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Enhanced selective sorption of Cu(II) from washing solution of fly ash using polyethyleneimine-crosslinked chitosan sorbents

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ABSTRACT

Recycling valuable metals from waste resources, such as fly ash, has attracted global attention. However, achieving highly selective recovery remains challenging because of competing ions in wastewater. To selectively recover Cu, we synthesized polyethyleneimine (PEI)-decorated chitosan (CTS) beads, which were cross-linked with tripolyphosphate (TPP) and glutaraldehyde (GA), forming PEI@CTS. The optimal synthesis parameters for the sorbents (2 % TPP (w/v), V_{PEI} :m_{CTS} = 1.25:1, denoted as PEI_{1.25}@CTS) were determined based on sorption capacity and bead morphology. The sorption process was driven by the amino groups from PEI/CTS and the phosphate groups from TPP, with high Cu(II) selectivity primarily attributed to stable Cu-PEI complexes and steric hindrance from the sorbed Cu. In simulated quaternary metal solutions, PEI1.25@CTS selectively sorbed Cu (II) over Pb(II), Zn(II), and Cd(II) at initial concentrations of 0.4–2.0 mmol/L, achieving Cu(II) distribution coefficients as high as 10⁵ mL/g. Furthermore, PEI_{1,25}@CTS was used for Cu recovery from fly ash washing solutions over three sorption cycles without desorption and retained a Cu removal efficiency of over 85 %. Copper sorption not only occurred at unoccupied binding sites but also progressively displaced previously sorbed competing ions due to its stronger complexation. Following complete digestion of reused PEI_{1.25}@CTS, the recovered Cu purity reached 39.1 wt%, a substantial increase from 7.7 wt% in the initial washing solution of fly ash. The high Cu selectivity and durability in real wastewater highlight PEI1.25@CTS as a promising material for Cu recovery, offering a sustainable approach to pollution control and resource recycling.

1. Introduction

Fly ash, a by-product of municipal solid waste incineration (MSWI), is classified as hazardous waste in several countries because of its elevated levels of multiple heavy metals (HMs) and chlorides [1,2]. Washing, a widely adopted pre-treatment, can effectively transfer HMs from the solid fly ash into an aqueous solution [3]. For example, Tao et al. [4] reported that at pH levels ranging from 1 to 7, the concentrations of Cu(II), Pb(II), and Zn(II) in fly ash leachates ranged from 22 to 56 mg/L, 53 to 66 mg/L, and 52 to 184 mg/L, respectively. Despite variations in concentrations, the leached HM concentrations far exceed

the wastewater discharge standard in China (Cu(II): 0.5 mg/L, Pb(II): 1.0 mg/L, and Zn(II): 2.0 mg/L) [5] or Directive 2010/75/EU from the European Union (Cu(II): 0.5 mg/L, Pb(II): 0.2 mg/L, and Zn(II): 1.5 mg/L) [6]. From the perspective of pollution control and circular economy, the washing solution can be employed initially as a feedstock for recovering valuable HMs, followed by the removal of toxic metals to meet discharge standards [7]. Compared to methods such as chemical precipitation and solvent extraction [8], the synthesis of a novel sorbent capable of highly selective recovery of valuable metals, including Cu(II) [9], from low- to high-grade feedstocks is of practical significance.

Polyethyleneimine (PEI), an amino-rich macromolecule, could form

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more stable complexes with Cu(II) over a broad pH range (4–12) compared to other HMs such as Zn(II) and Cd(II), explaining its high selectivity for Cu(II) [10–12]. Liu et al. [13] synthesized a hydrogel composed of PEI and soy protein (SPI) (designated as SPI/PEI) and found that increasing the PEI content from 0 to 50 % enhanced the Cu(II) sorption from 33.5 to 136.2 mg/g. In particular, the SPI/PEI composite hydrogel with a 50 % PEI content selectively adsorbed Cu(II) over Zn(II), Cd(II), and Pb(II), exhibiting a maximum selectivity coefficient for Cu (II)/Zn(II) of approximately 250. Similarly, chitosan (CTS), with its nitrogen- and/or oxygen-donor ligands, forms stable complexes with Cu (II) [14]. In the hydrogel bead form, CTS-based sorbents enable the diffusion of HMs to internal sorption sites and simplify solid–liquid separation after sorption [15].

Despite the frequently reported enhancement in the adsorption capacity of PEI-modified CTS adsorbents [16-19], the role of tripolyphosphate (TPP) in PEI-modified CTS adsorbents remains unclear. Song et al. (2017) [20] synthesized PEI-loaded CTS hollow beads (CHBs) using TPP as an ionic cross-linking agent [21]. While the authors attributed the high adsorption capacity for Pt(IV) ($815.2 \pm 72.6 \text{ mg/g}$) solely to the abundance of amine groups, other studies have recognized the contribution of TPP to metal adsorption capacity. Xia et al. (2022) [22] prepared CTS cross-linked with potassium tripolyphosphate (CTPP), achieving a maximum adsorption capacity of UO_2^{2+} (780.8 mg/ g), significantly higher than that of pure CTS (374.93 mg/g). Characterization results confirmed that tripolyphosphate groups from TPP significantly enhanced adsorption. Although literature on adsorption selectivity of TPP-crosslinked CTS adsorbents is limited, studies have reported Cu(II) selectivity in binary systems, such as Cu(II)-Ni(II) [23] and Cu(II)-Pb(II) [24], except in Ag(I)-Cu(II) systems, where Ag(I) was preferentially adsorbed [25]. Based on these findings, we hypothesize that incorporating a two-step cross-linking process using TPP and glutaraldehyde (GA) will reinforce the structural stability of PEImodified CTS, enhancing its durability in Cu recovery while contributing to Cu(II) adsorption capacity.

Besides sorbent synthesis, competitive sorption performance is critical for selectively recovering low-concentration target ions from multicomponent wastewater. For example, in fly ash leachate, where competing ions are much higher than those of target rare earth elements (REEs), adsorbents demonstrate strong REE selectivity with distribution coefficients (Kd) reaching $\sim 10^5 \text{--} 10^6 \text{ mL/g}$ [26]. However, competing ions occupy the remaining adsorption sites with a K_d of 10^3 – 10^4 mL/g, resulting in an REE purity of 9.9 % on saturated adsorbents [26]. Moreover, in fly ash, the most abundant heavy metals (HMs) are Pb(II), Zn(II), and Cu(II) [27,28], with Pb(II) possessing several physicochemical properties favorable for adsorption compared to coexisting ions (e. g., smaller hydrated radius and higher covalent index) [29]. Thus, further investigations are required to evaluate the performance of the synthesized sorbents in recovering Cu(II) from complex systems containing these typical coexisting metals at varying concentrations and to develop strategies for enhancing Cu(II) recovery while minimizing the sorption of competing ions.

