

Advancement of 3D-printed filter via acetone treatment for enhanced CuHCF immobilization and selective ammonium capture

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Abstract

Ammonium contamination is a major environmental concern due to its harmful effects on aquatic systems. In this study, copper hexacyanoferrate (CuHCF) was immobilized onto acetone-treated 3D-printed polylactic acid (PLA) filters. The acetone treatment increased surface roughness and hydrophilicity, improving CuHCF loading and stability. The modified filter showed an adsorption capacity of 1.91 mg/g and maintained over 90% regeneration efficiency over five cycles. Column experiments demonstrated stable performance for up to 40 hours. This approach provides a simple and scalable method for fabricating efficient adsorbents for ammonium removal.

1. Introduction

Ammonium contamination in aquatic environments is a significant concern due to its toxicity and contribution to eutrophication [1-5]. In wastewater systems, ammonium coexists with competing ions and fluctuating concentrations, making selective and efficient removal challenging [6]. Among available treatment methods, adsorption has attracted attention as a simple and energy-efficient approach, particularly for low to moderate ammonium concentrations where selectivity and regeneration are critical [7].

Metal hexacyanoferrates, also known as Prussian blue analogues (PBAs), have demonstrated excellent selectivity toward ammonium ions due to their well-defined lattice structures and ion-exchange mechanisms [8]. In particular, copper hexacyanoferrate (CuHCF) exhibits high affinity for NH_4^+ ions, driven by size compatibility and electrostatic interactions within its crystalline framework [9]. Despite these advantages, the practical application of CuHCF is limited by its powder form, which complicates recovery and reuse in water treatment systems.

Immobilization of PBAs onto solid supports has been explored to address these limitations, improving material stability and enabling easier handling [10]. In parallel, three-dimensional (3D) printing has emerged as a promising fabrication technique for designing structured adsorbents with controlled geometry and mechanical stability [11,12]. Among available materials, polylactic acid (PLA) is widely used due to its biodegradability and ease of processing, although its relatively inert surface requires modification to enhance adsorbent loading [13,14].

Surface treatment methods, such as solvent-based etching, can increase surface roughness and introduce reactive sites for further functionalization. In particular, acetone treatment provides a simple and controllable approach to modify PLA surfaces, enhancing hydrophilicity and facilitating subsequent chemical modification [15]. However, achieving stable and uniform immobilization of PBAs remains a challenge when relying solely on physical attachment.

In this study, a dual-step surface modification strategy is proposed, combining acetone pretreatment with acrylic acid polymerization to introduce carboxyl functional groups onto 3D-printed PLA scaffolds. This approach enables strong coordination with copper ions and promotes in-situ growth of CuHCF on the modified surface. The resulting composite structure aims to enhance adsorbent stability, loading efficiency, and overall ammonium removal performance, providing a practical platform for selective ammonium recovery under both batch and continuous-flow conditions.

2. Materials and Methods

2.1 Chemicals

Polylactic acid (PLA) filaments (1.75 mm) were used as the printing material. Acetone, NaCl, $K_4[Fe(CN)_6] \cdot 3H_2O$, $CuSO_4 \cdot 5H_2O$, acrylic acid (AA), potassium persulfate (KPS), and NaOH were used as received. A standard NH_4^+ solution (1000 mg/L) was used to prepare test solutions. All solutions were prepared using ultrapure water (18.2 M Ω ·cm).

2.2 Fabrication and surface modification of PLA scaffolds

2.2.1 3D printing

PLA scaffolds were fabricated using fused deposition modeling (FDM) at 200 °C (nozzle) and 50 °C (bed), with a printing speed of 40 mm/min. The scaffolds were designed as monolithic lattices (diameter: 1.45 cm, height: 0.2 cm, 40% infill).

2.2.2 Acetone treatment and acrylic acid modification

Scaffolds were immersed in 95% (v/v) acetone for 24 h to induce surface etching and improve hydrophilicity [42]. Subsequently, acrylic acid polymerization was performed in the presence of KPS at 70 °C for 7 h under a nitrogen atmosphere. After polymerization, the samples were washed and treated with 5 M NaCl for 48 h to stabilize surface functional groups. The modified scaffold was denoted as PLA-AcA.

2.2.3 In-situ growth of CuHCF

CuHCF was immobilized via a sequential ion-exchange process [11]. PLA-AcA scaffolds were first immersed in $CuSO_4$ solution (1.5 M, 24 h), followed by $K_4[Fe(CN)_6]$ (700 mM, 1 h), and a final $CuSO_4$ treatment (1 M, 30 min). The resulting samples were washed and dried, yielding PLA-AcA-CuHCF filters.

2.3 Characterization

The structural and chemical properties of the materials were analyzed using XRD and XPS to determine crystallinity and elemental composition. FT-IR spectroscopy was used to identify functional groups, while FE-SEM coupled with EDS was employed to observe surface morphology and elemental distribution. Thermogravimetric analysis (TGA) was conducted to evaluate thermal stability. CuHCF loading was quantified using ICP-MS after acid digestion.

