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Efficient copper ions adsorption property of the composite sepiolite-based polyethyleneimine alginate microspheres in wastewater treatment

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ABSTRACT

Heavy metal ions widely existing in the surface water systems can cause serious harm to humans and the environment. The present work has been carried out and presents the novel fabrication processes of sepiolite-based polyethyleneimine alginate microspheres (SPEIAM) and the characterizations of Fourier-transform infrared spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy for this composite material. SPEIAM has been efficiently utilized to remove copper ions from the simulated copper-containing industrial wastewater through adsorption method. The adsorption behaviors of SPEIAM for copper ions, including the effect of pH, the effect of adsorbent dosage, adsorption isotherm, adsorption kinetics, adsorption selectivity properties have been investigated. The results indicate that the adsorption kinetics of SPEIAM for copper ions at different temperatures can be modeled by the pseudo-second-order rate equation, the experimental data fit well with the Langmuir isotherm model which indicates the monolayered way of the adsorption and the maximum adsorption capacity of SPEIAM for copper ions could reach 490.20 mg/g, which is much higher than those values of other adsorbents reported in the literatures, and the extraordinary features of SPEIAM for copper ions removal can ensure their applicability and feasibility in the industrial scale.

Keywords: Sepiolite; Polyethyleneimine; Alginate; Microspheres; Composite; Copper adsorption

1. Introduction

Heavy metals are common pollutants found in various industrial effluents, which have represented a serious threat to the environment and the human being because of their toxic and lethal effects. Many methods such as chemical precipitation, ion exchange, membrane separation and adsorption have been utilized to treat the heavy metal pollutions. Adsorption is one promising method due to its facile processes and high efficiency, especially using low-cost natural clay materials as absorbents that have been highlighted recently [1–5]. Clay minerals such as sepiolite, which is a magnesium-rich silicate porous clay mineral with abundant Si–OH functional groups, are environmentally friendly adsorbent materials that have displayed high

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heavy metal removal efficiency, and they also have the obvious advantages of non-toxicity, widespread resources and low cost [1–3]. Copper ions always appears in the heavy metal pollutants of water and are commonly found in the industrial wastewater. Just like other heavy metals, they are not degradable and can accumulate in the living beings. If the wastewater containing copper ions is dumped into the rivers, the lakes or the oceans without any treatment, it would permanently damage the water-based biological system [6,7]. Therefore, it is necessary to develop highly efficient adsorbents for copper ions. Although it has been used as copper ions adsorbent, sepiolite exists in the state of lumpy powder, which makes it very difficult for the sepiolite adsorbent to be separated from solution systems and to be conducted in the subsequent processes of recovery and reuse. In order to solve this problem and explore more excellent heavy metal adsorbents with sepiolite, polyethyleneimine alginate microspheres have been considered in the present work.

Sodium alginate is a natural polymer that is mainly extracted from brown algae whose molecular skeleton contains a large number of highly active carboxylic function groups (–COOH) and hydroxylic ones (–OH), making sodium alginate an excellent cationic heavy metal adsorbent. It has excellent features such as high biocompatibility, biodegradable, and renewable [8–10]. Moreover, polyethyleneimine is a soluble polyamine. There are abundant amine functional groups on its molecular chain, such as primary amine, secondary amine, and tertiary amine that have a good affinity for cationic heavy metals such as Cu^{2+} [11,12]. In the present work, sodium alginate and polyethyleneimine have poly-blended together with sepiolite in order to construct a novel copper adsorbent sepiolite-based polyethyleneimine alginate microspheres (SPEIAM) with synergistic adsorption effect and good feasible operability. The adsorption sites on the surface of the alginate/polyethyleneimine gel adsorbent are relatively limited, and their internal active sites cannot be fully utilized because the related mass transfer resistance is very great, which reduces their performance of heavy metal ions adsorption. In order to overcome the above-mentioned limitations, in the present work, sodium alginate and polyethyleneimine have poly-blended together with sepiolite to construct a novel adsorbent SPEIAM with synergistic adsorption effect and good feasible operability, and sepiolite was introduced into the alginate/polyethyleneimine gel materials for the first time.

The object of this study was to explore the novel efficient sepiolite-based adsorbent SPEIAM and to investigate its copper ions adsorption properties. Multifarious organic functional groups in SPEIAM could chelate effectively with heavy metal ions such as copper ions and thereby efficiently promote their adsorption properties for those ions, Furthermore, its unique porous structure could enhance the adsorption ability of SPEIAM. Its adsorption performance has been evaluated using batch experiment and their physiochemical properties are studied by characterization techniques. The adsorption behaviors of SPEIAM for copper ions, including the effect of pH, the effect of adsorbent dosage, adsorption isotherm, adsorption kinetics, adsorption selectivity properties have been investigated.

2. Experimental

2.1. Materials and instruments

Sepiolite and polyethyleneimine (PEI, M.W. 600/10000) were purchased from Hunyuanjunhong New Materials Co., Ltd., China and Shanghai Titan Scientific Co., Ltd., China, respectively. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China and of analytical grade, which were used directly without further purification. Stock solutions of heavy metal ions (10,000 mg/L) were prepared by dissolving 10.0 g of their corresponding solid metal salts in 1,000 mL of deionized water, and the experimental solutions of desired concentration were prepared by diluting the stock solution with deionized water.

Fourier-transform infrared spectroscopy (FT-IR) has been utilized for functional group analysis on a Nicolet MAGNA-IR 550 spectrophotometer. The scanning electron microscopy (SEM) and the energy-dispersive X-ray spectroscopy (EDS) of the samples are performed on a HITACH SU8010 analytical instrument. The specific surface area of the sample SPEIAM was measured at liquid N_2 temperature (76 K) using an automatic physisorption analyzer ASAP 2020. The X-ray photoelectron spectroscopy (XPS) measurement has been made on a Perkin-Elmer PHI 550-ESCA/SAM photoelectron spectrometer operated at 10 kV and 30 mA. High-resolution XPS spectra are generated with the analyzer pass energy setting at 10 and 50 eV, respectively. The concentrations of the studied heavy metal ions are detected on a flame atomic absorption GBC-932A spectrophotometer.

2.2. Preparation of the adsorbent SPEIAM

2.2.1. Preparation of $CaCO_3$-embedded sepiolite

5.0 g of sepiolite and 2.65 g of sodium carbonate were added into 100 mL of deionized water, and then sonicated and stirred for 4 h at room temperature. After that, a certain amount of saturated calcium chloride solution was added dropwise until the precipitation is complete. After being washed, filtered and dried for 24 h, the $CaCO_3$-embedded sepiolite filler was obtained for subsequent use.

2.2.2. Preparation of the composite microspheres

A certain amount of $CaCO_3$-embedded sepiolite and sodium alginate (in the mass ratio: 2:1, 1:1, 1:1.5, 1:2) were added in 150 mL of deionzied water, and then sonicated for 5 min. Subsequently, 0.5 g of PEI in 50 mL deionized water was added into the mixture, which was continuously stirred for 6 h at 60°C. The composite microspheres were formed by dripping the above-mentioned mixture into a calcium chloride solution (3% w/v) with a medical syringe, and the obtained microspheres were further cross-linked for 12 h.

2.2.3. Hole-making process of SPEIAM

The above-mentioned prepared samples were treated by 0.05 M of hydrochloric acid for 2 h and washed with deionized water until pH ≈ 7, and then freeze-dried at –50°C for 48 h, and the as-synthesized product is labeled as SPEIAM.

2.3. Heavy metal ion adsorption measurements

Static adsorption experiment has been used to get the adsorption capacities of SPEIAM for different heavy metal ions. The static adsorption experiments are conducted by mixing SPEIAM (20.0 mg) with the solutions that contain heavy metal ions (20.0 mL). The mixture is equilibrated at 25°C for 24 h with the shaking method. Then the solutions are separated from the adsorbents and the concentration of metal ions is quantified by atomic absorption spectrometer.

The following formula has been used to compute the corresponding adsorption amount of these adsorbents q (mg/g) and removal rate R (%):

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \quad (1)$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where C_0 and C_e are the concentrations in the initial solution and the equilibrium solution of the respective heavy metal ions (mg/mL); V and m represent the volume of the solution (mL) and the weight of the adsorbent used in the adsorption studies (g), respectively. During the experimental procedure, these studied systems are mixed at the speed of 150 rpm through a rotary shaker. Each adsorption experiment has been conducted in triplicates and the average value is used.