In this study, we synthesized the PEI-decorated CTS, cross-linked with GA and TPP (designated as PEI@CTS). The resulting PEI@CTS sorbents were used to selectively sorb Cu(II) from a washing solution of fly ash. The objectives of this study were to (1) optimize the main synthesis parameters of PEI@CTS sorbents, (2) evaluate the sorption performance of PEI@CTS in single and quaternary metal systems, (3) explore the competitive sorption mechanism of PEI@CTS, and (4) apply PEI@CTS for the selective recovery of Cu(II) from the washing solution of fly ash. These findings contribute to a deeper understanding of competitive sorption in multicomponent systems and provide a foundation for novel strategies to recover Cu from feedstocks with varying Cu contents.

2. Materials and methods

2.1. Synthesis of PEI@CTS beads

The chemical reagents used in this study are summarized in **Text S1**, while the PEI@CTS composite sorbent synthesis is illustrated in Fig. 1. First, 1 g of CTS powder was added to 50 mL of 2 % (ν/ν) acetic acid in a beaker and stirred vigorously at room temperature to form a homogeneous hydrosol. Then, PEI was dispersed in the CTS hydrosol with intense agitation (1000 rpm) for 2 h at room temperature. The PEI-CTS hydrosol was then gradually dropped into 300 mL of TPP solution for preliminary cross-linking under continuous stirring. An aqueous TPP solution with a pH range of 8.5–8.7 was employed to facilitate interaction [20]. The resulting composite beads were left in the solution overnight. The wet beads were then transferred to a 0.6 % (ν/ν) GA solution for secondary cross-linking at a ratio of 1 g of beads to 1.5 mL of GA solution and reacted for 1 h at room temperature. After filtration, the PEI@CTS beads were washed with deionized water until a neutral pH was reached and subsequently freeze-dried for 24 h.

2.2. Batch experiments

2.2.1. Optimization of the composite sorbent

Unless otherwise specified, all sorption conditions were: initial concentrations of 100 mg/L, a sorbent dosage of 1 g/L, a contact time of 48 h, a shaking rate of 200 rpm, and a temperature of 298 K. Each test was conducted in triplicate. After sorption, the sorbents were collected for further characterization to reveal the sorption mechanisms (see **Text S2**). The residual concentrations of heavy metals (HMs) were measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, ICAP7200, Thermo Fisher Scientific, USA).

To optimize the preparation conditions of the composite sorbent, we investigated the effects of TPP and PEI on sorption performance through two groups of controlled experiments. In the first group, we varied the PEI volume (V_{PEI} : $m_{CTS} = 1:1, 1.25:1$, and 1.5:1), while maintaining a constant TPP concentration of 2 % (w/v). In the second group, we varied the TPP concentration (2 %, 3 %, and 4 % w/v) with a fixed V_{PEI} : m_{CTS} ratio of 1:1. Additionally, we conducted two comparative experiments to evaluate different combinations of PEI, CTS, and TPP. In the first comparative experiment, we added CTS hydrosol mixed with PEI (V_{PEI} : $m_{CTS} = 1.25:1$) to a 2 % NaOH solution (w/v). In the second experiment, we added pure CTS hydrosol to a 2 % TPP solution (w/v). The abovementioned sorbents were then tested for Cu(II) sorption.

The sorption capacity q_e (mg/g) was expressed as Eq. (1):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

Where C_0 and C_e represent the initial and equilibrium concentrations of heavy metal (mg/L), *V* represents the solution volume (mL), and *m* represents the mass of the sorbent (mg).

2.2.2. The effects of initial solution pH and sorbent dosage

The study investigated the impact of the initial solution pH on sorption, ranging from 2.0 to 6.0. Within this pH range, Cu(II), Pb(II), Zn (II), and Cd(II) are mainly present as free ions [30]. The relationships between metal ion speciation and pH are depicted in Fig. S1. The pH was adjusted using 0.1 mol/L NaOH and 0.1 mol/L HNO₃ solution. The effect of sorbent dosage on sorption was evaluated using sorbent dosages of 1.0–5.0 g/L.

2.2.3. The sorption kinetic, thermodynamic, and isotherm experiments

After identifying the optimal pH and sorbent dosage, we applied kinetic, isotherm, and thermodynamic models to single-metal systems, equimolar (EM)-quaternary metal systems, and equal concentration (EC)-quaternary metal systems, respectively (**Text S3**). The fitting



Fig. 1. Schematic diagram illustrating the synthesis of PEI@CTS.

results for single-metal systems are discussed in Text S4.

2.2.4. Sorption selectivity of composite sorbent

To better correlate the data obtained from single-metal systems with the quaternary ones and reveal the interaction between heavy metals in the quaternary metal systems, the heavy metal interaction factor (*P*) was employed (*Eq.* (2)) [31].

$$P = \frac{Q_{\text{max, multiple}}}{Q_{\text{max, single}}}$$
(2)

Where $Q_{max, single}$ and $Q_{max, multiple}$ is the sorption capacity of the target heavy metal in single and quaternary metal systems when sorption equilibrium is reached, mg/g; *P* is the heavy metal interaction factor (*P* > 1, synergistic effect; *P* = 1, no effect; *P* < 1, antagonistic effect).

The distribution coefficient (K_d , L/mg) and selectivity coefficient (α , dimensionless) were employed to gauge the affinity of a sorbent towards a specific ion and assess the selectivity of the sorbent in the presence of competing ions [32]. The equations were stated as *Eqs. (3) and (4*):

$$K_{d} = \frac{(C_{0} - C_{e})}{C_{e}} \times \frac{V}{m}$$
(3)

$$\alpha = \frac{K_{\rm d} (\rm T)}{K_{\rm d}(\rm I)} \tag{4}$$

Where *V* is the volume of the solution (mL), *m* is the weight of the sorbent (mg), K_d (T) is the K_d value of Cu(II), and K_d (I) is the K_d value of the other three metals in quaternary metal systems. A higher value of α indicates a stronger preference for Cu(II) over the other metals.

2.3. Application of sorbents in washing solution of fly ash

Fly ash was collected from a municipal solid waste incineration (MSWI) plant in Taizhou, Jiangsu province, China. A 25-g dried fly ash sample was mixed with 500 mL ultrapure water and approximately 26 mL hydrochloric acid. The mixture was stirred at room temperature for 3 h under magnetic stirring. The pH was then adjusted to 4–5, followed

by vacuum filtration to separate the washing solution. The main compositions of washing solution are summarized in Table S1.

