate that hindered the whole adsorption process, the initial pH value of the solution was 2.0–8.0. 0.1 g/L for the 200 mL Cd\(^{2+}\) sample solution that adsorbed 0.1 g AC-1.5. Figure 6 shows that the effect of pH on Cd\(^{2+}\) adsorption. Figure 6(a) summaries that pH had little effect on the adsorption equilibrium time, and that AC-1.5 had a strong pH dependence on the adsorption behaviour of Cd\(^{2+}\). Figure 6(b) shows that when the pH value was 2.0–5.0, the maximum adsorption of Cd\(^{2+}\) on AC-1.5 gradually

**Table 2** | Surface area and porosity of the ACs

| Adsorbent                        | Adsorption capacity | References     |
|----------------------------------|--------------------|----------------|
| AC-1.5                           | 51.4 mg/g          | (This paper)   |
| Polyethyleneimine modified AC     | 45 mg/g            | Xie et al. (2019)|
| Activated carbon grafted polymer | 35 mg/g            | Berber (2020)  |
| Activated carbon hazelnut husks   | 29.9 mg/g          | Imamoglu (2013)|

**Table 3** | Adsorption properties of AC with different concentrations of PEPA and a regeneration experiment of adsorption-desorption cycle (T = 298.15 K, C0 = 0.1 g/L, time = 180 min)

| Sample | AC | AC-0 | AC-0.5 | AC-1.0 | AC-1.5 | AC-2.0 | AC-2.5 |
|--------|----|------|--------|--------|--------|--------|--------|
| Q (mg/g)| 5.31| 25.46| 44.82  | 46.64  | 51.4   | 47.58  | 46.4   |
increased. When the pH value was 6.0, the best adsorption capacity of AC-1.5 for Cd\(^{2+}\) had was 51.4 mg/g, and when the pH value increased from 6.0 to 8.0, the adsorption capacity decreased with the increasing pH value. There were many amino groups and O-containing functional groups on the surface of modified AC, which were obviously affected by the pH value. AC-1.5 adsorbed Cd\(^{2+}\), its amine group and O-containing functional group formed a complex with Cd\(^{2+}\). The pH

**Figure 4** | Effect of adsorption time on adsorption capacity (T = 298.15 K, C\(_0\) = 0.1 g/L, time = 5–240 min).

**Figure 5** | AC-1.5 of activated carbon with different initial concentrations (T = 298.15 K, C\(_0\) = 0.01–0.12 g/L, time = 240 min).

**Figure 6** | (a, b) Effects of different pH values on adsorbents and maximum adsorption capacity at different pH values (T = 298.15 K, C\(_0\) = 0.1 g/L, pH = 2–8, time = 240 min).
value was low, due to the presence of a number of hydrogen ions in the solution, the amine matrix on the surface of the adsorbent was protonated, the complexing effect was lost, and an electrostatic repulsion force on Cd\(^{2+}\) was generated, which reduced the adsorption capacity. The increase of pH value also promoted the hydrolysis of carboxyl group, which improved the surface electronegativity of adsorbent, increased the electrostatic attraction between Cd\(^{2+}\) and adsorbent, and improved the complexation between AC-1.5 surface functional group and Cd\(^{2+}\). With the increase in pH value, the amount of negative charge on the surface of AC-1.5 increased and the electrostatic repulsion between metal cations and their surface decreased, so the adsorption capacity increased. The pH rose again, there were many Cd(OH)\(^{+}\) formation in the solution, which slightly reduced the adsorption capacity of AC-1.5 for Cd\(^{2+}\). The above experiments showed that the optimal pH value of Cd\(^{2+}\) adsorption by AC-1.5 was pH = 6. Therefore, all further adsorption experiments were carried out when pH = 6.

Figure 7 shows that the morphology of AC, AC-0 and AC-1.5 by SEM. As shown in Figure 7, there were a few honeycomb or circular pores on the surface of AC, and the morphology of AC-0 and AC-1.5 was similar to AC, Figure S1 shows the morphology of all AC by SEM. However, there were more honeycomb or circular pores (Wang et al. 2021a). The surface morphology of AC and AC-0 was smoother than that of AC-1.5. The surface of AC-1.5 was rough, some pore structure collapsed slightly, showing irregular circular pores; this phenomenon was related to the changes of internal pore structure. The surface of AC-1.5 was covered by spongy sediments, which was mainly due to the grafting of PEPA on the surface of AC. The modification of AC provided more adsorption sites for Cd\(^{2+}\).