2.4. Effect of pH on adsorption for copper ions

The effect of pH on the adsorption of copper ions has been studied by adding 20.0 mg of SPEIAM to 50 mg/L (200 and 500 mg/L) of Cu(II) at different pH values (2.0–6.0) in 100 mL Erlenmeyer flask. The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25°C. Then the solutions are separated from the adsorbents and the concentration of copper ions is detected by atomic absorption spectrometer.

2.5. Effect of adsorbent dosage on adsorption for copper ions

The effect of pH on the adsorption of copper ions has been studied by adding a certain amount of SPEIAM (0.5–3.0 g/L) to 200 mg/L of Cu(II) at pH = 5.0. The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25°C. Then the solutions are separated from the adsorbents and the concentration of copper ions is detected by atomic absorption spectrometer.

2.6. Adsorption kinetics of SPEIAM for copper ions

The adsorption kinetics on the uptake of copper ions by the adsorbent has been studied by placing 20.0 mg of SPEIAM with 10 mL of copper ion solution in a series of flasks at pH = 5.0 and 15°C–35°C with the concentration of copper ions being 200 mg/L. At a certain time interval, the adsorbent is filtrated and the concentrations of copper ions in the solutions are measured by atomic absorption spectrometer.

2.7. Adsorption isotherms of SPEIAM for copper ions

The isotherm adsorption property of the adsorbents is also investigated by batch tests. The adsorption isotherms can be studied using 20.0 mg of SPEIAM with different copper ions concentrations at pH = 5.0 and 15°C–35°C for 24 h. After that the adsorbent is filtrated and the concentrations of copper ions in the solutions are measured by atomic absorption spectrometer.

2.8. Investigations on the emulative adsorption for copper ions

The prepared SPEIAM (20.0 mg) has been mixed with the binary ions solutions (20.0 mL) containing equal initial concentrations (200 mg/L) of Cu(II) and other co-existing metal ions, and then these systems are oscillated 16 h. After that these solutions are separated from the adsorbents and the concentrations of metal ions have been detected by atomic absorption spectrometer.

3. Results and discussions

3.1. Design of the novel adsorbent SPEIAM

Sepiolite, a kind of magnesium-rich silicate clay mineral with abundant Si–OH functional groups, has been considered as one of the most promising candidates for heavy metal removal because of its obvious advantages such as low cost, special porous structure, large specific surface area, and excellent chemical stability. The new challenge concerning sepiolite applications for environmental protection is to improve its adsorbability [2]. In order to enhance its adsorption efficiency, operating feasibility, and recyclability, the sepiolite-based polyethyleneimine alginate microspheres have been considered in the present work. Fig. 1 presents the schematic illustration of synthesis process of the composite adsorbent SPEIAM. The sepiolite used in this experiment is a natural clay mineral with a formula of magnesium hydrosilicate $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4\cdot 8H_2O$ that contains a continuous two-dimensional tetrahedral sheet, its specific surface area was 153.24 m^2/g, and its X-ray diffraction (XRD) pattern is shown in Fig. S1a. Sepiolite materials were impregnated with sodium carbonate, calcium chloride solution was added in dropwise, and calcium carbonate was formed inside or onto the surface of sepiolite, and $CaCO_3$-embedded sepiolite has been obtained. And then, sepiolite-based alginate/PEI hydrogel microspheres beads were developed through a mild poly-blending method. With sepiolite having unique structure and high cation exchange capacity to make pores in the composite adsorbent, it was successful for the composite SPEIAM to the enhance mechanical properties, to improve the tolerance of the composite in complex aqueous systems, and to make up for the deficiencies of the alginate/PEI gel materials in terms of mass transfer and the inability of rational utilization of adsorption sites. The presence of the silanol, carboxyl, hydroxyl, amino and other functional groups can cause to enhance the interfacial interaction among sepiolite, alginate and polyethyleneimine. The synergistic effect of diverse porous structures and various functional groups from the components of the composite SPEIAM

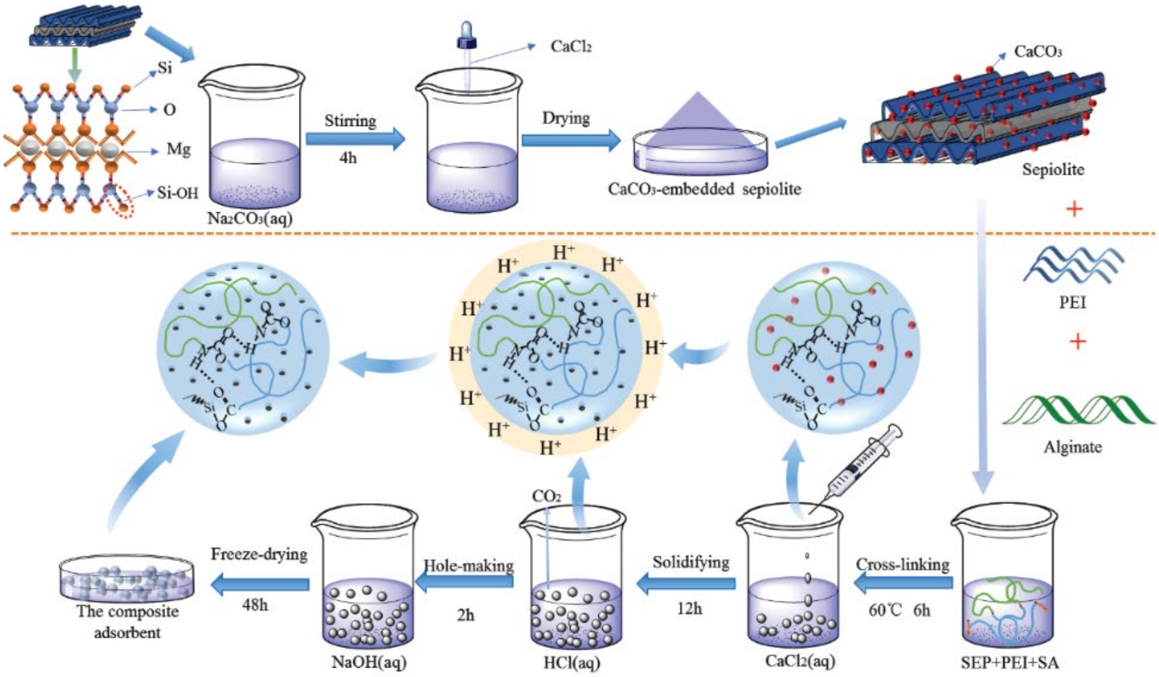


Fig. 1. Schematic illustration of preparation route for the composite adsorbent SPEIAM.

provide a cost-effective and highly efficient way to tackle heavy metal contaminated water systems. The ideas for the design of the composite adsorbent material are to construct highly efficient adsorbent, to provide the synergistic efficiency of each component, and greatly enhance the adsorption performance of the sepiolite-based composite.

3.2. Characterizations

FT-IR spectroscopy analysis is an important method to identify the characteristic functional groups of materials and the changes of functional groups after functionalization. Fig. 2 shows the FT-IR spectra of SPEIAM before (a) and after (b) copper ions adsorption. As shown in Fig. 2a, a wider absorption band in the range of 3,205–3,371 cm^{-1} appears and it has the maximum at 3,271.65 cm^{-1}, which can be attributed to the stretching vibration of hydroxyl groups (O–H), the stretching vibration of N–H, and the stretching vibration of C–H. The absorption peaks at 1,676.81 and 1,415.50 cm^{-1} belong to the stretching vibration of C=O and the characteristic absorption peaks of $-COO^-$ and C–N, respectively [13–15]. In addition, the absorption peak at 1,589.54 cm^{-1} is attributed to the stretching vibration of the N–H bond [16], which displays the successful modification of $-NH_2$ on the matrix. Fig. 2b will be discussed in the later section of the copper ions adsorption. Fig. S1 shows the XRD patterns of sepiolite (a) and SPEIAM (b). As seen in the Fig. S1a, the phase peaks of sepiolite ($Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4\cdot 8H_2O$), calcite($CaCO_3$), quartz ($SiO_2$) and dolomite ($CaMg(CO_3)_2$) are identified, which are similar to those in the related references [17,18]. However, compared with Fig. S1a, the characteristic diffraction peak of quartz at 27.5° almost disappears in Fig. S1b. In addition, the diffraction peaks attributed to calcite, dolomite and the (110) crystal plane of sepiolite all decrease, which are caused by the decomposition of the above-mentioned minerals structures in SPEIAM during the hydrochloric acid pore-making procedure.