In the sorbent application study, PEI@CTS was added at a dosage of 3 g/L to the fly ash washing solution and incubated for 12 h, after which it separated from the solution. The liquid phase was sampled and acidified with 1 % HNO₃ to pH < 2, and the residual metals in the liquid phase were measured using ICP-OES. Then, the recovered PEI@CTS was reused in a fresh washing solution for a second sorption cycle using the same procedure. A third sorption cycle was conducted to further evaluate the reusability of the sorbent.

After the third sorption cycle, the spent PEI@CTS was transferred into a 100 mL crucible and mixed with 5 mL concentrated nitric acid and a few drops of perchloric acid. This crucible was placed on a hot plate at 180 °C and heated until the sorbent was completely digested. The resulting solution was diluted to a final volume of 10 mL, and the metal contents were determined by ICP-OES. The metal purity (wt %) was calculated as the percentage of the target metal mass relative to the total metal mass [26].

2.4. Model fit evaluation

In addition to the commonly used coefficient of determination (R^2), the residual root mean square error (RMSE, *Eq.* (5), the sum of the squares errors (ERRSQ/SSE, *Eq.* (6), and the average percentage deviation (%D, *Eq.* (7) have also been used to compare and determine which model fits the data better:

RMSE =
$$\sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (q_{e, cal} - q_{e, exp})^2}$$
 (5)

$$ERRSQ = \sum_{i=1}^{n} (q_{e, cal} - q_{e, exp})^{2}$$
(6)

$$\%D = \left[\frac{1}{4}\sum_{i=1}^{i=4}\frac{1}{N_{m}}\sum_{j=1}^{N_{m}} \left|\frac{q_{i,j,exp} - q_{i,j,cal}}{q_{i,j,exp}}\right|\right] \times 100\%$$
(7)

3. Results and discussion

3.1. Optimization and characterization of PEI@CTS sorbents

Table 1 presents the variations in viscosity, shape, textural properties, specific surface area (SSA), and sorption capacity of the composite sorbents with different V_{PEI}:m_{CTS} ratios. As the PEI loading increased, the sorption capacity for Cu(II) gradually improved from 43.8 to 56.6 mg/g. This increase is accompanied by significant decreases in specific surface area (SSA) and pore volume, decreasing from 32.28 to $6.24 \text{ m}^2/\text{g}$ and 0.25 to $0.02 \text{ cm}^3/\text{g}$, respectively. This suggests that PEI is the active component for Cu(II) sorption and is primarily located within the pores of the sorbents, resulting in a decrease in the SSA, pore volume, and average pore diameter [33]. However, when the ratio of V_{PEI} to m_{CTS} reached 1.5:1, the viscosity of the resulting hydrogel solution decreased significantly by ~ 45 % compared to the ratio of V_{PEI}:m_{CTS} = 1:1. This reduction in viscosity weakens the mechanical strength of the resulting sorbents, rendering them unable to withstand the impact and drag forces during cross-linking with TPP [34]. These findings agree with our previous results, which showed that low viscosity is detrimental to the construction of CTS-based beads [35]. Therefore, a VPEI:mCTS ratio of 1.25:1 was selected for the subsequent synthesis of PEI@CTS.

Fig. 2(a) compares the effects of TPP concentration on the sorption performance of the obtained sorbents towards Cu(II). An increase in TPP concentration reduced sorption capacity from 43.3 mg/g to 38.5 mg/g. Although TPP cross-linking reinforces the CTS network structure [36], excessive cross-linking with amine groups might ultimately diminish the sorption capacity [37]. The sorbents synthesized with 2 % TPP and CTS were tested in a quaternary metal system (Fig. 2(b)). The selective sorption order was Pb(II) > Cu(II) >> Cd(II), indicating that TPP exhibits a higher sorption affinity for Pb(II) and Cu(II) than Zn(II) and Cd(II). Furthermore, in Fig. 2(c), the sorption capacities of sorbents prepared with different combinations towards Cu(II) were determined as 48.9 \pm 0.6 mg/g (for CTS + PEI + TPP), 41.7 \pm 1.1 mg/g (for CTS + PEI + NaOH), and 42.0 \pm 0.7 mg/g (for CTS + TPP). This demonstrates that the combined use of TPP and PEI could increase the sorption capacity towards Cu(II) by approximately 16-17 % compared to the sorbents using only TPP or PEI. Consequently, the synthesis parameters were optimized to 2 % TPP (w/v) and a VPEI:mCTS ratio of 1.25:1, yielding the preferred sorbent designated as PEI_{1.25}@CTS.

Fig. 2(d) illustrates the impact of sorbent dosage on the sorption performance of PEI_{1.25}@CTS for the removal of Cu(II), Pb(II), Zn(II), and Cd(II) from single-metal systems (initial concentration = 100 mg/L). Generally, the removal percentage (%) of HMs increased with the dosage of PEI_{1.25}@CTS, while sorption capacity gradually decreased. At a dosage of 3 g/L, the sorption capacities of Cu(II) and Pb(II) were 32.5 ± 0.1 mg/g and 31.5 ± 0.1 mg/g, respectively, with no further increase up to 5 g/L. Based on these observations, a sorbent dosage of 3 g/L was selected for the subsequent experiments. Fig. 2(e) compares the effects of initial pH values on the sorption capacity of PEI_{1.25}@CTS. The Cu(II) and Pb(II) sorption peaked at pH 5 and decreased slightly at pH 6. In contrast, the sorption capacities for Zn(II) and Cu(II) increased from pH 2 to 4 and remained constant above pH 4. Thus, the optimal pH values for Cu(II), Pb(II), Zn(II), and Cd(II) sorption were determined to be 5, 5, 6, and 6, respectively. As the sorption process is governed by multiple

factors, a factorial design approach was employed to estimate the maximum Cu(II) sorption capacity. The optimal conditions for achieving the maximum sorption capacity (78.8 mg/g) were identified as pH 5.0, initial Cu(II) concentration 150 mg/L, and sorbent dosage 1 g/L (Tables S2 and S3, Fig. S2, Text S5). The point of zero charge (pHpzc), as presented in Fig. 2(f), of PEI_{1.25}@CTS was estimated to be 7.31. This indicates that the surface of PEI_{1.25}@CTS was always positively charged within the pH range of 2–6, suggesting that strong electrostatic repulsion at low pH values (e.g., pH = 2–4) might significantly affect the sorption of HMs.