2.4 Ammonium adsorption experiments

2.4.1 Kinetics and isotherms

Batch adsorption experiments were conducted to evaluate NH_4^+ removal performance. Filters at different modification stages (PLA, PLA-CuHCF, PLA-Ac-CuHCF, and PLA-AcA-CuHCF) were first compared using 10 mg/L NH_4^+ solutions.

Kinetic studies were performed by sampling at predefined time intervals, while isotherm experiments were conducted using initial NH_4^+ concentrations ranging from 1 to 100 mg/L. All experiments were performed at 25 °C with constant agitation. NH_4^+ concentrations were measured using ion chromatography (IC). Kinetic data were fitted using pseudo-first-order and pseudo-second-order models, while equilibrium data were analyzed using Langmuir and Freundlich isotherms (Text S1–S2).

2.4.2 Selectivity, desorption, and reusability

Selectivity was evaluated in mixed-ion solutions containing NH_4^+ , K^+ , Na^+ , Li^+ , and Cs^+ (10 mg/L each). Desorption was performed using NaCl or KCl solutions (0.1–1 M), and the released NH_4^+ was quantified by IC. Reusability was assessed over five adsorption-desorption cycles using 10 mg/L NH_4^+ and 1 M KCl as the regenerant.

2.4.3 Continuous column experiment

A column experiment was conducted to evaluate continuous performance. A PLA-AcA-CuHCF filter (0.24 g) was packed in a glass column and fed with 1 mg/L NH_4^+ solution at 0.2 mL/min. After adsorption, desorption was carried out using 1 M KCl. Effluent samples were collected periodically and analyzed using the indophenol blue method [16]. Breakthrough behavior was modeled using the Thomas model (Text S3).

3. Results and Discussion

3.1 Structural and surface characterization of modified PLA filters

3.1.1 Chemical and structural properties

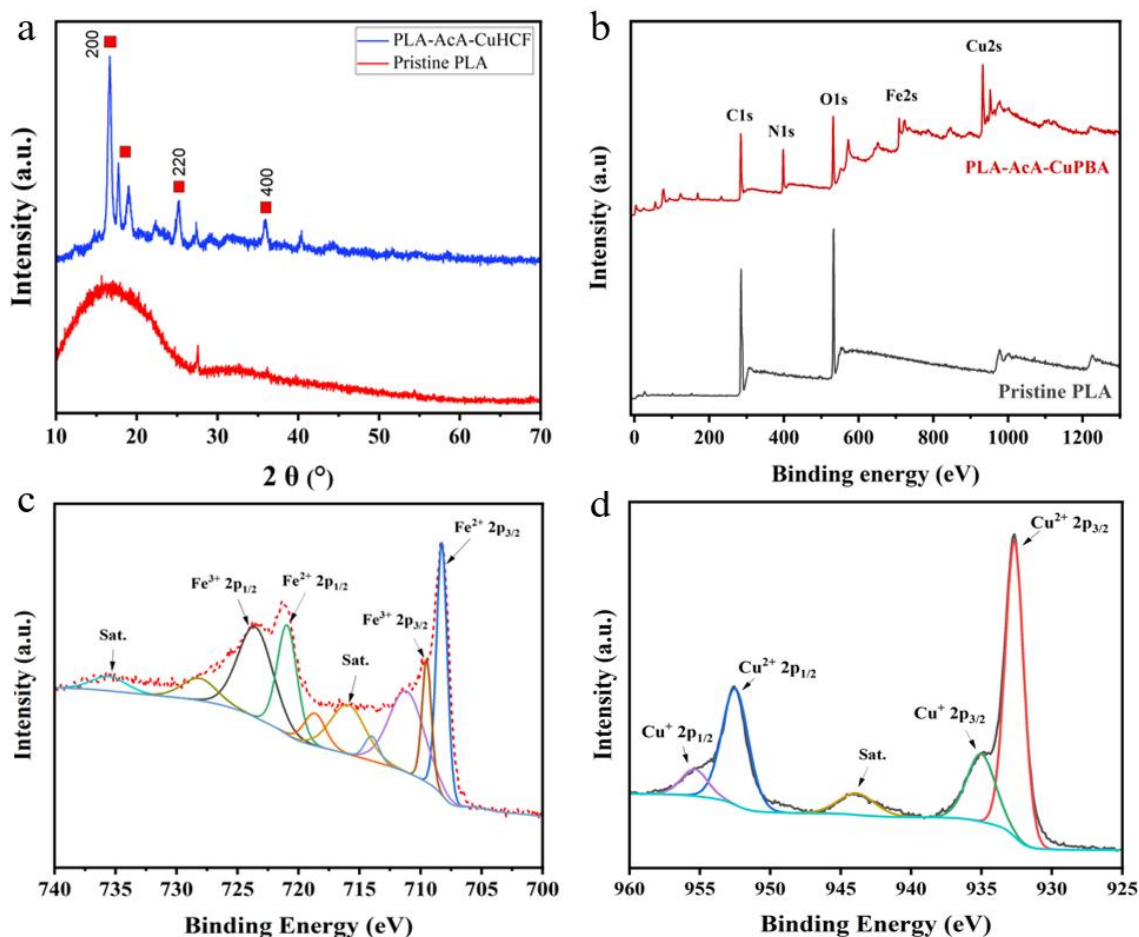


Fig. 1 (a) XRD patterns of pristine PLA and modified filters showing CuHCF crystallization; (b) XPS survey spectra; (c) Fe 2p, and (d) Cu 2p spectra confirming mixed oxidation states in the PAA–CuHCF filter.