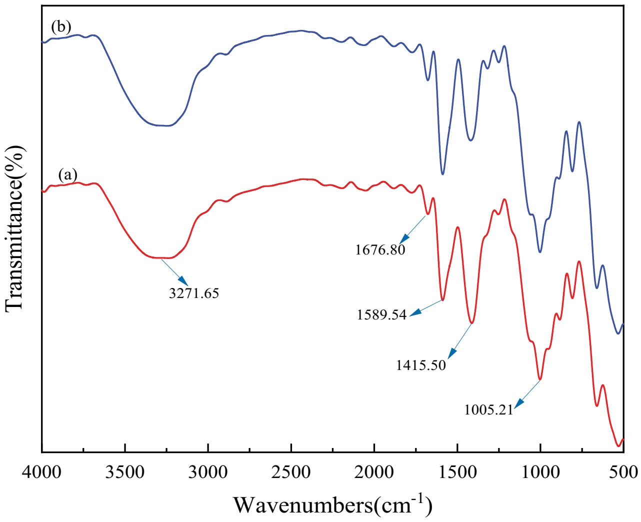


Fig. 2. FT-IR spectra of SPEIAM before (a) and after (b) copper ions adsorption.

Fig. 3 presents SEM (a–g) of SPEIAM at different resolutions (sample surface (a, d); sample cross-section (b, c, e), before (f) and after (g) pore-making), photograph (i) of SPEIAM microspheres before and after copper ions adsorption (inset), and EDS (J) of the composite adsorbent

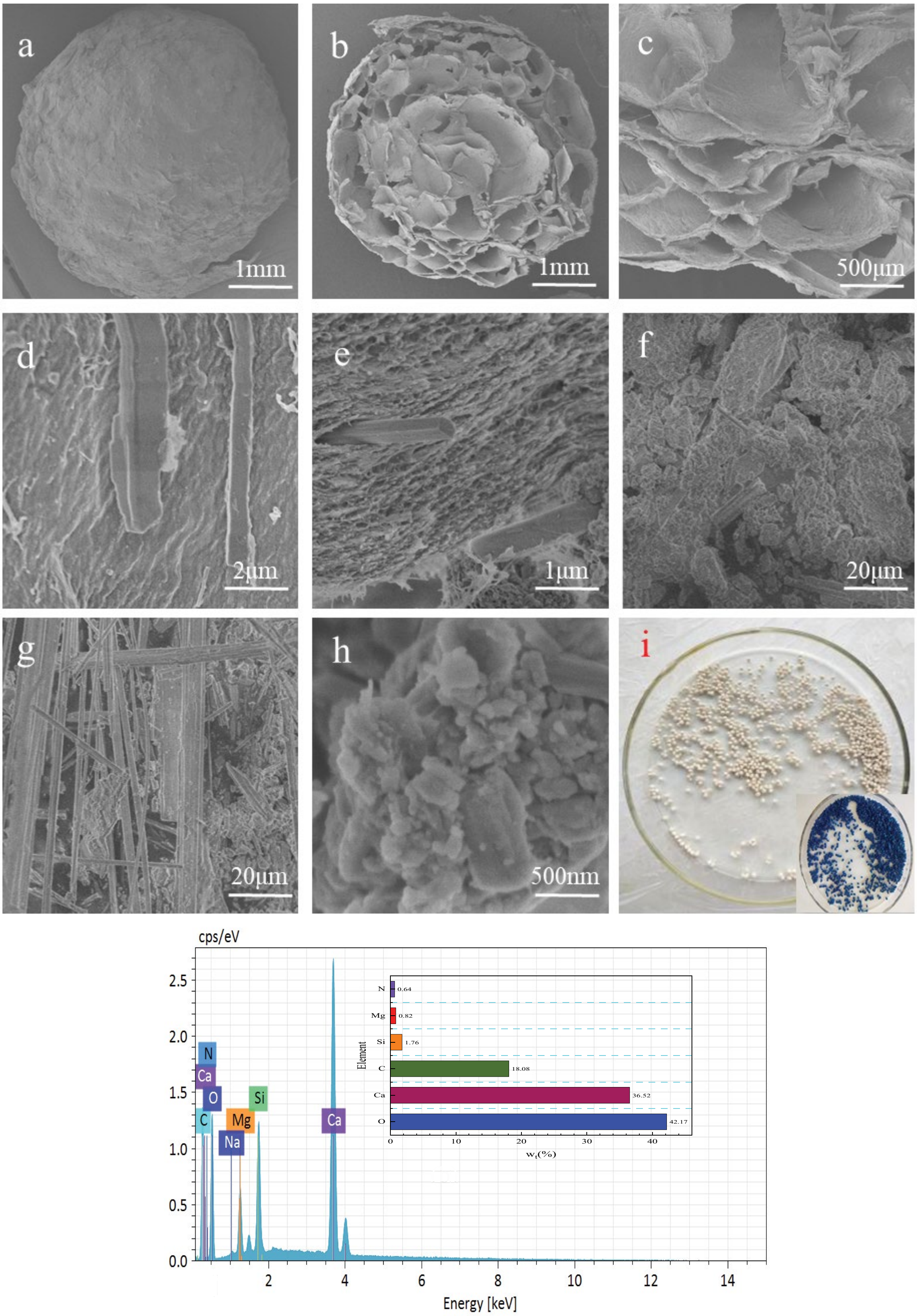
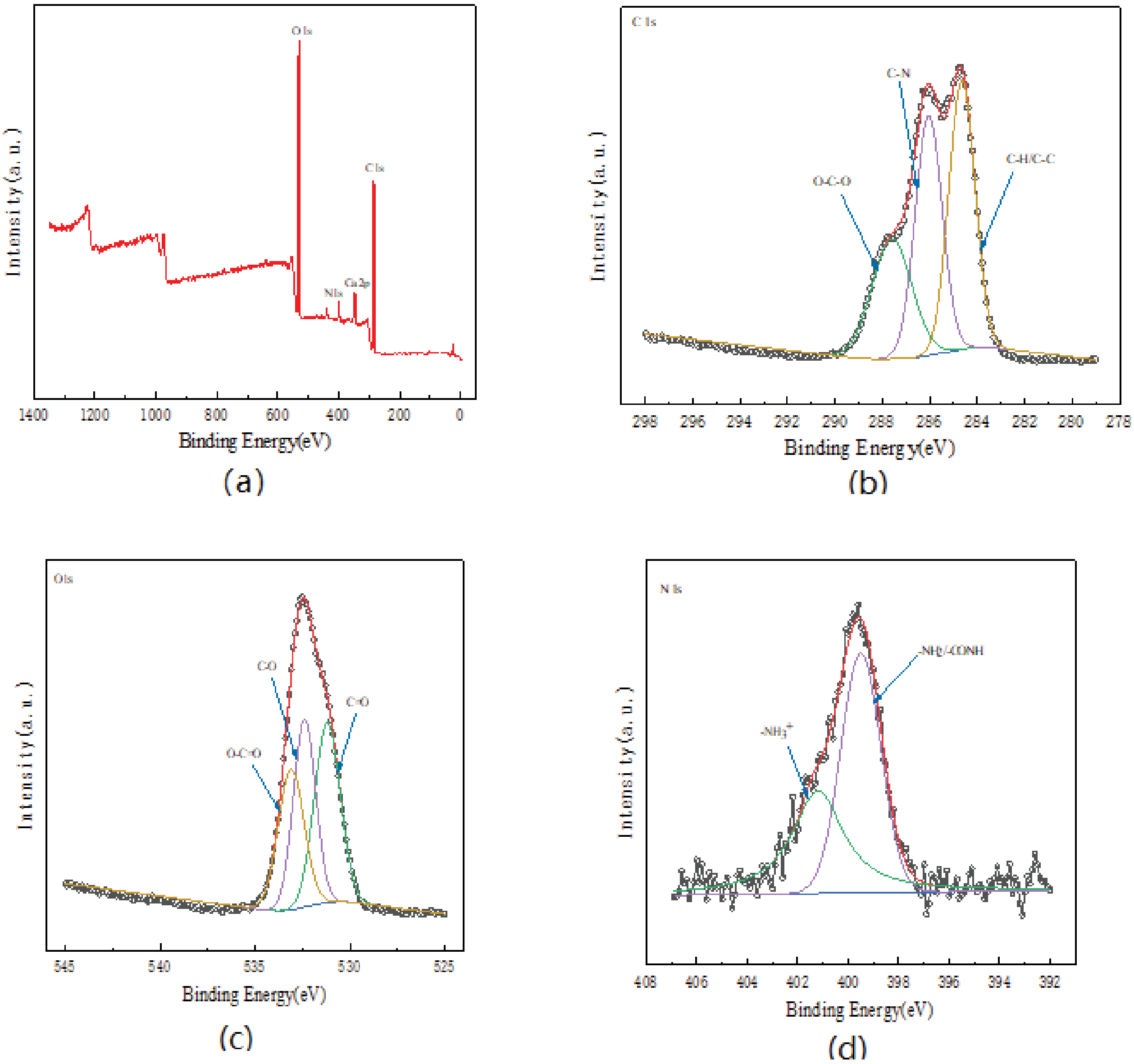


Fig. 3. SEM (a–g) of SPEIAM at different resolutions (sample surface (a, b, d); sample cross-section (c, e), before (f) and after (g) pore-making), photograph (h, i) of SPEIAM microspheres before and after copper ions adsorption (inset), and EDS (j) of the composite adsorbent SPEIAM.