Fig. S3(a) shows an SEM image of the cross-section of PEI_{1.25}@CTS, showing the bead-like morphology and porous structure of PEI_{1.25}@CTS. As presented in Table 1, the SSA of PEI_{1.25}@CTS was 6.24 m²/g, and the average pore diameter was 15.21 nm. Figs. S3(b) and (c) compare the characteristic variations in the FT-IR spectra of CTS, PEI, TPP, PEI₁@CTS, and PEI_{1.25}@CTS, confirming that cross-linking occurred within PEI1.25@CTS. The characteristic peaks identified in the FT-IR spectra are summarized in Table S4. After PEI cross-linking, the peak at approximately 3443 cm^{-1} of CTS shifted to approximately 3276 cm⁻¹ in PEI_{1.25}@CTS and became broader, likely due to the N-H stretching vibrations of the amine groups of PEI (peak at 3273 cm^{-1}). Furthermore, the peak at 1604 cm⁻¹ of PEI_{1 25}@CTS can be ascribed to the stretching vibration of the C=N band generated by the Schiff base reaction, indicating covalent cross-linking between the amine groups of CTS, PEI, and the aldehyde groups of GA [10]. In the TPP spectra, the peaks at 1212, 894, and 477 cm⁻¹ corresponded to the P=O stretching, the stretching vibration of the P–O–P bridge, and the symmetric variable angular vibration of PO₃. After ionic cross-linking with TPP, significant changes were observed in the peaks at 1070, 887, and 515 $\rm cm^{-1}$ in PEI1.25@CTS, indicating P-containing functional groups from TPP. The new peaks at 1548 cm⁻¹ in PEI₁@CTS and PEI_{1.25}@CTS were assigned to the ionic interactions between the positively charged amine groups of CTS or PEI and the negatively charged groups of TPP. The peak intensity at 1548 cm⁻¹ in PEI_{1.25}@CTS was lower than that in PEI₁@CTS, indicating that more amine groups were involved in PEI cross-linking than in ionic cross-linking with TPP in PEI_{1.25}@CTS.

3.2. Sorption performance of $PEI_{1.25}$ @CTS in single and quaternary metal systems

Fig. 3(a) and (b) show the sorption behavior of PEI_{1.25}@CTS in quaternary metal systems with equal concentrations (EC) and equimolar concentrations (EM), respectively. In both systems, the target HMs exhibited high affinities towards PEI_{1.25}@CTS in the order of Cu(II) > Pb (II) > Zn(II) > Cd(II), although Pb(II) demonstrated superiority in single-metal systems (Fig. S4(a)). Notably, competing ions did not affect Cu(II) sorption. Both the rate constant (k_2) and equilibrium capacity (q_e) for Cu (II) remained nearly identical in single Cu and EC-quaternary metal systems (k_2 : 0.03 and 0.03 g·h⁻¹·mg⁻¹; q_e : 33.05 and 34.61 mg/g, Tables S5 and S6). In the single-metal and the two quaternary metal systems, the sorption of Cu(II) closely followed a pseudo-second-order kinetic model ($R^2 = 0.994-0.995$). This suggests that the sorption of Cu(II) was primarily due to chemisorption, irrespective of the competing ions. In contrast, Pb(II) sorption in the EC-quaternary system showed poor fits to both the pseudo-first-order ($R^2 = 0.363$) and pseudo-second-

Table 1

Comparison of viscosity, shape, textural property, and Cu(II) sorption capacity of PEI@CTS sorbents synthesized with different ratios of PEI and CTS (with 2% TPP).

Materials (PEI*@CTS)	V _{PEI} :m _{CTS}	Viscosity (cP)	Shape	Sorption capacity (mg/g) for Cu(II)	SSA (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
PEI0@CTS	0:1	792	Spherical	42.0 ± 0.7	32.28	0.25	37.56
PEI1@CTS	1:1	765	Spherical	43.8 ± 1.2	17.12	0.06	16.46
PEI1.25@CTS	1.25:1	598	Spherical	48.4 ± 0.8	6.24	0.02	15.21
PEI _{1.5} @CTS	1.5:1	421	Irregular	56.6 ± 0.9	NA	NA	NA

* The subscript numbers mean the ratios between V_{PEI} and m_{CTS}; NA: not available.



Fig. 2. (a) Variation in sorption capacity of PEI₁@CTS for Cu(II) with TPP concentration; (b) Sorption capacity of sorbents synthesized with 2 % TPP and CTS in equimolar quaternary metal systems (initial concentration = 1 mmol/L for each); (c) Effect of different ingredient combinations of sorbents on the sorption capacity for Cu(II); Effect of (d) sorbent dosage and (e) initial solution pH on the sorption capacity of PEI_{1.25}@CTS for heavy metals in single-metal systems; (f) Point of zero charge of PEI_{1.25}@CTS. Note: Unless specified, initial concentration = 100 mg/L, temperature = 298 K, contact time = 48 h, dosage = 1 g/L.

order models ($R^2 = 0.761$), suggesting partial inhibition by Cu(II). However, in the EM-quaternary system, Pb(II) sorption followed the pseudo-second-order model more closely ($R^2 = 0.970$), likely due to its high initial concentration (207.2 mg/L), which provided a stronger driving force to access available sorption sites. The kinetic models for Zn (II) sorption displayed low R^2 values (ranging from 0.216 to 0.894), while those for Cd(II) sorption failed to fit any kinetic models in either the EC- or EM-quaternary metal systems. This indicates that the sorption of Cu(II) ions inhibited the competitive sorption of coexisting Zn(II) and Cd(II) and prompted the desorption of previously sorbed ions as the process progressed.

Intra-particle diffusion models were used to simulate sorption behavior in single-metal systems (Fig. S4(b)) as well as EC- and EMquaternary metal systems (Fig. 3(c) and 3(d)). Both quaternary systems exhibited similar two-stage diffusion. In the first stage, Cu(II) rapidly diffused through the exterior film of PEI1 25@CTS and was sorbed onto the surface, whereas Pb(II), Zn(II), and Cd(II) were inhibited to varying degrees [38]. In both single-metal systems and EC-quaternary metal systems, the diffusion rate constants (i.e., $k_{i,1}$) for Cu(II) were 1.37 and 1.19 mg/(g min^{1/2}), respectively (Tables S5 and S6). This indicated that the film diffusion of Cu(II) was slightly diminished in the presence of competing ions. In contrast, the $k_{i,1}$ values for Pb(II), Cd(II), and Zn(II) decreased notably in the EC-quaternary system relative to their single-metal counterparts, indicating that competitive inhibition primarily occurred during surface diffusion. The hydrated radii of Cu(II) (4.19 nm), Pb(II) (4.01 nm), Cd(II) (4.26 nm), and Zn(II) (4.30 nm) are much smaller than the average pore diameter of PEI1.25@CTS (15.21 nm, Table 1). Therefore, we hypothesized that the sorption of Cu(II) onto PEI1.25@CTS led to the sorption inhibition of ions other than the physical barrier [12,39].