The crystalline and chemical characteristics of the modified PLA filters were analyzed using XRD, XPS, and FTIR. XRD patterns (Fig. 1a) showed that pristine PLA exhibited a broad peak typical of amorphous polymers [17]. After modification and CuHCF immobilization, distinct peaks at 16.47° , 24.55° , and 36.27° corresponding to the (200), (220), and (400) planes appeared, confirming the formation of crystalline CuHCF on the PLA surface [18,19].

XPS analysis further confirmed successful immobilization of CuHCF. While pristine PLA showed only C and O signals, the modified PLA-AcA-CuHCF exhibited additional N, Fe, and Cu peaks [8]. The Fe 2p spectrum indicated the coexistence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ species, and the Cu 2p spectrum showed both Cu^+ and Cu^{2+} states, consistent with the mixed-valence structure of CuHCF [20–22].

FTIR results (Fig. 2) supported the surface modification and CuHCF formation. The characteristic C=O stretching band of PLA (1758 cm^{-1}) increased after acrylic acid treatment, indicating the introduction of carboxyl groups. Enhanced O-H and CH₂ bands further suggested increased hydrophilicity [23]. After CuHCF immobilization, distinct peaks at 2098 cm^{-1} (C $\equiv$ N stretching) and 598 cm^{-1} (metal-cyanide vibrations) were observed, confirming in-situ formation of CuHCF. These peaks were significantly weaker in unmodified PLA-CuHCF, indicating limited attachment. Additionally, the band at 1606 cm^{-1} corresponding to lattice water further supports the formation of the CuHCF framework [24].

Overall, the results demonstrate that acetone and acrylic acid modification effectively enhanced surface functionality, enabling uniform and stable immobilization of crystalline CuHCF on the PLA scaffold.

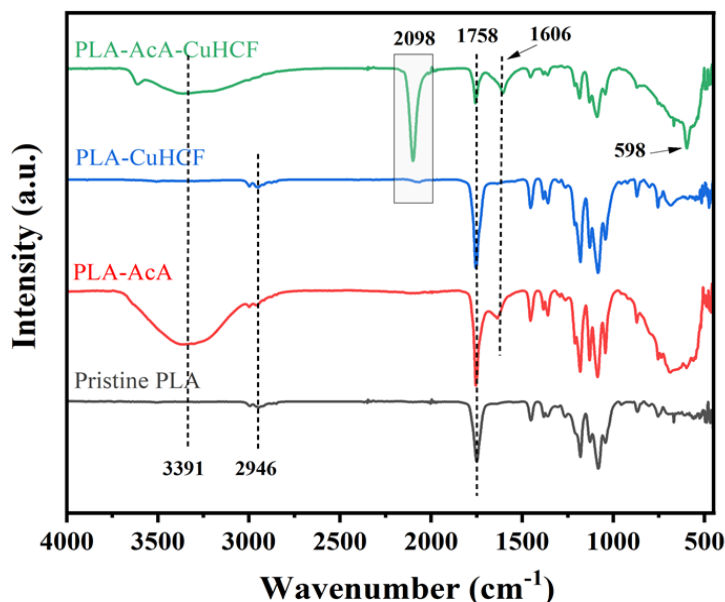


Fig. 2 FTIR spectra of pristine PLA, PLA-AcA, PLA-CuHCF, and PLA-AcA-CuHCF filters showing functional group evolution and CuHCF bonding.

3.1.2 Morphological and thermal properties

The morphological evolution and elemental distribution of the filters were analyzed using SEM-EDS (Fig. 3). Pristine PLA exhibited a smooth and homogeneous surface, while direct CuHCF deposition resulted in only sparse and weakly attached particles due to the inert nature of the polymer. After acetone treatment, the surface became rough and porous, increasing surface area and promoting particle adhesion. Following acrylic acid modification and CuHCF immobilization, the surface was uniformly coated with a dense

CuHCF layer. EDS mapping confirmed the homogeneous distribution of Cu and Fe, indicating successful and uniform immobilization [8].