SPEIAM, Fig. 3a–e and g show the surface and cross-sections of SPEIAM at different resolutions, and it is obvious that the surface and internal fibrous rod-like structure of the composite material can be seen, which means the distribution of sepiolite fillers in the composite microspheres. Moreover, compared with Fig. 3f, the composite material SPEIAM displays loose porous structure after pore-making (Fig. 3g), which can be beneficial to the heavy metal ions adsorption. Just as shown in Fig. 3, the internal and surface morphology of SPEIAM is better at relatively low resolution, while only alginate matrix can be seen at high-resolution (Fig. 3h). Overall, the SEM images has shown that in general there is a complex interleaving network structure in the gel microspheres, and its surface is relatively loose, which can provide more adsorption sites and have better synergistic adsorption effect of sepiolite and alginate/PEI. Elemental analysis of the surface of SPEIAM using EDS is displayed in Fig. 3b, which shows that the composite is mainly composed of N, O, C, Mg, Si, and Ca, and because hydrogen with a very low molecular weight make it difficult to de detected through the EDS analysis, hydrogen peaks have not appeared on the spectrum. The special structure and carboxyl, hydroxyl, amino and other functional groups in the chemical structure of SPEIAM, as revealed by the FT-IR analysis with SEM and EDS tests, indicate the potential of SPEIAM as a promising efficient adsorbent.

Fig. 4 shows the XPS spectrum of SPEIAM, and Fig. 4a is the full spectrum of the composite microspheres, there are characteristic peaks attributable to C1s, Ca2p, and O1s at the binding energies of 284.9, 347.3, and 532.6 eV,



(a)

(b)

(c)

(d)

Fig. 4. XPS spectra of SPEIAM, including their own full survey scan spectrum (a), and the high-resolution spectrum of C1s (b), O1s (c) and N1s (d).

respectively. Furthermore, it can be observed at 399.7 eV, there is a characteristic peak of N1s, which indicates that PEI has been successfully cross-linked with sepiolite and alginate by forming N-containing functional groups [19,20]. In order to further analyze the composition and the functional groups containing C, O, and N in the composite SPEIAM, the peak separation treatment has been carried out. The XPS high-resolution spectrum of C1s (Fig. 4b) displays that the peak at 284.93 eV is divided into three peaks, which can be attributed to O–C–O (287.6 eV), C–N/C–O (286 eV), and C–H/C–C (284.6 eV) [19,20]. Fig. 4c is the high-resolution spectrum of O1s, at the binding energies of 531.2, 532.4, and 533.1 eV, there are characteristic peaks that are attributable to C=O, C–O, and O–C=O respectively [20]. Fig. 4d is the high-resolution XPS spectrum of N1s, the peak at 399.7 eV contains two peaks, and they are attributed to the protonated amino $–NH_3^+$ (401.2 eV), primary amino $–NH_2$ and amide –NOCH (399.6 eV). Furthermore, Fig. S2 displays zeta potential – pH plot of the composite adsorbent SPEIAM, and as shown in the figure, the negative charge of zeta potential increases with the increase of pH value in the range of pH = 3.0–7.0. When the pH value of SPEIAM microspheres is lower than 3.6, it is not conducive to the adsorption of heavy metal cations due to electrostatic repulsion. When the pH of SPEIAM microspheres is higher than 3.6, there is electrostatic attraction with heavy metal cations like Cu(II) ions, which has a positive effect on the adsorption properties. In summary, the above-mentioned characterization results indicate that the composite SPEIAM with special structure and several functional groups might display remarkable adsorption performance for heavy metal ions.

3.3. Adsorption studies for heavy metal ions

Static saturated adsorption capacity is an important parameter reflecting the adsorption performance of adsorbent materials, and it also provides an important reference for the experimental research of selective adsorption. Fig. 5 shows the static saturated adsorption capacity results of SPEIAM for Cu(II), Pd(II), Hg(II), Cr(VI), Cr(III), Co(II), Zn(II), and Ni(II) are 127.27, 27.55, 24.61, 15.69, 7.33, 1.70, 1.69, and 1.99 mg/L, respectively, and as seen from the figure, SPEIAM has good adsorption for copper ions. The rich-COOH, –OH, $–NH_2$ and other functional groups in the composite material have good chelating ability for heavy metals, especially for Cu(II). Both porous structure and the diverse functional groups of SPEIAM can make it a potential adsorbent for copper ions. According to the results of the static saturated adsorption experiments, heavy metal copper ions have been chosen as the adsorbed object ions in the subsequent research work. In the process of the preparation of SPEIAM, different mass ratio of $CaCO_3$-embedded sepiolite and sodium alginate (2:1, 1:1, 1:1.5, 1:2) have been added in the reaction system. Moreover, PEI with different molecular weight (600, 10,000) were included, these samples have been utilized in the adsorption for copper ion, and the responding results are shown in Fig. 6. It is clear that the as-synthesized composite adsorbent with PEI (MW 600) has better adsorption effect for copper ions, and the one with the mass ration (1:1.5) of $CaCO_3$-embedded sepiolite and sodium alginate has the highest adsorption capacity. Therefore, the synthesis of SPEIAM would be conducted on the conditions of PEI (MW 600) and the mass ration (1:1.5) of $CaCO_3$-embedded sepiolite and sodium alginate. In the composite material synthesis procedure, $CaCO_3$ also has positive effect on improving the adsorption, the related experiments have been carried out, and the research results show that the addition of calcium carbonate has a positive effect on copper ions adsorption. Fig. S4 displays the influence of modification methods on adsorption capacity for Cu(II) ions, and as shown in the figure, the best adsorption capacity has been achieved by mixing PEI, alginate, and sepiolite loaded with $CaCO_3$. Moreover, the effect of PEI mass for

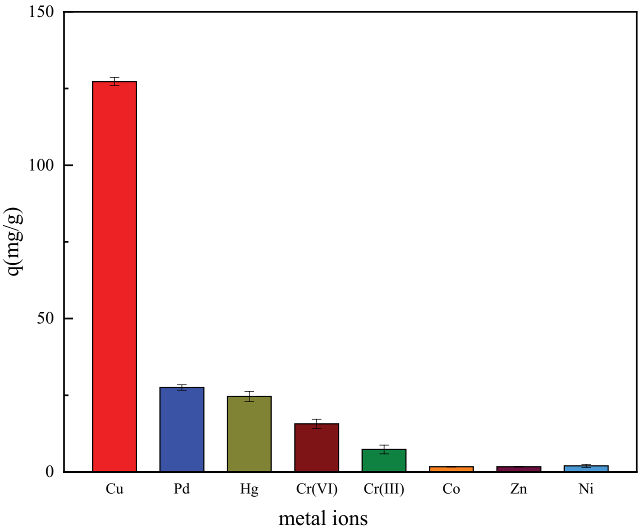


Fig. 5. The static adsorption capacities of SPEIAM for heavy metal ions.