Sorption isotherms for single-metal systems are summarized in **Table S7** (Figs. S3(c) and (d)), while the fitting parameters for the multicomponent sorption isotherms and average percentage deviation (D%) are listed in Table S8. High %D values indicate that the extended Langmuir (ELMI, 292 %) and modified Langmuir (MLMI, 70 %)

multicomponent isotherms failed to fit the experimental data. In contrast, the Sheindorf-Rebuhn-Sheintuch isotherm (SRSI), a Freundlich-type isotherm model, provided a much better fit, with a %D value of 5 %. However, one thing should be noted—the SRSI model includes 16 competition coefficients for a quaternary metal system, which could lead to over-parameterization and unreliable results [40]. Therefore, the effects of initial concentration on sorption in quaternary metal systems are investigated in detail in the following section.

Fig. 3(e) and (f) and Fig. S5 depict the effects of initial concentrations on the sorption capacities of PEI1.25@CTS in EC-, EM-quaternary, and single-metal systems. The results clearly demonstrate that an initial Cu(II) concentration of 300 mg/L marks a critical point in multicomponent systems. Within the concentration range of 25-500 mg/L, the sorption capacity for Cu(II) increased gradually with the rising initial concentration, reaching a plateau at 300 mg/L. This trend is attributed to a stronger driving force at higher initial concentrations, which overcomes the mass transfer resistance between the aqueous solution and solid phases. Beyond 300 mg/L, changes in equilibrium sorption capacity for Cu(II) became negligible (< 7 %), indicating the saturation of sorption sites. A similar saturation trend was observed in the single Cu(II) system, where capacities stabilized above 300 mg/L. The aforementioned sorption capacity for Cu(II) (66.3-69.5 mg/g) could be comparable to those in the EC-quaternary metal systems (63.0-66.8 mg/g). This suggests that competing ions slightly reduce the availability of sorption sites for Cu(II). For comparison, the sorption sites strongly occupied by Cu(II) significantly inhibited the sorption of Pb(II) in the multicomponent systems, compared to the single Pb system. However, an unexpected rise in Pb(II) sorption was observed when the initial concentration exceeded 300 mg/L (Fig. 4(a)). Since the sorption sites for Cu(II) were saturated beyond 300 mg/L, the increase in Pb(II) sorption indicates that other sorption sites are available for Pb(II). In contrast, Cd (II) and Zn(II) sorption followed a simple trend: sorption increased at lower concentrations due to sufficient sorption sites but declined at higher concentrations as desorption occurred from competition for limited active sites. In the EM-quaternary metal system, despite Cu(II)



Fig. 3. Experimental data from sorption of equal concentration (EC) and equimolar (EM) quaternary metal systems fitted with (a)-(b) pseudo-first-order, pseudosecond-order, and (c)-(d) intra-particle diffusion kinetic models; (e)-(f) Effect of initial concentrations on sorption in quaternary metal systems.

having the lowest mass concentration among the four HMs, its sorption capacity increased linearly, highlighting PEI_{1.25}@CTS preferential selectivity for Cu(II).

Thermodynamic analyses of the single-metal systems are summarized in **Text S4.** In summary, the values of ΔG were negative for four HMs, indicating that the sorption is a spontaneous process. The negative values of ΔH and ΔS indicate the sorption of Cu(II) and Cd(II) is an exothermic and entropy-decreasing process. In contrast, the positive ΔH and ΔS values for Pb(II) and Zn(II) suggest an endothermic and entropyincreasing process (Fig. S6(a) and Table S9). In the quaternary metal system, the thermodynamic model did not fit well with the experimental data (Fig. S6(b)), likely due to the complexity of the sorption process. In addition to the desorption of Cd(II) and Zn(II) and the increased sorption of Pb(II) at higher initial concentrations, partial structural degradation of sorbents was observed at 328 K when exposed to metal concentrations of 400 and 500 mg/L. This degradation is likely attributable to the sorbents' limited thermal stability, combined with intensified metal competition under such elevated concentrations.

Both the distribution coefficients (K_d) and selectivity coefficients (α) are critical indicators of selectivity. In all quaternary metal systems, the

 K_d values for the four HMs exhibited a similar decreasing order: K_d (Cu (II)) > $K_d(Pb(II))$ > $K_d(Zn(II))$ > $K_d(Cd(II))$, except at extremely high initial concentrations (500 mg/L, Table 2). The unexpected K_d order at 500 mg/L, along with the opposite trends in K_d (Cu(II)) and K_d (Pb(II)), indicated a more complex interaction between Pb(II) and Cu(II) sorption, in contrast to the straightforward inhibitory effect of Cu(II) on Cd (II) and Zn(II) sorption. Table 3 compares the selectivity coefficients (α) of PEI1.25@CTS for Cu(II) with other documented sorbents used in multicomponent systems [13,24,41-46]. PEI1.25@CTS exhibited better performance than most other sorbents, considering selectivity for Cu and cost. The sorption capacities of Cu for sodium alginate/PEI composite hydrogel and tetraethylenepentamine-modified chitosan/ CoFe₂O₄ were higher than ours. Still, their selectivity coefficients of Cu (II)/Pb(II) were lower than 1, showing their weak preferential for Cu(II). It should be noted that the branched PEI (molecular weight: 25,000; content of H₂O: less than 1 %) in the soy protein-based PEI hydrogel [13] could lead to better Cu selectivity than ours. In contrast, our sorbent employs a 50 % aqueous solution of PEI, which provides fewer active functional groups per unit dose but is much cheaper than the aforementioned branched PEI, favoring the practical applications of



Fig. 4. (a) Effect of interactions between heavy metal ions on sorption in EC-quaternary metal systems; Competitive adsorption–desorption of $PEI_{1.25}$ @CTS preloaded with specific heavy metal in aqueous solutions containing competing metal in binary metal systems (b) including Cu and (c) without Cu; SEM-EDS line scan analysis of $PEI_{1.25}$ @CTS after sorption of target heavy metals in quaternary metal systems: (d) 75 mg/L for Cu(II) and 300 mg/L for Pb(II), Zn(II) and Cd(II); (e) 300 mg/L for Cu(II), Pb(II), Zn(II) and Cd(II). Note: contact time = 48 h; pH = 5; temperature = 298 K; dosage = 3 g/L.

Table 2

Distribution (K_d) and selectivity (a) coefficients for competitive sorption by PEI_{1.25}@CTS sorbents at different initial concentrations in quaternary metal systems.