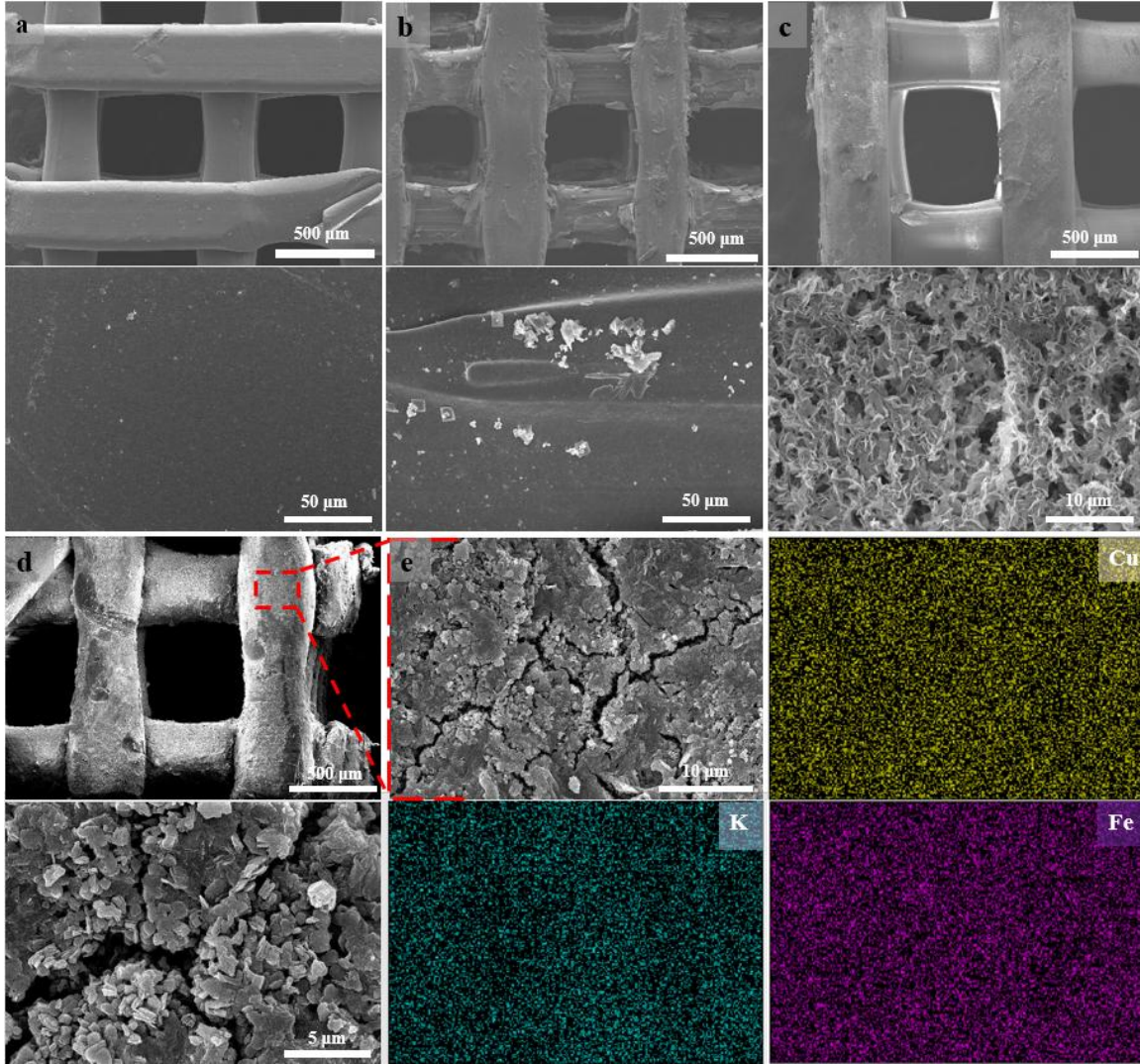


Fig. 3 SEM and EDS mapping images of prepared filters: (a)Pristine PLA, (b) PLA-CuHCF, (c) PLA-AcA, (d) PLA-AcA-CuHCF, (e) EDS mapping of PLA-AcA-CuHCF

Thermal behavior was evaluated using TGA (Fig. 4). Pristine PLA showed a single degradation stage between 308.7–410.6 °C, while PLA-AcA exhibited a slightly lower degradation onset due to increased surface porosity after chemical treatment [25,32]. In contrast, CuHCF-loaded samples showed multi-step decomposition behavior. The PLA-CuHCF filter exhibited two degradation stages associated with polymer decomposition and CuHCF breakdown, with a residual mass of ~4.6% at 800 °C [26].

The PLA-AcA-CuHCF filter showed a three-stage decomposition profile, including initial loss of bound water and residual species, followed by PLA degradation and final CuHCF decomposition [27,28]. The higher residual mass (~8.9%) compared to PLA-CuHCF indicates increased CuHCF loading.

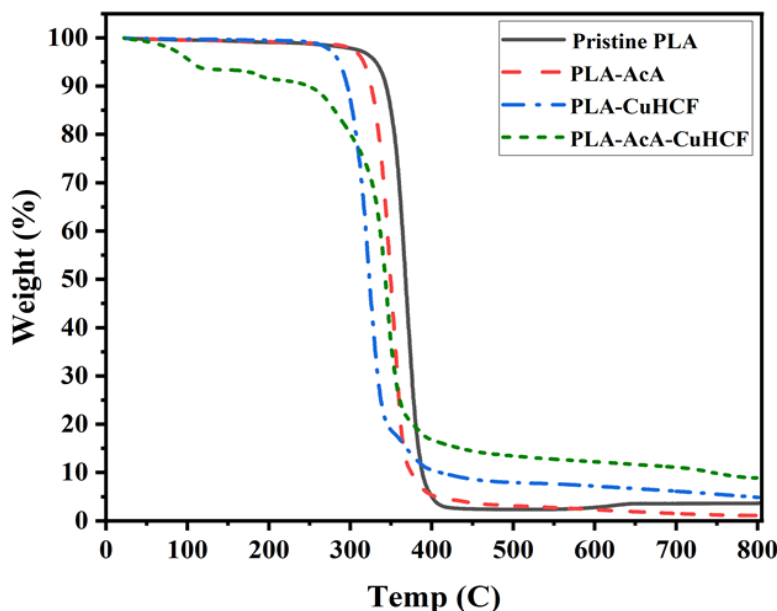


Fig. 4 Thermogravimetric analysis (TGA) curves of pristine PLA, PLA-AcA, PLA-CuHCF, and PLA-AcA-CuHCF filters under N₂ atmosphere.