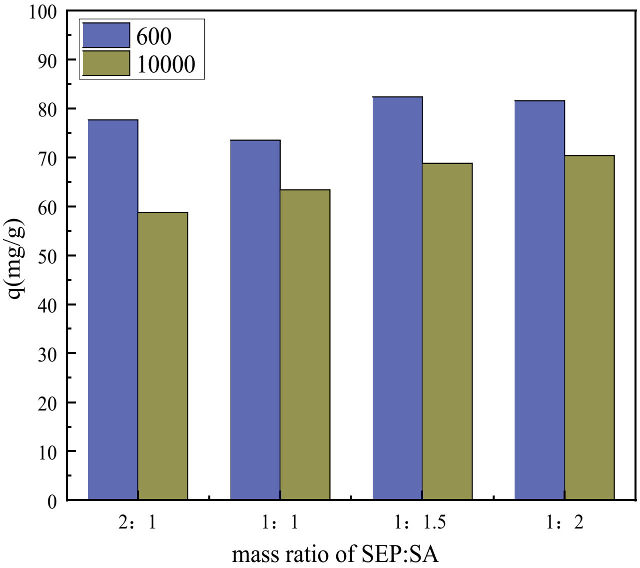


Fig. 6. The influence of the mass ratio of $CaCO_3$-embedded sepiolite and sodium alginate, and the molecular weight of PEI on the adsorption of SPEIAM for copper ions.

copper ions adsorption has been studied, and the results are shown in Fig. S3, it is obvious that the adsorption capability of SPEIAM with 0.5 g of PEI has the highest value, then, in the subsequent adsorption experiments, SPEIAM is prepared with 0.5 g of PEI including in the synthesis procedure. On the other hand, it can be clearly seen from Fig. 3i that after the adsorption of copper ions, the composite microspheres can still maintain the original microsphere shape and have good mechanical properties, which is very useful for the further its practical applications.

3.4. Effect of pH for copper ions adsorption

The pH value of the solution plays a greater role in the surface chemical properties of the adsorbent and the state of the adsorbate, so it is important to explore the optimal adsorption pH of solution for the copper ions adsorption. The adsorbent SPEIAM contains a large number of –COOH, Si–OH, $-NH_2$ groups, and shows acidity sensitivity to the pH of the water environment. For the adsorption of the target heavy metal ions Cu(II), the influence of pH value of the solution environment not only on the characteristic functional groups onto the surface of the composite SPEIAM but also on the existence form of ions must be considered. Considering that when the pH value is higher than 6, the heavy metal ions Cu(II) are easily hydrolyzed or precipitated, the adsorption performance of SPEIAM for Cu(II) has been investigated in the pH range of 2.0–6.0 at different copper concentrations (500, 200, and 50 mg/L). The corresponding adsorption experiments at 25°C in the pH range of 2.0–6.0 are conducted in order to evaluate the effect of pH on the adsorption for Cu(II) onto SPEIAM and optimize the specific pH value for the maximum adsorption efficiency, and the results are illustrated in Fig. 7. This study of pH effect can help us identify the optimum pH for effective removal. As depicted in this figure, and it is clear that as the pH value increases, the adsorption capacity increases sharply. The adsorption capacity of the composite material SPEIAM for Cu(II) reached the maximum when the pH value was 5.0, and then the adsorption capacity decreased slightly at pH = 6.0. The reason might be, under low pH conditions, the hydrogen ions concentration in the solution is high, thus, because of the competitive adsorption of H^+ and Cu^{2+} under low pH conditions, the active adsorption sites are reduced; on the other hand, there is the electrostatic repulsion between the positively charged Cu^{2+} and the protonated $-NH_2$, which could reduce the adsorption capacity of the composite adsorbent. After that, as the pH value increases, the protonation could be weakened, and the active sites of the adsorbent increase, causing the adsorption capacity to increase sharply. The more negative charges at high pH value are on the surface of SPEIAM, the stronger would be the interactions between the copper ions and the composite adsorbent surface, consequently, the higher would be the adsorption capacity of SPEIAM, and the increase of adsorption capacity for Cu(II) reaches the maximum value at the pH of 5.0. Further increase in the pH value causes the reduction of the adsorption capacity for copper ions, According to the zeta potential data (Fig. S2) and the optimal pH value 5.0 measured in the experiment, it is obvious that the pH value corresponds to the negative charge area, indicating that electrostatic interaction does exist in the adsorption process. Therefore, the subsequent copper ions adsorption experiments are conducted in the solution condition of pH = 5.0.

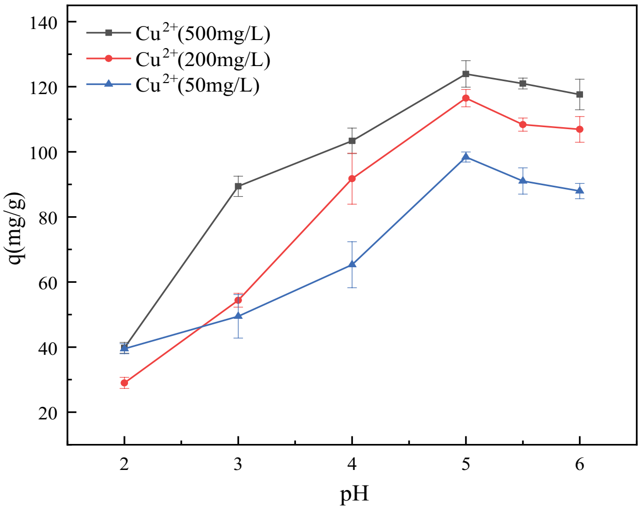


Fig. 7. The effect of pH on the adsorption for copper ions on SPEIAM.

3.5. Effect of SPEIAM adsorbent dosage for copper ions adsorption

The dosage of adsorbent is an important indicator that affects the degree of removal of heavy metal ions. The study of the optimal adsorbent dosage usually requires that the adsorbent can be effectively used while ensuring high removal efficiency. In order to determine the adsorbent dosage for optimal adsorption of copper ions onto SPEIAM which was varied from 0.5 to 3.0 g/L. Fig. 8 shows the adsorption and removal effect of dosage of SPEIAM for copper ions, that is, the variations in the adsorption capacity of SPEIAM for Cu(II) ions vs. the variations in the composite adsorbent dosage. As observed, with the increase of the removal rate, the adsorption capacity of the adsorbent for copper ions shows a downward trend, which can be attributed to the tendency of copper ions to distribute at a great surface of the adsorbent competitive adsorption resulting in a decrease of the adsorption capacity on the unit mass of the adsorbent [6]. Furthermore, increasing the adsorbent amount in a fixed volume reduces the number of available sites as the effective surface area is likely to decrease. This phenomenon has been reported in the previous literature [21,22]. When the adsorbent dosage is 3.0 g/L, the removal rate is 85% and the adsorption capacity is 56.36 mg/g. Therefore, regarding the determination of the optimal adsorbent dosage, we must not only consider comprehensively, that is, while ensuring a higher removal efficiency, the adsorbent can be effectively used. In the subsequent experiments, 3 g/L of SPEIAM can be utilized to investigate its adsorption performance.

3.6. Adsorption isotherm for copper ions adsorption

The adsorption isotherm investigation can point out how the adsorbate distributes between the solution and

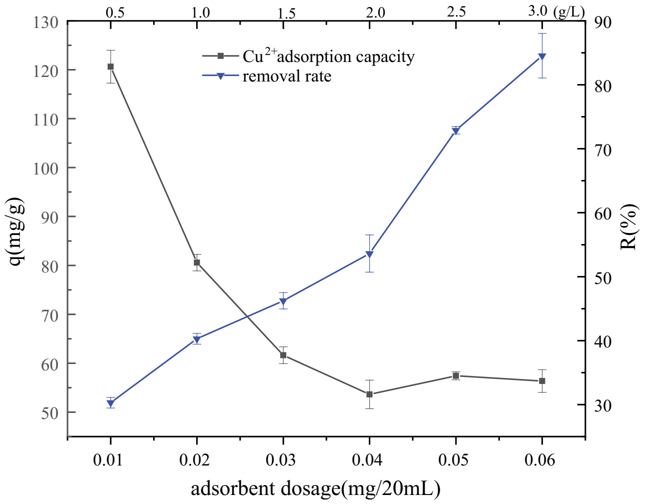


Fig. 8. Effect of adsorbent dosage on the adsorption for copper ions on SPEIAM.

the adsorbent when the adsorption process is at equilibrium state [21]. The study of adsorption isotherm is very vital and necessary to understand the interactions between adsorbate and adsorbent, and to establish an appropriate correlation of adsorption equilibria in order to optimize the adsorption system. In order to explore the relationship between equilibrium adsorption capacity and equilibrium concentration for the composite SPEIAM, the studies on the corresponding adsorption isotherm have been carried out at different temperatures. The analysis of the isotherm data by fitting the appropriate model that can be used for design the process. In the present work, it can be found in Fig. 9a that at the certain temperature, the adsorption capacities of copper ions on the adsorbent rise with the increase of the equilibrium concentration, and the removal of copper ions depends on the concentration, which is due to the fact that the initial Cu(II) concentration provides the necessary driving force to overcome the resistance to the mass transfer of copper ions between the solution and adsorbent. Then, the adsorption line of SPEIAM for copper ions becomes almost linearly smooth at higher concentration. The elevation of the initial copper ions concentration can lead to enhanced dispersion and diffusion of copper ions from the soluble phase to the adsorbents, resulting in a collision of copper ions and SPEIAM and hence increased adsorption capacities. This type of copper adsorption graph indicates a high ion exchange affinity between the adsorbate and the surface of the adsorbent, and chemical adsorption. Moreover, the absorption capacities of copper ions onto SPEIAM are all higher than those of SEP@SA and PEI@SA at 25°C. In general, all these adsorbents have reached almost their maximum adsorption capacity. As observed, the absorption capacities of copper ions onto SPEIAM increase along with the increase of temperature. The above-mentioned research results show that this novel SPEIAM is very favorable and useful for the copper adsorption, and the high adsorption capacity make it a good promising candidate material for copper removal.