Quaternary metal systems*	Initial concentration	$K_d (\mathrm{mL/g})$				α		
		Cu	Pb	Cd	Zn	Cu/Pb	Cu/Cd	Cu/Zn
Equal concentration (EC)	500 mg/L	204.3	214.0	1.5	0.6	1.0	Cu/Cd 135.9 93.6 397.8 1088.0 139.1 225.5 165.8 35.0 7.9 453.8 363.9 210.3 117.0 73.4 41.4 9.3	318.8
	400 mg/L	326.1	185.8	3.5	4.5	1.8	93.6	72.9
	300 mg/L	532.4	154.8	1.3	5.0	3.4	397.8	106.8
	250 mg/L	821.1	168.2	0.8	8.6	4.9	1088.0	95.3
	200 mg/L	1630.9	217.9	11.7	23.7	7.5	139.1	68.9
	150 mg/L	4575.2	338.7	20.3	56.1	13.5	225.5	81.6
	100 mg/L	10395.0	629.7	62.7	143.1	16.5	165.8	72.6
	50 mg/L	10121.0	1529.8	289.6	463.9	6.6	35.0	21.8
	25 mg/L	7044.7	3510.8	897.9	1280.9	2.0	7.9	5.5
Equimolar	2.0 mmol/L	9019.4	312.6	19.9	69.7	28.9	453.8	129.4
(EM)	1.6 mmol/L	16538.7	419.8	45.5	136.3	39.4	363.9	121.3
	1.2 mmol/L	18018.9	431.6	85.7	179.6	41.8	210.3	100.3
	1.0 mmol/L	15962.9	569.3	136.5	248.1	28.0	117.0	64.4
	0.8 mmol/L	15034.9	746.2	204.9	346.9	20.2	73.4	43.3
	0.6 mmol/L	12495.8	890.5	302.1	467.0	14.0	41.4	26.8
	0.4 mmol/L	9504.0	2515.0	1022.4	1506.3	3.8	9.3	6.3

* Equal concentration (EC) refers to quaternary metal systems in which all metals had the same initial mass concentrations, ranging from 25 mg/L to 500 mg/L. Equimolar (EM) refers to quaternary metal systems in which all the metals had the same initial molar concentrations, ranging from 0.4 mmol/L to 2.0 mmol/L.

PEI1.25@CTS.

3.3. Competitive sorption mechanism

To further investigate the interactions of HMs in multicomponent systems, competitive adsorption–desorption experiments were conducted in binary metal systems (details in **Text S6**). Binary systems containing Cu revealed the dominant role of Cu(II) in competitive sorption scenarios (Fig. 4(b)), compared to binary systems composed of

Zn and Cd or Pb and Zn (Fig. 4(c)). For example, in a Pb-Cu binary system, introducing Pb-preloaded PEI_{1.25}@CTS into an aqueous Cu(II) solution resulted in 41 % of the preloaded Pb(II) being released by Cu (II). The sorption capacity of Pb-preloaded PEI_{1.25}@CTS for Cu(II) reached 0.49 mmol/g, identical to that of fresh PEI_{1.25}@CTS in a single Cu(II) system. For comparison, the sorption capacity of Cu-preloaded PEI_{1.25}@CTS for Pb(II) was 0.08 mmol/g, half of that in a single Pb(II) system using fresh PEI_{1.25}@CTS (0.16 mmol/g). Free Pb (II) ions released only 2 % of the preloaded Cu(II). Overall, Cu(II) sorption

Table 3

Comparison	of sorption capacity	v and selectivity	v coefficient for C	Cu(II) sorption by	v PEI1 25@CTS	sorbents and	other sorbents re	ported in the lite	erature.
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Materials	Heavy	Concen-	Conditions				Cu sorption	Selectivity coefficient	Reference
	metals	tration (mg/ L)	рН	т (°С)	Dosage (g/L)	t (h)	capacity (mg/ g) ^b		
Sodium alginate/ polyethyleneimine composite hydrogel ^a	Cu-Pb	100	5.5	25	0.5	24	322.6	Cu(II)/Pb(II) 0.7	[41]
Chitosan-tripolyphosphate (CTPP) beads ^a	Cu-Pb	300	4.5	27	0.4	1.67	19.2	Cu(II)/Pb(II) 1.0	[24]
Tetraethylenepentamine modified chitosan/ CoFe ₂ O ₄ ^a	Cu-Pb	200	5	25	1	1.5	92.6	Cu(II)/Pb(II)0.9	[42]
Chitosan-pyromellitic dianhydride modified biochar	Cu-Pb-Cd	100	6	25	1	24	60.6	Cu(II)/Cd(II) 18.0; Cu(II)/Pb(II) 33.6	[43]
Diethylenetriaminepentaacetic acid-modified chitosan/polyethylene oxide ^a	Cu-Ni-Pb	200	5	25	2	1.5	46.0	Cu(II)/Pb(II) 2.9; Cu(II)/Ni(II) 4.8	[44]
Magnetic iron oxide chitosan (Fe ₃ O ₄ -CS) nanocomposite ^a	Cu-Pb- Cd-Ni	10	5	25	1	1	7.5	Cu(II)/Pb(II) 0.8; Cu(II)/Cd(II) 17.2; Cu(II)/Ni(II) 38.9	[45]
Soy protein-based polyethyleneimine hydrogel	Cu-Pb- Zn-Cd	100	5.5	25	0.5	24	106.7	Cu(II)/Zn(II) 250.5; Cu(II)/Cd (II) 103.5; Cu(II)/Pb(II) 137.1	[13]
PEI _{1.25} @CTS	Cu-Pb- Zn-Cd	100	5	25	3	24	32.8	Cu(II)/Pb(II) 16.5; Cu(II)/Zn (II) 72.6; Cu(II)/Cd(II) 165.8;	This study
		200					57.2	Cu(II)/Pb(II) 7.5; Cu(II)/Zn(II) 68.9; Cu(II)/Cd(II) 139.1	
N-methylene phosphonic acid chitosan aerogels $\ensuremath{^{\mathrm{a}}}$	Cu-Pb- Zn-Ni-Cd	200	5	25	1	24	118.0	Cu(II)/Zn(II) 18.0; Cu(II)/Cd (II) 20.6; Cu(II)/Pb(II) 3.06; Cu (II)/Ni(II) 16.0	[46]

^a Estimated from data shown in figures or tables.