ICP-MS analysis further confirmed CuHCF immobilization, with Fe and Cu contents of 5.98 wt% and 1.70 wt%, respectively (Table S1). The elevated Fe/Cu ratio (~4:1) is attributed to additional Fe-containing surface species not detectable by XRD [28-30]. Based on Cu content, the CuHCF loading was estimated at ~5.5 wt%, confirming substantial immobilization [31].

Overall, the combined analyses demonstrate that acetone and acrylic acid modification significantly enhance surface roughness, functionalization, and CuHCF loading, resulting in a stable and uniformly coated composite structure.

3.2 Evaluation of ammonium adsorption behavior and mechanism

3.2.1 Effect of surface modification on adsorption performance

A batch adsorption experiment was conducted to compare ammonium removal across pristine PLA, PLA-CuHCF, PLA-Ac-CuHCF, and PLA-AcA-CuHCF (Fig. 5). Pristine PLA showed negligible adsorption due to the absence of active sites. The PLA-CuHCF filter exhibited a very low capacity (~ 0.018 mg/g), reflecting limited CuHCF loading and weak adhesion on the unmodified surface, consistent with structural analyses.

After acetone pretreatment, the adsorption capacity increased to 0.28 mg/g, indicating improved surface roughness and partial enhancement of CuHCF attachment. The PLA-AcA-CuHCF filter demonstrated the highest performance, reaching 1.39 mg/g, nearly five times higher than PLA-Ac-CuHCF.

This significant improvement is attributed to the introduction of $-\text{COOH}$ and $-\text{OH}$ functional groups, which enhance Cu^{2+} coordination and enable uniform in-situ growth of CuHCF, resulting in a dense and accessible active layer for NH_4^+ adsorption.

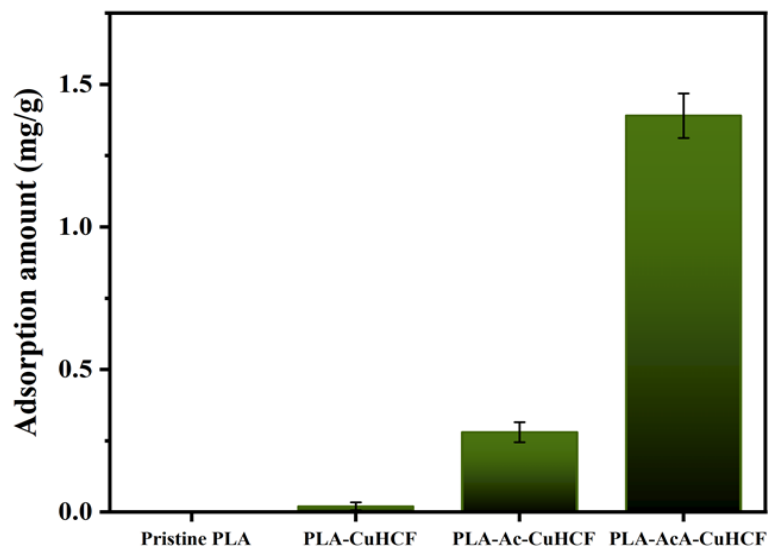


Fig. 5 Single-point ammonium adsorption capacities of pristine PLA, PLA-CuHCF, PLA-Ac-CuHCF, and PLA-AcA-CuHCF filters obtained from batch experiments ($[\text{NH}_4^+]_0 = 10$ mg/L, contact time = 24 h).

Overall, the results confirm that the combined acetone and acrylic acid modification effectively improves CuHCF immobilization and adsorption performance, with PLA-AcA-CuHCF showing the highest efficiency among all samples.

3.2.2 Adsorption kinetics and isotherm analysis

The adsorption behavior of NH_4^+ onto PLA-AcA-CuHCF was evaluated through kinetic and isotherm experiments (Fig. 6). Rapid adsorption occurred within the first 10 min, reaching 1.24 mg/g, followed by a gradual approach to equilibrium with a maximum capacity of 1.38 mg/g after 24 h. The fast-initial uptake indicates that most active sites are readily accessible, while the stable performance confirms strong CuHCF attachment and structural integrity.

Kinetic data were fitted using pseudo-first-order (PFO) and pseudo-second-order (PSO) models (Table S2). Although both models showed high correlation ($R^2 = 0.999$), the PSO model provided a better fit with lower RMSE and a predicted equilibrium capacity (1.383 mg/g) consistent with experimental results. This suggests that adsorption is primarily governed by chemical interactions, such as ion exchange between NH_4^+ and the CuHCF lattice.