The adsorption isotherms have been studied and the data are analyzed with Langmuir Eq. (3) and Freundlich Eq. (4) (Fig. 9b and c). The Langmuir isotherm model is based on the presumption that the surface monolay will adsorb homogeneous substances with a limited number of adsorption sites, and is represented by the linear equation as follows [23]:

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qK_L} \tag{3}$$

where q_e is the adsorption capacity, mg/g; C_e is the equilibrium concentration of copper ions, mg/L; q is the saturated adsorption capacity, mg/g and K_L is the Langmuir adsorption constant, L/mg.

The Freundlich isotherm model is an empirical equation that elucidates the adsorption process, which assumes that adsorbent surface changes are involved in the multilayer diffusion on the heterogeneous adsorption sites, and it can be expressed as follows [23]:

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{4}$$

where q_e is the adsorption capacity, mg/g; C_e is the equilibrium concentration of copper ions, mg/L; n is Freundlich constant and K_F is the binding energy constant reflecting the affinity of the adsorbents to metal ions, mg/g.

The equilibrium and statistical parameters of these two adsorption isotherm models for the adsorption of copper ions (Table 1) obtained using least square method show that the maximum absorption capacities of copper ions onto SPEIAM are all higher than the values of SEP@SA and PEI@SA at 25°C, and the regression coefficients R^2 obtained from the Langmuir model for SPEIAM are very close to 1(0.9891–0.9981), suggesting the Langmuir model could well interpret the studied adsorption procedure. The coefficient n in the Freundlich model is a measure of the curvature of the fitted equation known as the adsorption intensity, and the values of SPEIAM at the three different temperatures are all around 2, indicating there is strong adsorption in these conducted studies [24]. As shown in Table 1, Fig. 9b and c, the Freundlich isotherm is not consistent with the obtained experimental data as well as the Langmuir model, the experimental results of copper ions adsorption obtained at all temperatures have been found to fit well the Langmuir isotherm model. From the comparison of correlation coefficients, it can be concluded that the data are fitted better by the Langmuir equation than by the Freundlich equation, indicating the adsorption of SPEIAM for copper ion obeys the Langmuir adsorption isotherm, and the maximum adsorption capacities of SPEIAM at 35°C is 490.20 mg/g, which is higher than the corresponding experimental values obtained. As a justification for this difference, the theoretical model assumes that the entire surface of the adsorbent material is composed by existing adsorption sites to form a single layer [24]. It is well known that the Langmuir isotherm suggests that the adsorption occurs in the monolayer way on the homogenous active sites, where the adsorption of each

Table 1
Isotherm parameters of the Langmuir model and the Freundlich model for the adsorption of copper ions on SPEIAM, PEI@SA, and SEP@SA obtained by using the linear method

		Langmuir			Freundlich		
T (°C)	Adsorbents	q_m (mg/g)	K_L (L/mg)	R_L^2	K_F (mg/g)	n	R_F^2
15	SPEIAM	396.83	0.00297	0.9891	11.4223	2.1151	0.9787
25	SPEIAM	431.03	0.00328	0.9974	12.1724	2.0739	0.9554
35	SPEIAM	490.20	0.00301	0.9981	11.2348	1.9598	0.9512
25	PEI@SA	293.26	0.00205	0.9683	5.2135	1.9108	0.9929
25	SEP@SA	325.73	0.00248	0.9768	7.3669	2.0028	0.9811

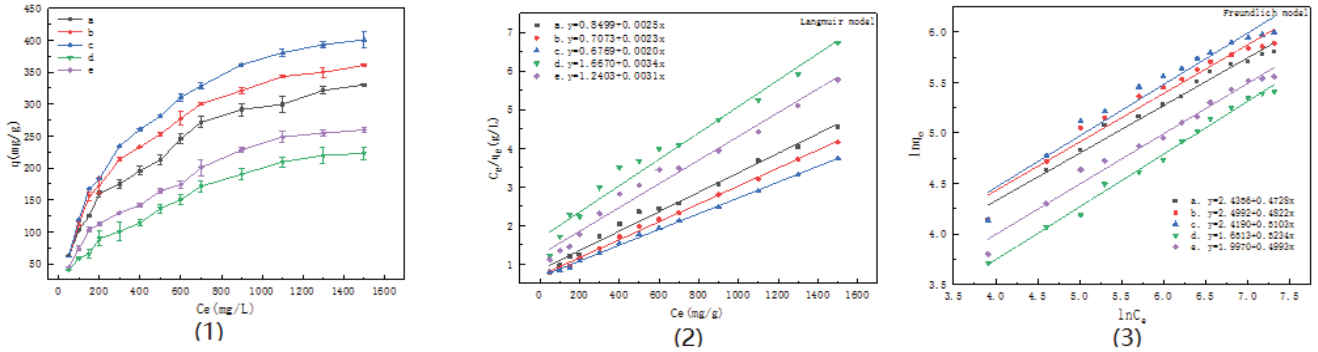


Fig. 9. Isotherm for the adsorption of copper ions on SPEIAM at different solution temperatures (1); Langmuir isotherm obtained by using the linear method for the adsorption of copper on SPEIAM at different solution temperatures (2); Freundlich isotherm obtained by using the linear method for the adsorption of copper ions on SPEIAM at different solution temperatures (3) (a) SPEIAM at 15°C, (b) SPEIAM at 25°C, (c) SPEIAM at 35°C, (d) SEP@SA at 25°C, and (e) PEI@SA at 25°C.

adsorbate molecule onto the surface had equal adsorption activation energy. The fact shows that the adsorption of this hybrid adsorbent is attributed to monolayer adsorption, it also recommends that the process is endothermic in nature because the value of q increases with the rise in temperature from 15°C to 35°C. Therefore, in the equilibrium state, the distribution of copper ions between the aqueous solution and SPEIAM is a crucial factor that determine the maximum adsorption capacity of SPEIAM, and the copper ions adsorption of SPEIAM is attributed to monolayer adsorption. Fig. 2b presented the FT-IR spectrum of SPEIAM after copper ions adsorption, it is shown that after SPEIAM adsorbed Cu(II) ions, the positions of the peaks of oxygen and nitrogen-containing functional groups have slightly moved or changed, which indicated that these functional groups have participated in the adsorption of Cu(II) ions. For example, the peak at 1,589.54 cm^{-1} has a significant increase after Cu(II) ion adsorption, which may be involved in complex chemical reactions such as reduction and complexation of Cu(II) ions by the amino functional group; The peak at 1,415.50 cm^{-1} has been weakened after Cu(II) ion adsorption, which may be the result of the interaction between the functional groups and copper ions and be involved in copper ions adsorption [14,16]. Moreover, a comparison between the adsorption capacities for copper ions removal of the composite SPEIAM and other adsorbents is presented in Table 2. As seen from the table, it is obvious that the maximum adsorption capacity of SPEIAM is much higher than those of the adsorbents reported in the literatures [6,20,25–37], and SPEIAM could be an excellent adsorbent for a potential enhancement of copper ions control in water considering the maximum adsorption capacity compared to several other copper ions adsorbent materials in the literatures (Table 2), and the excellent adsorption capacity has made it a good promising candidate material for the copper removal.

3.7. Adsorption kinetics for copper ions adsorption

The adsorption kinetics studies are very crucial in the adsorption process because it affects the design of the copper ions removal treatment plant, and the rapid kinetics will facilitate smaller reactor volumes ensuring efficiency and economy. Fig. 10a depicts the evolution of the copper adsorption capacity with the contact time, which could determine the adsorption equilibrium time. The adsorption studies have been carried out by varying the contact time from 0 to 800 min at three different temperatures (15°C, 25°C, and 35°C). It came out that the adsorption capacities of SPEIAM for copper ions increased rapidly in the first 100 min, and then followed a gradual rise with time until it reaches equilibrium, and the adsorption process needs at least 13 h to reach the adsorption equilibrium. The kinetic curves are all smooth and continuous, leading to saturation, suggesting the possibility of the formation of monolayer coverage of metal ions on the surface of the composite adsorbent [38].