^b The sorption capacity for Cu was obtained from multicomponent systems.

released 41–74 % of the preloaded competing ions on PEI_{1.25}@CTS, whereas competing ion sorption caused negligible desorption (1–2%) of preloaded Cu(II). Cu(II) also induced substantially higher desorption of preloaded Zn(II), Cd(II), and Pb(II) than any of these ions could cause in return. For instance, Cd(II) and Pb(II) desorbed 40% and 48% of preloaded Zn(II), respectively, while Cu(II) desorbed 70%. These findings demonstrated the much stronger binding affinity of PEI_{1.25}@CTS for Cu (II), allowing Cu(II) to firmly occupy the sorption sites or substantially displace other previously sorbed competing ions.

The cross-sectional line scan of the spent PEI_{1.25}@CTS revealed the metal distributions at initial Cu concentrations of 75 and 300 mg/L (with 300 mg/L for each competing ion). In systems in which the Cu(II) concentration was 75 mg/L (Fig. 4(d)), Cu(II) predominantly occupied the sorption sites of the outer layer, achieving a high removal efficiency of 97.6 %. The remaining sorption sites were available for Pb(II), Cd(II), and Zn(II), resulting in removal efficiencies of 63.4 %, 18.3 %, and 27.5 %, respectively. As the Cu(II) concentration increased to 300 mg/L (Fig. 4(e)), the sorption sites became insufficient for competing ions, and the steric hindrances generated by the sorbed Cu(II) further inhibited the sorption of Zn(II) and Cd(II), reducing their removal efficiencies to 1.5 % and 0.4 %, respectively. The sorbed Cu(II) might generate hindrances that limited the approach of Cd(II) and Zn(II) towards PEI_{1.25}@CTS because of their larger hydrated radii than those of Cu(II), (Cu(II): 0.419 nm, Zn(II): 0.430 nm, and Cd(II): 0.426 nm). In contrast, Pb(II), with the smallest hydrated radius (0.401 nm), could access the PEI1.25@CTS surface and bound to sorption sites that exhibited a higher affinity for Pb(II) than for Cu(II), as evidenced by Pb(II) observed in the outer layer (removal efficiency: 32.1 %) (Fig. 4(e)).

Fig. 5(a) compares the variations in the FT-IR spectra of PEI_{1.25}@CTS before and after sorption. The broad band at 3276 cm⁻¹ in PEI_{1.25}@CTS shifted to 3419–3423 cm⁻¹ after the sorption. This indicated the participation of O–H or N–H in HM sorption. Meanwhile, the peak at 1604 cm⁻¹ in PEI_{1.25}@CTS exhibited significant and similar shift trends for four HMs (1628–1631 cm⁻¹), highlighting the involvement of amine groups in the sorption [10,47]. Furthermore, the shifts in the peaks at 1070 and 515 cm⁻¹ of PEI_{1.25}@CTS were apparent, indicating the involvement of phosphate groups in HM sorption (Table S4).

Fig. 5(b)–(d) compare the XPS spectra before and after HM sorption. The N 1s spectra of as-prepared $PEI_{1.25}$ @CTS could be assigned to three peaks with BEs at 398.32, 399.39, and 400.51 eV. This corresponds to

the nitrogen atom in C=N, –NH–, and –NH₂/NH₃⁺, respectively (Fig. 5 (b)). After the sorption of HMs, the peak of –NH₂/NH₃⁺ shifted to higher BEs. For example, the increase of BEs varying for metals could be ranked in a decrease order of Cu(II) (+1.23 eV) > Zn(II) (+1.01 eV) > Cd(II) (+0.86 eV) > Pb(II) (+0.82 eV), indicating that nitrogen atoms were preferential sorption sites for Cu(II). The O 1s spectra (Fig. 5(c)) were curve-fitted into three components, which are identified as O–H (529.92 eV), O–P (531.70 eV), and O=P (533.02 eV) [48]. The BEs of the O–H peak in the O 1s spectra significantly increased after adsorbing four HMs. This was primarily attributed to decreased electron cloud density around the oxygen atoms after bonding with Cu(II) [49]. In Fig. 5(d), the P 2p spectra were deconvoluted into two peaks at 131.97 and 132.74 eV [22], both of which shifted upon metal sorption, confirming the involvement of phosphate groups.

FT-IR and XPS results indicate that the sorption mechanism of $PEI_{1.25}$ @CTS for the four HMs involves amine, hydroxyl, and phosphate groups. Notably, these functional group contributions are concentration-dependent. At a metal concentration of 800 mg/L (Fig. 5), all three groups participate in sorption. However, at 100 mg/L (Fig. 57), only amine and hydroxyl groups are involved. In an EC- quaternary metal system with an initial concentration of 300 mg/L, Pb(II) sorption by $PEI_{1.25}$ @CTS was higher than that of sorbents (PEI + CTS) synthesized without TPP (Fig. S8), suggesting a role for TPP under competitive conditions. In summary, in low-concentration quaternary metal systems, amine and hydroxyl groups serve as the primary sorption sites, while TPP may still function primarily as an ionic cross-linking agent. In high-concentration quaternary metal systems, where Cu(II) strongly competes for amine groups, Pb(II) is likely redirected to functional groups with a weaker affinity for Cu(II), such as TPP (Fig. 2(b)).

PEI_{1.25}@CTS exhibited an affinity order of Cu(II) > Pb(II) > Zn(II) > Cd(II), and the highest affinity for Cu(II) could be explained as follows. First, the –NH₂ clusters originated from PEI and/or CTS are the most important functional groups and could form stable complexes with Cu (II) (e.g., $[Cu \leftarrow (NH_2)_4]^{2+}$, $[Cu \leftarrow (NH_2)_3(OH)]^{2+}$, $[Cu \leftarrow (NH_2)_2(OH)_2]^{2+}$), although PEI, CTS, and TPP might differently contribute to the Cu(II) sorption. A previous study revealed that the stability constants (log K) of PEI-metal complexes follow the order of Cu (II) (20.51) > Cd(II) (15.41) > Zn(II) (14.17) > Pb(II) (9.43) [50]. This aligns with the largest observed shift in N 1s binding energy after Cu(II) sorption (Fig. 5(b)), further confirming the strong coordination between



Fig. 5. (a) FT-IR spectral variations for PEI_{1.25}@CTS sorbent before and after sorption of Cu(II), Pb(II), Cd(II), and Zn(II) in single-metal systems; XPS spectral analysis for PEI_{1.25}@CTS before and after sorption of Cu(II), Pb(II), Cd(II), and Zn(II) in single-metal systems: (b) N 1s, (c) O 1s, (d) P 2p.

nitrogen atoms and Cu(II). As shown in Fig. 4(b), Cu(II) can be strongly sorbed when competing for sorption sites and even replacing those already sorbed HMs [51]. Second, the strongly sorbed Cu(II) might generate steric hindrance at the surface of the sorbents, which impedes the approaching of coexisting ions, especially for Cd(II) and Zn(II) with larger hydrated radii than Cu(II), towards PEI_{1.25}@CTS, decreasing the sorption of competing ions [52]. Additionally, the surface of PEI_{1.25}@CTS was always positively charged within the pH range of 2–6 (in Section 3.1). Thus, electrostatic attraction was not considered as one of the primary sorption mechanisms in this study.