Isotherm analysis (Fig. 6b) showed that the Langmuir model better described the adsorption behavior ($R^2 = 0.989$) compared to the Freundlich model ($R^2 = 0.968$), indicating monolayer adsorption on a relatively homogeneous surface. The maximum adsorption capacity (q_m) was 1.914 mg/g, and the separation factor ($R_L = 0.606$) confirmed favorable adsorption ($0 < R_L < 1$) (Text S2).

When normalized based on the CuHCF content (5.5 wt%), the adsorption capacity corresponded to 34.8 mg/g (1.93 mol/kg), which is comparable to reported values for powdered CuHCF [8,33–35]. This indicates that the immobilized CuHCF retains its intrinsic adsorption performance without significant mass-transfer limitations.

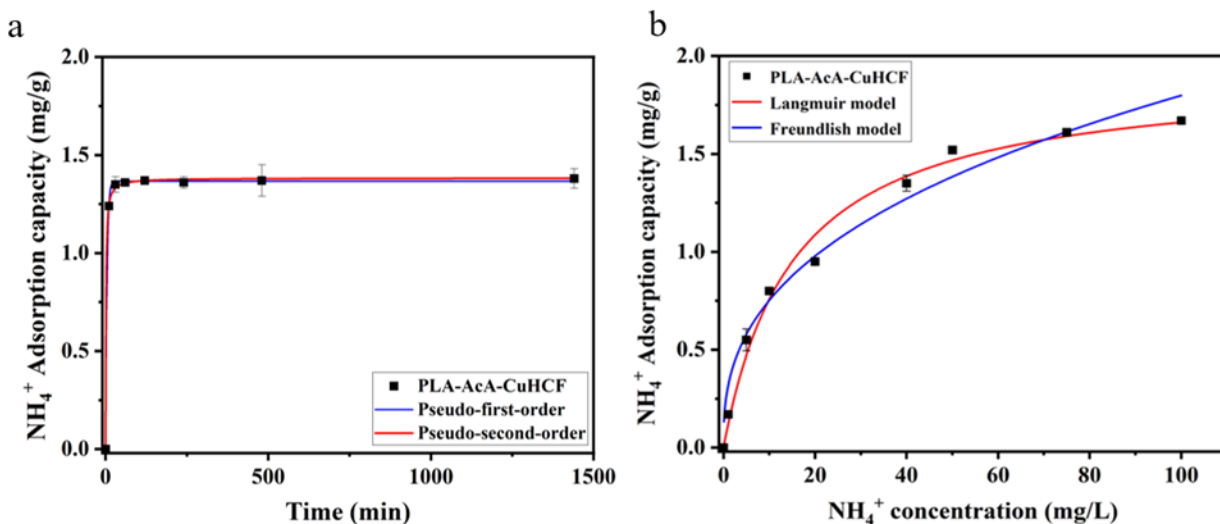


Fig. 6 (a) Ammonium adsorption kinetic curves of PLA-AcA-CuHCF with fitting results from PFO and PSO kinetic models, (b) Ammonium adsorption isotherm curves of PLA-AcA-CuHCF with fitting results using Langmuir and Freundlich isotherm models.

Overall, the results demonstrate that NH_4^+ adsorption is rapid, favorable, and dominated by ion-exchange interactions within the CuHCF framework, with the modified PLA scaffold providing accessible and uniformly distributed active sites [36,37].

3.2.3 Selectivity and ion-exchange mechanism

The selectivity of the PLA-AcA-CuHCF filter was evaluated using a mixed solution containing NH_4^+ , Na^+ , K^+ , Li^+ , and Cs^+ (10 mg/L each) (Fig. 7). The filter maintained a high adsorption capacity for NH_4^+ (~1.0 mg/g) in the presence of Na^+ and Li^+ , indicating minimal interference from these ions.

In contrast, the presence of K^+ and Cs^+ led to a noticeable reduction in NH_4^+ removal, demonstrating strong competitive effects. This behavior is attributed to their similar hydrated ionic radii to NH_4^+ , which allows them to access the interstitial sites of the CuHCF lattice through comparable diffusion pathways [38]. In particular, Cs^+ shows stronger lattice affinity and preferential occupation of vacancy sites, resulting in more significant competition for active sites [39]. Additionally, comparable hydration energies of K^+ and Cs^+ facilitate partial dehydration, further enhancing their ability to compete with NH_4^+ during ion-exchange processes [38,40].

Overall, the results confirm that CuHCF exhibits strong selectivity toward NH_4^+ , with competitive effects primarily governed by ionic size and hydration properties, making it suitable for ammonium removal in multi-ion systems.