Table 2
Comparison of the maximum adsorption capacity of different adsorbents for copper ions

Adsorbents	Maximum adsorption capacity (mg/g)	References
	Cu(II)	
Glycyrrhiza glabra root	181.6	[6]
PCCM aerogel	81.3	[25]
GO-NH_2	26.25	[26]
ZFN-Alg beads	106.6	[27]
SA-LDH	60.01	[28]
PEI-RCSA	177.1	[29]
PC-ED/1.5	123.45	[30]
g-C_3N_4/SA	168.2	[31]
Magnetic SA/CMC hydrogel	89.49	[32]
NSC	169.94	[33]
SW biochars	223	[34]
Magnesium silicate-modified PAL	210.64	[35]
PLLA nanofibrous membrane	111.66	[36]
Hematite (α-Fe_2O_3) iron oxide coated sand	3.93	[37]
SPEIAM	490.20	This work

This may be because of the fact that in the first adsorption step, more free adsorption sites are readily available for copper ions to occupy, there is a remarkable concentration gradient between the copper ions in the solution and those at the surface of SPEIAM, and thus the adsorption process at this stage proceeds at high rate. Consequently, the number of sites become less, and copper ions have to compete among themselves for getting adsorbed, the repulsive forces between the copper ions adsorbed and the free ones in the solution increases and might be hampered to diffusion into the deeper pores, and then the adsorption process reaches the adsorption equilibrium. Moreover, it is obvious that with the rise of temperature, the equilibrium adsorption capacity for copper ions increases significantly, and the rise of the temperature has provided a greater driving force for the mass transfer and subsequent surface adsorption. These adsorption kinetic studies could provide the necessary information for modeling and designing of the adsorption process. Both the pseudo-first-order equation and the pseudo-second-order equation have been utilized to illustrate the adsorption kinetics mechanisms of the adsorbent surface at different temperatures and to express the adsorption process of SPEIAM for copper ions, and they can be expressed by the Eqs. (5) and (6) [39,40], respectively:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where q_e is the amount of metal adsorbed at equilibrium per unit weight of adsorbent, mg/g, q_t is the amount of metal ion adsorbed at t time, k_1 (min^{-1}) and k_2 (g/mg min) are the rate constants of pseudo-first-order and pseudo-second-order adsorption. The experimental data have been applied to these two kinetics models, and the kinetics model parameter results including the experimental and calculated q_e values, k_1, k_2 and regression coefficient (R^2) values are presented in Table 3. The pseudo-first-order kinetic and pseudo-second-order kinetic plots for the adsorption of copper ions onto SPEIAM at different temperatures are shown in Fig. 10b and c, respectively. As seen from Table 3, all of the correlated coefficients R^2 are close to one, However, the obtained coefficients values of the pseudo-second-order model (>0.9952) are better than those of the pseudo-first-order model for the adsorbent (0.9761–0.9887). The pseudo-second-order model results indicate better conformity than the pseudo-first-order model, and it is more suitable to describe the adsorption kinetics of SPEIAM for copper ions. In the selected two models to be fitted, the pseudo-first-order model is based on the assumption that diffusion and mass transfer of the adsorbate to the adsorption site controls the adsorption behavior, but in the pseudo-second-order model, chemisorption is the rate limiting step, hence, the above-mentioned fitting results suggest that the related adsorption mechanism is predominantly by chemisorption involving electrostatic action of positive and negative charges and coordination action rather than diffusion and mass transfer [41]. Furthermore, the difference between the experimental and calculated value of q_e suggested the suitability of the pseudo-second-order kinetic model. Therefore, the adsorption kinetics could well be approximated more favorably by pseudo-second-order kinetic model for copper ions onto SPEIAM.

3.8. Adsorption selectivity for copper ions adsorption

In order to study the adsorption selectivity of SPEIAM for Cu(II), in the present work, the adsorption selectivity of SPEIAM to the target ion Cu(II) has been evaluated by the competitive adsorption with lead ions/gold ions/silver

Table 3
Kinetic parameters of the adsorption for copper ions on SPEIAM at various temperatures

T (°C)	($q_{e(\text{exp})}$)	Pseudo-first-order			Pseudo-second-order		
		$k_1 \times 10^{-3}$	$q_{e(\text{cal})}$	R_1^2	$k_2 \times 10^{-4}$	$q_{e(\text{cal})}$	R_2^2
	(mg/g)	(min^{-1})	(mg/g)		(g/mg min)	(mg/g)	
15	157.94	3.88	80.42	0.9761	1.915	157.48	0.9961
25	173.08	4.17	91.30	0.9810	1.639	174.52	0.9952
35	181.34	4.62	97.53	0.9887	1.627	183.49	0.9968

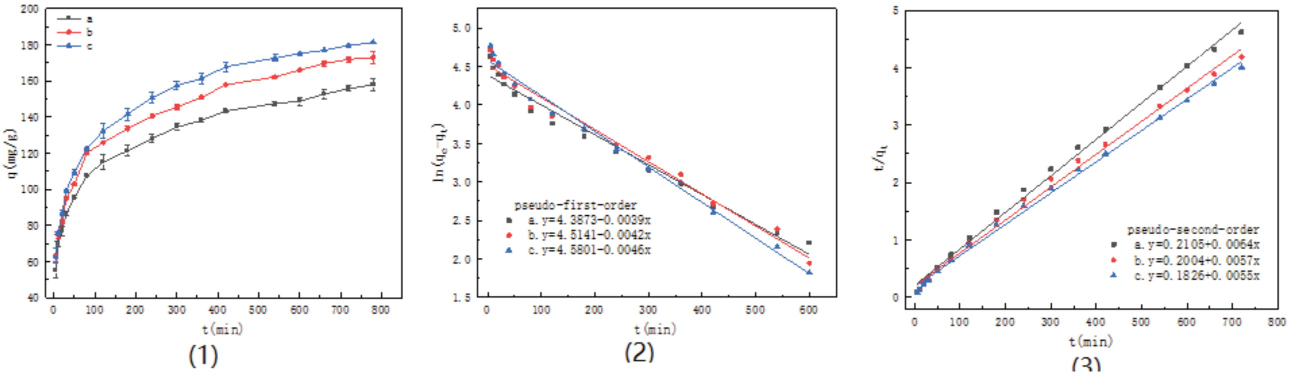


Fig. 10. The kinetic adsorption of copper ions onto SPEIAM at different solution temperatures (1); pseudo-first-order kinetic model of SPEIAM for copper ions at various temperatures (2); pseudo-second-order kinetic plots for the adsorption of copper ions on SPEIAM at various temperatures (3) (a) SPEIAM at 15°C, (b) SPEIAM at 25°C, and (c) SPEIAM at 35°C.

ions/palladium ions/platinum ions/chromium ions as the co-ions. 20.0 mg of the prepared SPEIAM has been added into 20 mL of solutions (binary systems which containing equal initial concentrations) and the mixture has been shaken for 12 h. Then the solutions are separated from the adsorbents and the concentrations of metal ions have been detected by atomic absorption spectrometer. The adsorption selectivity experiments by SPEIAM have been carried out in several binary ions systems, and the obtained results for Cu(II) adsorption at 25°C are presented in Table 4. The selective coefficient α is the result of the adsorption capacity of Cu(II) divided by the one of the other metal ion in the binary ion systems. The experimental results display that the prepared SPEIAM shows high selectivity towards Cu(II) in the binary ion systems, and the selectivity coefficients are all greater than 1, indicating that the composite material with higher adsorption efficiency for Cu(II) over these other coexisting metal ions has preferential affinity for copper ions apparently and it is very favorable for the removal of copper ions. In the complex water systems, even if it adsorbs other heavy metal ions, SPEIAM can still keep the high adsorption capacities for the target copper ions and maintain its excellent removal performance for copper ions from binary ion systems. Moreover, to investigate the feasibility of reusing the composite adsorbent SPEIAM, desorption experiments have been conducted. The copper ions loaded SPEIAM samples were treated with hydrochloric acid and hydrochloric acid-thiourea, sulfuric acid and sulfuric acid-thiourea, nitric acid and nitric acid- thiourea at 25°C for 24 h to remove copper ions and then followed with a second round of copper ions adsorption testing. The results of elution from Fig. S5 (the effect of different eluents on the desorption efficiency for copper ions) show that the system of hydrochloric acid-thiourea is very efficient. Therefore, hydrochloric acid-thiourea was selected for the subsequent adsorption–desorption cycle experiments, and the research results show that a little decrease of the adsorption efficiency was seen in the second use, and the samples retain their copper ions uptake