Table 4 shows the zeta potential of AC, AC-1.5, AC-1.5-adsorbed Cd\(^{2+}\). The zeta potential of AC particles was \(-28.7\) mV. The zeta potential of the AC-1.5 surface changed to 7.04 mV, because the -NH or -NH\(_2\) on the surface of AC-1.5 made it easy to attract cationic substances, and generated more positive charges on the AC-1.5 surface. The zeta potential of AC-1.5-adsorbed Cd\(^{2+}\) changed to 11.1 mV because of the increase in zeta potential of the AC-1.5 surface with adsorbed Cd\(^{2+}\). The zeta potential of the AC-1.5-adsorbed Cd\(^{2+}\) surface increased significantly, which also proved that AC-1.5 successfully adsorbed Cd\(^{2+}\) (Martin et al. 2021).

**Adsorption kinetic studies**

The adsorption kinetic model applied herein has been usually applied to study the relationship between adsorption capacity and contact time. The process of adsorption can be described by different adsorption mechanisms such as mass transfer, chemical reaction and particle diffusion. To study the adsorption rate and mechanism of AC-1.5 for Cd\(^{2+}\), kinetic experiments was carried out. The pseudo-first-order kinetic equation and pseudo-second-order kinetic equation were used to simulate the adsorption kinetics of the adsorbent for Cd\(^{2+}\). The pseudo-first-order kinetic model is based on the assumption that the limiting factor of adsorption is the mass transfer resistance in the adsorbent particles. If the fitted results of adsorption kinetics data accord with pseudo-first-order reaction kinetics, the adsorption process is diffusion controlled and the rate limiting
step is physical adsorption. The pseudo-second-order kinetics is based on the assumption that the limiting factor of adsorption is the chemisorption mechanism, which controls the adsorption rate by sharing or exchanging electrons between adsorbent and adsorbate. The rate of metal ions occupying the active sites on the adsorbent is proportional to the square of the number of unoccupied active sites.

Figure 8 shows the kinetic fitting results of adsorbent. Figure 8(a) and 8(b) shows the pseudo-first-order kinetic curve, and the pseudo-second-order dynamic curve, respectively. Table 5 summarizes the characteristic parameters of the model. The correlation coefficient of the pseudo-second-order kinetic equation was larger (0.9892 ± 0.0015 > 0.9279 ± 0.0132), and the calculated value of equilibrium adsorption capacity was in good agreement with the actual value, indicating that the pseudo-second-order kinetic equation fitted the experimental data well, so the rate controlling stage was chemical adsorption. It was believed that the adsorption was due to the chemisorption between the active group (amino group) on the surface of the material and the metal ions, so that the metal ions were adsorbed on to the surface of the material.

Adsorption isotherm studies
To determine the adsorption effect of AC on Cd\(^{2+}\), adsorption isotherm experiments were carried out under different initial concentrations of AC. Langmuir and Freundlich isotherm models were used to describe the model. The Langmuir isotherm model has been successfully applied in many monolayer adsorption processes. It assumes uniform adsorption at a specific adsorption position in the adsorbent. All adsorption sites are the same for the adsorbed species, and there is no interaction between the adsorbed molecules. The Freundlich isotherm model assumes that a multilayer adsorption is formed due to the uneven distribution of adsorption heat on the uneven surface of the adsorption material. The Langmuir and Freundlich equations were used to fit the experimental data.