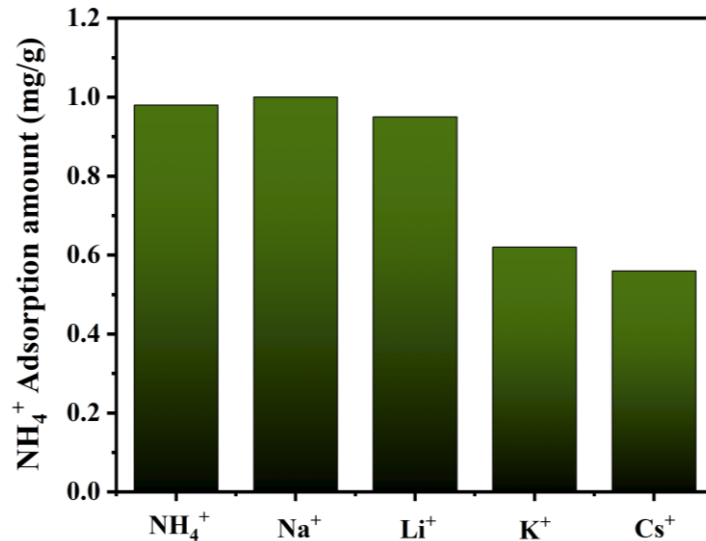


Fig. 7 Adsorption selectivity of the PLA-AcA-CuHCF filter toward NH_4^+ in the presence of coexisting monovalent cations (Na^+ , K^+ , Li^+ , and Cs^+) at equal concentrations (10 mg/L, contact time = 24 h).

3.3 Regeneration, continuous operation, and practical implications

3.3.1 Desorption and reusability

The desorption performance of the PLA-AcA-CuHCF filter was evaluated using NaCl and KCl solutions (Fig. 8a). Desorption efficiency increased with salt concentration, confirming a concentration-dependent ion-exchange mechanism. KCl showed superior performance, achieving ~75% desorption at 0.1 M and >95% at 1 M, whereas NaCl was less effective under identical conditions. This difference is attributed to the closer hydrated ionic radius of K^+ (3.31 Å) to NH_4^+ , which facilitates ion exchange within the CuHCF lattice, while Na^+ is less compatible due to its larger radius [41].

Reusability was assessed over five adsorption-desorption cycles using 10 mg/L NH_4^+ and 1 M KCl (Fig. 8b). The desorption efficiency remained stable between 84–88% with negligible performance loss, indicating good regeneration stability. Post-cycle characterization (Fig. S1) confirmed that the CuHCF structure and its immobilization on the PLA scaffold remained intact, with no significant degradation or particle loss.

These results demonstrate that the PLA-AcA-CuHCF filter exhibits high regeneration efficiency and structural stability, supporting its suitability for repeated use in ammonium recovery applications.

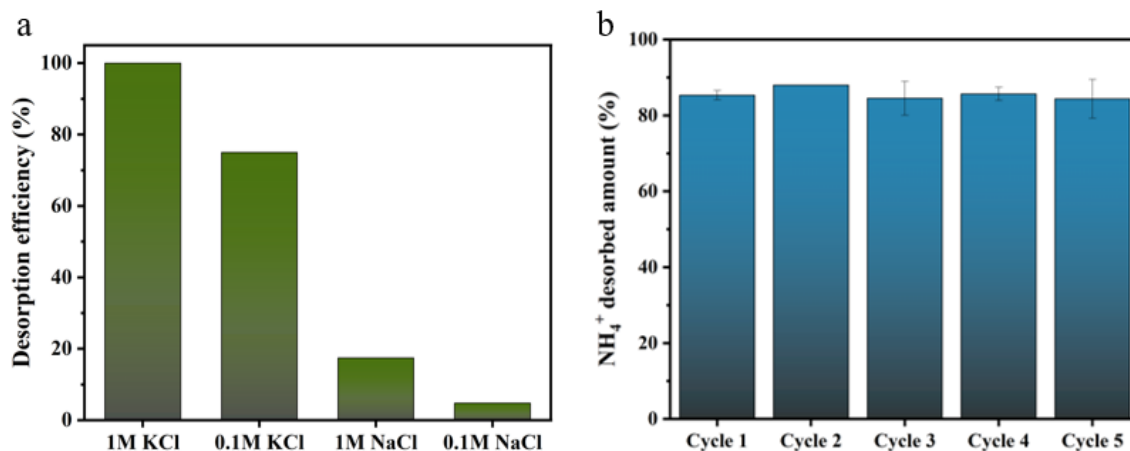


Fig. 8 (a) Desorption efficiency of NH_4^+ from the PLA-AcA-CuHCF filter using NaCl and KCl solutions at different concentrations (0.1 M and 1 M). (b) Reusability performance of the PLA-AcA-CuHCF filter over five consecutive adsorption-desorption cycles (adsorption: 10 mg/L NH_4^+ , 24 h; desorption: 1 M KCl, 8 h).

3.3.2 Continuous operation

The continuous adsorption performance of the PLA-AcA-CuHCF filter was evaluated using a fixed-bed column (Fig. 9a). During the first 10 h, the breakthrough ratio (C_t/C_0) remained below 0.2, corresponding to >80% NH_4^+ removal. The half-breakthrough point

($C_t/C_0 = 0.5$) occurred at ~ 20 h, and a plateau ($C_t/C_0 \approx 0.85\text{--}0.9$) was reached after ~ 40 h. Even after 100 h of operation, complete saturation was not observed, indicating stable performance under continuous flow. The incomplete saturation is attributed to the relatively short empty-bed contact time (EBCT ≈ 12 min), which limits full utilization of adsorption sites under dynamic conditions. The total ammonium uptake was 1.2 mg, and the breakthrough behavior was well described by the Thomas model ($R^2 = 0.97$), confirming predictable adsorption kinetics.