The sorption of $\rm PEI_{1.25}@CTS$ for Pb(II) needs additional explanations. Although the stability constant of the PEI-Pb complexes is the

smallest, $PEI_{1.25}$ @CTS has the second-highest affinity for Pb(II), and an increasing trend in Pb(II) sorption was observed at Cu(II) concentrations above 300 mg/L. This may be because: (1) Among the four HMs, Pb(II) possesses the highest atomic weight, electronegativity and smallest hydrated radius, all of which favor sorption; (2) TPP contributes to Pb(II) sorption when Pb(II) competes with Cu(II) at higher concentrations.

3.4. Application of PEI_{1.25}@CTS in washing solution of fly ash

The application of $PEI_{1.25}$ @CTS to recover Cu from a washing solution of fly ash was evaluated. As presented in Fig. 6(a), $PEI_{1.25}$ @CTS provided a Cu removal efficiency of 87.1–97.1 % for all three sorption



Fig. 6. (a) Reusability performance for $PEI_{1.25}@CTS$ over three sorption cycles in washing solution of fly ash. Note: contact time for one cycle = 12 h; pH = 4-5; temperature = 298 K; dosage = 3 g/L; (b) Purity (wt%) of major competing ions and Cu(II) in washing solution of fly ash and the digestion solution of spent $PEI_{1.25}@CTS$; (c) Schematic representation of Cu(II) recovery using $PEI_{1.25}@CTS$ without elution.

cycles. This indicates that the high selectivity for Cu of PEI_{1.25}@CTS was retained even without the elution of metals. Based on the metal concentrations in the fly ash washing and digestion solutions shown in Tables S1 and S10, the metal purity before and after PEI_{1.25}@CTS application was calculated with *Eq.* (8). As shown in Fig. 6(b), the Cu purity in the initial washing solution was 7.7 wt%. After the third sorption cycle, the Cu(II) purity in the digestion solution of spent PEI_{1.25}@CTS was 39.1 wt%, showing the highest increase in purity (+407.6 %). In addition to Cu(II), PEI_{1.25}@CTS also removed Al and Fe from the washing solution. In contrast, the purity of the other competing ions (Ba, Co, Cd, Mn, Pb, and Zn) decreased significantly (by 36.8–83.8 %), indicating that these ions were displaced by Cu(II) and released during the second and third sorption cycles.

Purity_i (wt%) =
$$\frac{C_i \times V}{\sum\limits_{k=1}^{11} C_k \times V} \times 100 \%$$
 (8)

Where C_i (mg/L) represents the concentration of the target heavy metal i; C_k (mg/L) represents the concentration of the k-th heavy metal (k varying in the range of 1-11 means Cu, Fe, Al, As, Cr, Ba, Cd, Co, Mn, Pb and Zn, respectively); V (mL) represents the solution volume.

The Cu purity before and after PEI_{1.25}@CTS sorption was further compared with reported materials applied for various Cu-containing wastewater (Table S11). Purity calculations required metal concentration data before and after treatment; however, such data were reported in limited studies. For non-selective adsorbents, the spent adsorbents did not exhibit Cu enrichment, with enrichment factors close to 1. In contrast, the treatment using CuSe electrodes resulted in a nearly 3.5-fold increase in purity, whereas our approach achieved a 5-fold enhancement.

Finally, we propose a strategy to recover Cu(II) from a multicomponent aqueous solution by reusing $PEI_{1.25}$ @CTS without undergoing any desorption step (Fig. 6(c)). First, $PEI_{1.25}$ @CTS that had already taken up Cu(II) could continue to sorb Cu(II) ions from the quaternary metal systems (Cu–Pb–Zn–Cd) due to the availability of remaining sufficient sorption sites. Second, Cu(II) could form stable complexes with the functional groups on the framework of PEI_{1.25}@CTS compared to the other ions. Thus, the sorbed Cu(II) ions could further exert a steric hindrance effect, thereby impeding the competing metal ions to access sorption sites. Third, the Cu(II) ions in a multicomponent aqueous solution could effectively displace the sorbed Cd(II), Zn(II) and Pb(II), respectively, due to the high stability constants (log K) of the PEI–metal complexes (Cu(II) > Cd(II) > Zn(II) > Pb(II)). Thus, the PEI_{1.25}@CTS sorbent could effectively enhance the selectivity of sorption toward Cu (II) in complex metal systems.

4. Conclusions

This study demonstrates the potential of PEI-cross-linked CTS sorbents for the selective recovery of Cu(II) from fly ash washing solutions. The optimized PEI_{1.25}@CTS (2 % TPP (w/v), V_{PEI}:m_{CTS} = 1.25:1) exhibited high Cu selectivity in the presence of competing metals, achieving a K_d of 10⁵ mL/g. Compared to previously reported sorbents, PEI_{1.25}@CTS demonstrated superior selectivity coefficients. Furthermore, PEI_{1.25}@CTS maintained stable Cu removal performance (removal efficiency: >85 %) over multiple sorption cycles in fly ash washing solutions. The sorption process led to progressive Cu enrichment and concurrent desorption of competing metals, enhancing the final recovery purity. Notably, the high stability of the Cu-PEI complexes and the steric hindrance created by the sorbed Cu contributed to the selective recovery of Cu from low-grade waste streams.

The high selectivity of $PEI_{1.25}$ @CTS in complex wastewater matrices highlights its potential for industrial applications, particularly waste valorization and resource recovery. Future research should focus on scaling up the process through column sorption experiments, optimizing the recyclability of the material, and assessing its applicability in diverse Cu-containing waste streams. These findings will contribute to the advancement of sustainable metal recovery technologies and efficient wastewater treatment.

CRediT authorship contribution statement

Yu Gong: Writing - review & editing, Writing - original draft,

Methodology, Funding acquisition, Conceptualization. Zitao Lin: Writing – original draft, Visualization, Investigation, Formal analysis. Jing Yang: Writing – review & editing, Writing – original draft, Visualization. Yongming Ju: Writing – review & editing, Writing – original draft, Supervision, Funding acquisition. Dorota Kołodyńska: Supervision. Jie Liu: Writing – review & editing. Xiaohan Shan: Investigation. Yujie Wang: Methodology, Investigation. Yong Zhang: Writing – review & editing, Resources. Weixin Li: Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2025.162469.

Data availability

Data will be made available on request.

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