Figure 9 shows the experimental results. Figure 9(a) and 9(b) shows the Langmuir fitting diagram, and the Freundlich fitting diagram, respectively. Table 6 shows the correlation coefficients of Langmuir and Freundlich models. The correlation coefficient of the Freundlich model was low (0.9658 ± 0.0149<0.9747 ± 0.0744), indicating that the Freundlich equation did not match the adsorption process. The correlation coefficient of the Langmuir model was 0.9747 ± 0.0744, demonstrating that the theoretical model was in good agreement with the experimental data and that the Langmuir model can better described the adsorption process compared to the Freundlich model. The adsorption characteristics of Cd\(^{2+}\) on AC-1.5 was single-
molecule adsorption, and the distribution of active groups on the surface of the adsorbent was uniform. This showed that the adsorption process of Cd$^{2+}$ on AC-1.5 was not a pure physical adsorption process, and there was a chemical interaction between the adsorbent and metal ion in solution. The -NH$_2$ and other functional groups in the adsorbent interacted with charged metal ions in the solution electronically and played an important role in the adsorption process.

**Binary competitive adsorption experiment**

Here, 0.1 g of AC-1.5 was added to 200 mL of 0.1 g/L Cd$^{2+}$ solution. The concentrations of potassium ion (K$^+$) and lead ion (Pb$^{2+}$) were 0, 0.02, 0.04, 0.06, 0.08 and 0.1 g/L respectively, and two-component competition of K$^+$ and Pb$^{2+}$ was formed. Figure 10 shows that with the increase in the initial concentration of K$^+$, the Cd$^{2+}$ adsorption capacity of AC-1.5 gradually decreased. The adsorption of Cd$^{2+}$ has a significant inhibitory effect when metal ions exist themselves; the higher the concentration was, the stronger the inhibitory effect was. Compared with Cd$^{2+}$, K$^+$ has a stronger competitive adsorption capacity. This may be related to the radius of the metal ions: The smaller the radius, the easier it was to be adsorbed (Ma

![Figure 9](https://iwaponline.com/wst/article-pdf/84/12/3916/979641/wst084123916.pdf)

**Figure 9** | (a, b) Langmuir isotherm constants and Freundlich isotherm constants for AC-1.5 adsorption (T = 298.15 K, C$_0$ = 0.1 g/L, pH = 6, time = 5–240 min).

**Table 6** | Langmuir and Freundlich isotherm constants for methylene blue and crystal violet adsorption regeneration experiment of the adsorption–desorption cycle (T = 298.15 K, C$_0$ = 0.01–0.1 g/L, pH = 6, time = 180 min)

| Sample  | Langmuir model | Freundlich model |
|---------|----------------|-----------------|
|         | $K_L$ (L/g)    | $Q_m$ (mg/g)    | $R^2$          | $K_F$ (L/g) | $n$     | $R^F$ |
| AC-1.5  | 0.06           | 73.69           | 0.9747 ± 0.0744 | 2.57        | 1.99    | 0.9658 ± 0.0149 |

![Figure 10](https://iwaponline.com/wst/article-pdf/84/12/3916/979641/wst084123916.pdf)

**Figure 10** | Binary competitive adsorption (T = 298.15 K, C$_0$ = 0.1 g/L, pH = 6, time = 180 min).
et al. 2021). The radius of $K^+$ was smaller than that of $Cd^{2+}$. In the presence of $K^+$, the competition coefficient of $Cd^{2+}$ was relatively small (Wang et al. 2021b). In the presence of $K^+$, it was difficult for the material to remove $Cd^{2+}$. Pb$^{2+}$ and $Cd^{2+}$ showed the same trend. As shown in Figure 10, Pb$^{2+}$ also had the inhibition effect on the adsorption of $Cd^{2+}$ on AC-1.5. The radius of Pb$^{2+}$ was larger than that of $Cd^{2+}$, the competitive adsorption of Pb$^{2+}$ was not strong, and the inhibition effect on the adsorption of $Cd^{2+}$ was weak.