In-column regeneration using 1 M KCl (Fig. 9b) resulted in rapid NH_4^+ desorption, with C_t/C_0 reaching ~ 0.9 within 5 h, followed by near-complete elution. The total recovery reached $\sim 97\%$ after 25 h.

These results demonstrate that the PLA-AcA-CuHCF filter maintains stable adsorption performance and enables efficient in-situ regeneration under continuous-flow conditions, highlighting its potential for practical ammonium recovery.

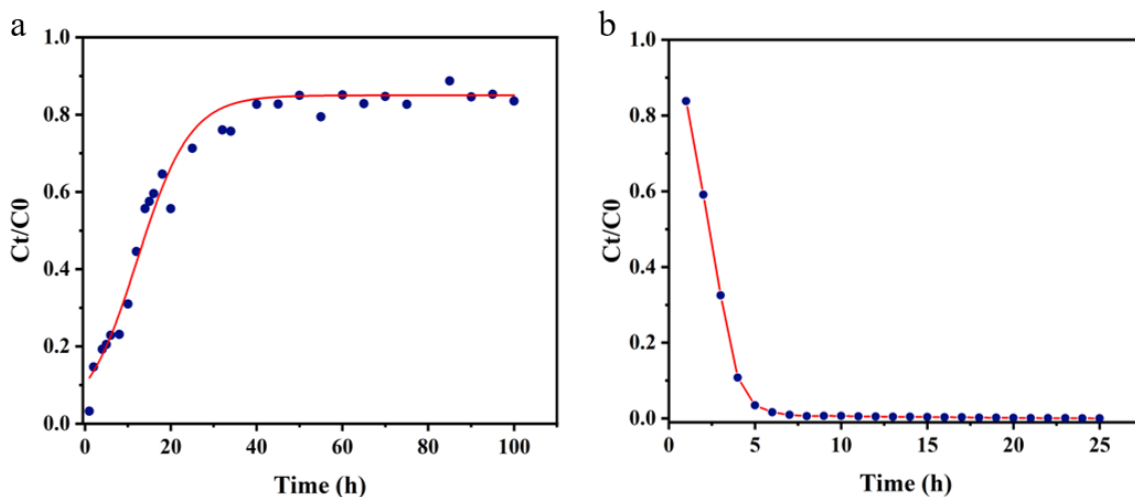


Fig. 9 (a) Breakthrough curve (C_t/C_0) for continuous NH_4^+ adsorption using the PLA-AcA-CuHCF filter (influent concentration = 1 mg/L, flow rate = 0.2 mL/min). (b) Desorption profile (C_t/C_0) during regeneration with 1 M KCl solution (flow rate = 0.1 mL/min).

3.3.3 Practical significance and sustainability perspective

This study demonstrates that the PLA-AcA-CuHCF filter is an effective and stable platform for ammonium removal and recovery. The combination of acetone and acrylic acid modification enabled strong surface functionalization, resulting in high CuHCF loading (~ 5.5 wt%) and durable immobilization on the 3D-printed PLA scaffold.

The structured filter exhibited clear practical advantages over conventional adsorbents, including easy handling, low pressure drops, and stable operation under continuous flow. It maintained efficient NH_4^+ removal for over 100 h and achieved $\sim 97\%$ recovery using 1 M KCl, with consistent regeneration performance over multiple cycles. The use of biodegradable PLA and the ability to recover ammonium as a reusable resource further support its relevance for sustainable water treatment and circular nitrogen management [42-44].

Overall, the results highlight the potential of combining 3D printing, surface modification, and in-situ CuHCF growth to develop robust and reusable adsorbents. While challenges such as competing ions and complex wastewater matrices remain, this platform provides a promising foundation for scalable and efficient ammonium recovery systems.

4. Conclusion

This study presents an effective strategy for selective ammonium removal using a surface-engineered 3D-printed PLA filter functionalized with copper hexacyanoferrate (CuHCF). The dual-step modification, consisting of acetone pretreatment and acrylic acid grafting, enabled enhanced surface functionality and stable immobilization of CuHCF on the PLA scaffold.

The resulting PLA-AcA-CuHCF filter exhibited rapid adsorption kinetics, a maximum capacity of 1.91 mg/g, and high selectivity in the presence of competing monovalent ions. Structural characterization confirmed uniform CuHCF distribution and strong interfacial stability, which contributed to consistent performance. Under continuous-flow conditions, the filter maintained stable operation for over 100 h and achieved regeneration efficiencies exceeding 90% across multiple cycles, demonstrating its durability and reusability.

Overall, the combination of 3D printing, surface modification, and in-situ CuHCF growth provides a practical platform for developing structured and reusable adsorbents. While challenges remain in complex wastewater systems, this approach offers a promising pathway for scalable and energy-efficient ammonium recovery.

Acknowledgments

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