Table 4
Adsorption selectivity of SPEIAM for copper ions at 25°C

Systems	Metal ions	Adsorption capacity (mmol/g)	Selective coefficient
Cu(II)-Pb(II)	Cu(II)	1.6340	1.59
	Pb(II)	1.0309	
Cu(II)-Au(III)	Cu(II)	1.8569	2.24
	Au(III)	0.8296	
Cu(II)-Ag(I)	Cu(II)	1.5871	3.30
	Ag(I)	0.4809	
Cu(II)-Pd(IV)	Cu(II)	2.1032	5.81
	Pd(IV)	0.3620	
Cu(II)-Pt(IV)	Cu(II)	2.1239	4.56
	Pt(IV)	0.4654	
Cu(II)-Cr(VI)	Cu(II)	2.1539	17.27
	Cr(VI)	0.1247	

capacities of more than ninety percent after three cycles, the copper ions uptake capacities decreased gradually in the successive uses. Therefore, the high adsorption capacity and good reproducibility make the composite adsorbent SPEIAM a significant potential for removing copper ions from aqueous solutions using adsorption method. In conclusion, the above-mentioned research results show that the high adsorption capacity and selectivity of SPEIAM make it good promising candidate materials for copper ions removal, and it can be utilized in the extraction, separation and recovery of copper ions from multi-ionic complex aqueous systems.

4. Conclusion

Heavy metal ions are of special environmental concern because they are non-degradable and therefore persistent. Nowadays, the removal of heavy metal containments from industrial waste water is one of the most important environmental issues to be solved. In the present paper, the novel adsorbent sepiolite-based polyethyleneimine alginate microspheres SPEIAM has been successfully synthesized. This composite, with special porous structure and several kinds of functional groups that are potential centers for copper ions removal, is a promising material to be applied for this operation with excellent adsorption capacity for copper ions. The feasibility of using SPEIAM for adsorption of copper ions from simulated industrial wastewater has been studied in detail. The adsorption performance of SPEIAM has been evaluated using batch experiments which include adsorption kinetics, isotherm, adsorption selectivity and so on. The results indicate that the adsorption kinetics of SPEIAM for copper ions at different temperatures can be modeled closely by a pseudo-second-order rate equation; the experimental data fit well with the Langmuir isotherm model which indicates the monolayered way of the adsorption and the maximum adsorption capacities of SPEIAM for copper ions could reach 490.20 mg/g at 35°C. The characteristic of this composite shows its ability to adsorb and separate heavy metal elements. This ability can be explored for applications in cleaning technologies. All these research work results present that SPEIAM has filled a void in field of efficient adsorption for copper, and the excellent features of SPEIAM with high efficiency for water purification and copper ions removal can ensure their applicability and feasibility in the industrial scale.

Acknowledgments

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Supplementary information

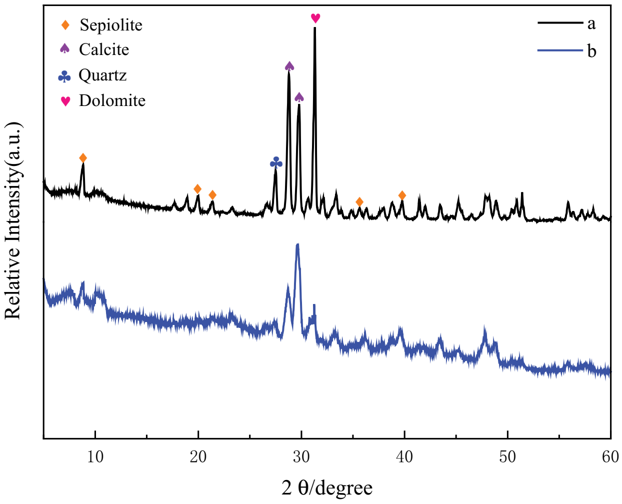

Fig. S1. XRD patterns of sepiolite (a) and SPEIAM (b).

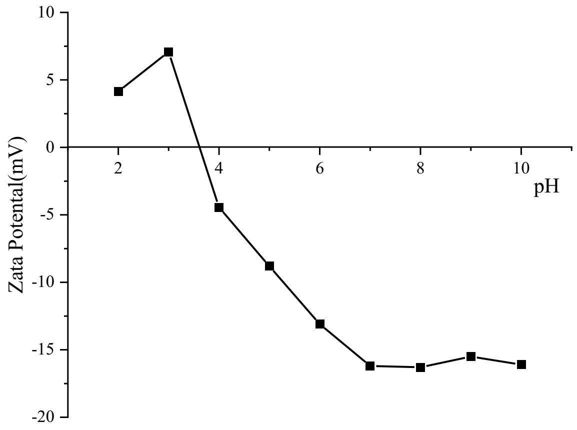

Fig. S2. Zeta potential – pH plot of the composite adsorbent SPEIAM.

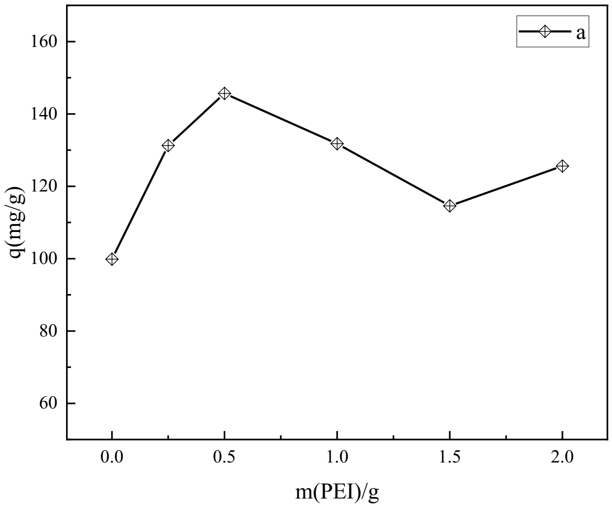

Fig. S3. Effect of PEI mass in SPEIAM on the adsorption for copper ions.

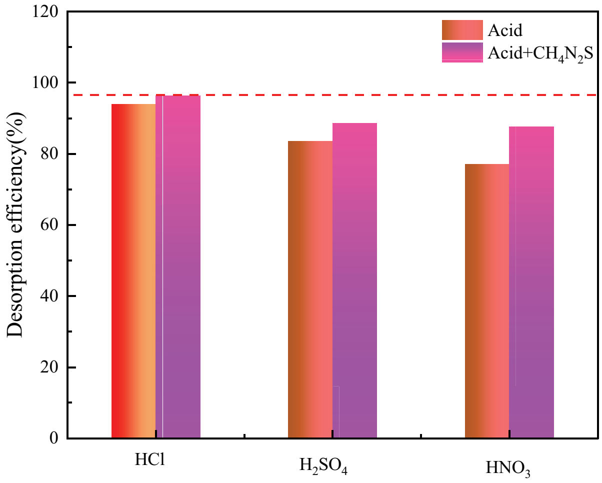

Fig. S5. Effect of different eluents on the desorption efficiency for copper ions.

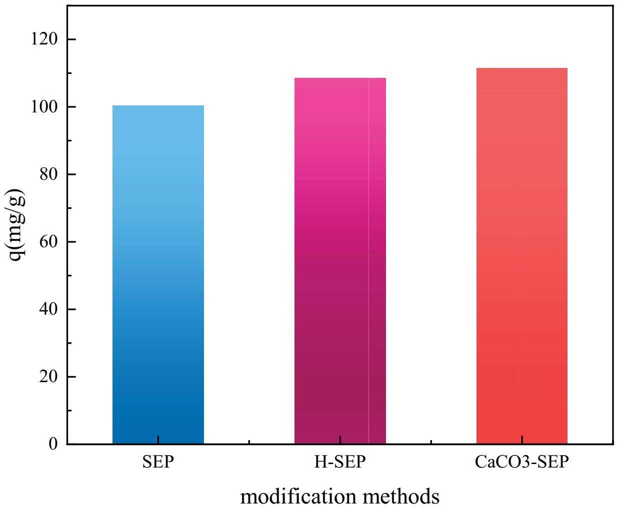

Fig. S4. The influence of modification methods on adsorption capacity for Cu(II) ions.