### Regeneration of adsorption–desorption cycle

The recycling of modified AC is of great significance in practical application, because it can reduce production cost and save time. To study the important index of modified AC recycled, we considered the properties of the active groups of the adsorbent (Wu et al. 2021). In this study, 0.1 mol/L HCl solution and 0.1 mol/L EDTA solution were used to regenerate the used modified AC. Here, 0.1 g of AC-1.5-adsorbed cadmium ion was put into 100 mL of 0.1 mol/L HCl solution and 0.1 mol/L EDTA solution, respectively, in a constant-temperature oscillator for 6 h for regeneration after desorption. Then the adsorption and desorption experiments were repeated five times, the solubility of the sample solution for re-adsorbing cadmium ions was 0.1 g/L. Figure 11 shows that 0.1 mol/L EDTA solution was a suitable regeneration agent for AC-1.5, because EDTA had strong complexation ability and could desorb metal ions without damaging the original structure of the adsorbent. These results proved that AC-1.5 not only has a high removal rate, but also a good recycling performance, thus providing good application prospects.

### CONCLUSIONS

In the present work, AC was modified by KOH and PEPA, and was used for adsorption removal of $Cd^{2+}$ from wastewater. After PEPA loaded on the AC surface, the specific surface area of all modified AC decreased and the surface zeta potential of the AC-1.5 increased. The pH was an important factor affecting the $Cd^{2+}$ adsorption, and when the pH was 6, AC-1.5 exhibited an optimal $Cd^{2+}$ adsorption in aqueous solution, which gave an adsorption capacity of 51.4 mg/g. FTIR shows that the best adsorption performance for $Cd^{2+}$ in waste liquid that was mainly due to the increase of amine group content on the surface, which provided more adsorption sites for $Cd^{2+}$ adsorption and played an important role in the adsorption process. The adsorption process could be fitted by a Langmuir isotherm adsorption model and a pseudo-second-order kinetic equation, indicating that the $Cd^{2+}$ adsorption on AC-1.5 was a monolayer coverage, and the adsorption process was a chemical process. AC-1.5 exhibited a good regeneration ability, and the adsorption capacity of AC-1.5 to $Cd^{2+}$ remained about 45 mg/g after four cycles of recycling, indicating that modified AC was a very promising adsorption material.

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### DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.
REFERENCES

Berber, M. R. 2020 Surface-functionalization of activated carbon with polyglucosamine polymer for efficient removal of cadmium ions. *Polymer Composites* 41, 3074–3086.

Dao, M. T., Nguyen, T. T. T., Nguyen, X. D., La, D. D., Nguyen, D. D., Chang, S. W., Chung, W. J. & Nguyen, V. K. 2020 Toxic metal adsorption from aqueous solution by activated biochars produced from macadamia nutshell waste. *Sustainability* 12, 7909.

Duan, C., Ma, T., Wang, J. & Zhou, Y. 2020 Removal of heavy metals from aqueous solution using carbon-based adsorbents: a review. *Journal of Water Process Engineering* 37, 101339.

Herbert, A., Kumar, U. & Janardhan, P. 2021 Removal of hazardous dye from aqueous media using low-cost peanut (*Arachis hypogaea*) shells as adsorbents. *Water Environment Research* 93, 1032–1043.

Ho, P. H., Lofty, V., Basta, A. & Trens, P. 2021 Designing microporous activated carbons from biomass for carbon dioxide adsorption at ambient temperature. A comparison between bagasse and rice by-products. *Journal of Cleaner Production* 294, 126260.

Imamoglu, M. 2013 Adsorption of Cd(II) ions onto activated carbon prepared from hazelnut husks. *Journal of Dispersion Science and Technology* 34, 1183–1187.

Jang, D.-I. & Park, S.-J. 2012 Influence of nickel oxide on carbon dioxide adsorption behaviors of activated carbons. *Fuel* 102, 439–444.

Lu, Z., Zhang, H., Shahab, A., Zhang, K., Zeng, H., Bacha, A.-U.-R., Nabi, I. & Ullah, H. 2021 Comparative study on characterization and adsorption properties of phosphoric acid activated biochar and nitrogen-containing modified biochar employing eucalyptus as a precursor. *Journal of Cleaner Production* 303, 127046.

Ma, X., Wei, X., Dang, R., Guo, W., Kang, Y., Li, X., Gao, Y., Bai, J., Zhang, Y., Zhang, Z., Ma, Y. & Zong, Z. 2021 A simple, environmentally friendly synthesis of recyclable magnetic γ-Fe2O3/Cd2+–Ni2+–Fe3+–CO3– layered double hydroxides for the removal of fluoride and cadmium ions. adsorption capacity and the underlying mechanisms. *Applied Clay Science* 211, 106191.

Martin, S. K., Tomida, J. & Wood, R. D. 2021 Disruption of DNA polymerase zeta engages an innate immune response. *Cell Reports* 34, 108775.

Pan, Y., Zhang, Y., Huang, Y., Jia, Y., Chen, L. & Cui, H. 2021 Synergetic effect of adsorptive photocatalytic oxidation and degradation mechanism of cyanides and Cu/Zn complexes over TiO2/ZSM-5 In real wastewater. *Journal of Hazardous Material* 416, 125802.

Sahu, J. N., Karri, R. R. & Jayakumar, N. S. 2021 Improvement In phenol adsorption capacity on eco-friendly biosorbt derived from waste palm-oil shells using optimized parametric modelling of isotherms and kinetics by differential evolution. *Industrial Crops and Products* 164, 113333.

Saleh, T. A., Adio, S. O., Asif, M. & Dafalla, H. 2018 Statistical analysis of phenols adsorption on diethylenetriamine-modified activated carbon. *Journal of Cleaner Production* 182, 960–968.

Sharma, P. 2021 Efficiency of bacteria and bacterial assisted phytoremediation of heavy metals: an update. *Bioresource Technology* 328, 124835.

Ullah, M., Nazir, R., Khan, M., Khan, W., Shah, M., Afridi, S. G. & Zada, A. 2019 The effective removal of heavy metals from water by activated carbon adsorbents of albizia lebbeck and melia azedarach seed shells. *Soil and Water Research* 15, 30–37.

Wang, J., Wu, Z., Niu, Q., Liu, L., Yang, L., Fu, M., Ye, D. & Chen, P. 2021a Highly efficient adsorptive removal of toluene using silicon-modified activated carbon with improved fire resistance. *Journal of Hazardous Material* 415, 125753.

Wang, T., Meng, Z., Sheng, L., Liu, Z., Cao, X., Wang, X. & Sun, X. 2021b Insights into the mechanism of co-adsorption between tetracycline and nano-TiO2 on coconut shell porous biochar In binary system. *Advanced Powder Technology* 11, 4120–4129.

Wu, H., Gong, L., Zhang, X., He, F. & Li, X. 2021 Bifunctional porous polyethyleneimine-grafted lignin microspheres for efficient adsorption of 2,4-dichlorophenoxyacetic acid over a wide pH range and controlled release. *Chemical Engineering Journal* 411, 128539.

Xie, X., Gao, H., Luo, X., Su, T., Zhang, Y. & Qin, Z. 2019 Polyethyleneimine modified activated carbon for adsorption of Cd(II) In aqueous solution. *Journal of Environmental Chemical Engineering* 7, 103183.

Xu, G., An, Z., Xu, K., Liu, Q., Das, R. & Zhao, H. 2021 Metal organic framework (MOF)-based micro/nanoscaled materials for heavy metal ions removal: the cutting-edge study on designs, synthesis, and applications. *Coordination Chemistry Reviews* 427, 213554.

Yuan, L., Wen, T., Jiang, L., Liu, Z., Tian, C. & Yu, J. 2021 Modified superhydrophilic/underwater superoleophobic mullite fiber-based porous ceramic for oil-water separation. *Materials Research Bulletin* 143, 11454.

Zeng, W., Guo, W., Li, B., Wei, Z., Dionysiou, D. D. & Xiao, R. 2021 Kinetics and mechanistic aspects of removal of heavy metal through gas-liquid sulfide precipitation: a computational and experimental study. *Journal of Hazardous Materials* 408, 124868.

Zhang, Z., Wang, T., Zhang, H., Liu, Y. & Xing, B. 2021 Adsorption of Pb(II) and Cd(II) by magnetic activated carbon and its mechanism. *Science of the Total Environment* 757, 143910.

Zhu, F., Zong, Z., Zhang, B. G. & Dai, Y. R. 2021 A critical review on the electrospun nanofibrous membranes for the adsorption of heavy metals In water treatment. *Journal of Hazardous Materials* 401, 125608.