

Cite this: *RSC Appl. Polym.*, 2026, **4**, 626

Functionalized nanocellulose for efficient removal of ammonium impurities from contaminated water

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Carboxycellulose nanofibers with carboxylate functionality are a promising material for a multitude of applications, including environmental remediation. In this paper, we present an in-depth systematic study on the application of TEMPO-oxidized CNFs for ammonium removal, demonstrating their versatility against a broad range of ammonium impurities (5–5000 ppm) using both simulated and real contaminated water. The efficiency of CNFs was tested under various conditions, including the amount of CNFs, pH, and time. The results showed that CNFs follow both the Langmuir and the Freundlich isotherm models with good fitting, indicating their monolayer as well as multilayer adsorption mechanism. Furthermore, characterization using FTIR, SEM/EDS, and adsorption and kinetic analyses employing various models reveals that chemisorption is the dominant mechanism of ammonium adsorption by CNFs. The Langmuir isotherm model, when fitted to adsorption data gathered for original ammonium impurities in the range of 5–5000 ppm using CNFs, yielded a maximum adsorption capacity of 303.3 mg g⁻¹. Additionally, this study includes a technical application to remove ammonium impurities from real contaminated fish water, with results indicating an average removal efficiency of between 80% and 90%. We have also developed an in-house flotation remediation system (FRS) to address handling and collection issues related to CNFs and used CNFs. Hence, this study presents a comprehensive and sustainable approach to addressing the most significant ammonium nutrient problem, utilizing the most abundant, scalable, and eco-friendly plant-based material.

Received 3rd July 2025,
Accepted 15th November 2025

DOI: 10.1039/d5lp00201j

rsc.li/rscaplpolym

Introduction

Several factors, including the ever-increasing human population, expansive industrial activities, and the subsequent rapid development of industries, have been attributed to an increase in the use of anthropogenic ammonia (NH₃) and an increase in ammonium ion (NH₄⁺) deposition in aquatic environments. A considerable amount of NH₄⁺ in the aquatic environment originates from human excreta, which contains nitrogenous compounds metabolized by bacteria into NH₄⁺. Additionally, agricultural runoff, particularly from areas with extensive use of nitrogen-based fertilizers, significantly contributes to NH₄⁺ pollution.¹ Fertilizers rich in NH₄⁺ and

nitrate are applied to crops to enhance growth; however, their significant amounts leach into surface and groundwater, resulting in elevated NH₄⁺ levels in rivers, lakes, and aquifers. Globally, Harmful Algal Blooms (HABs) pose a significant environmental challenge, particularly in nutrient-rich water bodies. These blooms, often caused by cyanobacteria (also known as blue-green algae), thrive in warm, slow-moving waters with high levels of phosphorus and nitrogen.^{2–4} Excess nutrients, primarily from agricultural runoff, lawn fertilizers, faulty septic systems, and wastewater treatment plants, exacerbate this issue.⁵ Phosphorus is the primary driver, as it promotes rapid algal growth, while NH₄⁺ acts as an additional nutrient source, sustaining these blooms. HABs disrupt aquatic ecosystems by blocking sunlight, depleting oxygen levels during decomposition, and releasing toxins harmful to humans, animals, and marine life. Despite implementing Total Maximum Daily Loads (TMDLs) to regulate phosphorus inputs, toxic HABs remain a recurring issue. Continued efforts to reduce nutrient pollution, restore natural shorelines, and promote public education are crucial to safeguarding freshwater ecosystems.^{6,7}

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In industrial settings, NH_4^+ concentrations in wastewater can vary significantly, with levels often exceeding regulatory limits. For instance, municipal wastewater has NH_4^+ concentrations ranging from 27 to 100 mg L^{-1} . Fish-processing waste has NH_4^+ concentrations ranging between 8 and 42 mg L^{-1} . In domestic wastewater, the NH_4^+ concentration typically ranges from 39 to 60 mg L^{-1} .⁸ Fertilizer production, food processing facilities, and similar industries frequently have NH_4^+ concentrations ranging from 5 to 1000 mg L^{-1} .^{8,9} These values increase depending on the type of processing industry, typically reaching as high as 2945 mg L^{-1} . NH_4^+ plays a crucial role in both aquatic and terrestrial environments, particularly within the nitrogen cycle.⁸ It can exist in equilibrium with ammonia (NH_3) in aqueous solutions, and the equilibrium between NH_4^+ and NH_3 is highly dependent on pH. At lower pH levels, NH_4^+ is predominant, while at higher pH levels, NH_3 dominates.¹⁰ NH_4^+ in drinking water poses significant health risks. For example, it can react with chlorine during water treatment processes to form chloramines, which can exacerbate asthma symptoms due to excessive exposure to trichloramine.¹¹ Additionally, when NH_4^+ is oxidized to nitrite in the human body, it can interfere with the oxygen-carrying capacity of hemoglobin, particularly in infants, leading to methemoglobinemia, commonly known as “blue baby syndrome”.¹² Therefore, there is an urgent need to address NH_4^+ in wastewater in a sustainable manner.

It can be removed through various methods, including biological treatment, adsorption techniques,^{13,14} and chemical precipitation. Adsorption is the most promising technique investigated for removing NH_4^+ from wastewater. Unfortunately, this technique is often marred by a lack of suitable and viable adsorbent materials. According to Han *et al.*,¹⁵ this challenge is further aggravated by the need to find efficient, affordable, abundant, and sustainable materials. Consequently, different avenues have been explored, including modifying adsorption techniques to accommodate various materials. Wang *et al.*¹⁶ reported that physical activation and chemical modification are the most prominent avenues for enhancing the performance of ion exchange mechanisms based on readily available adsorbent materials. For instance, the authors sought to examine whether physical activation could enhance the adsorption method for removing NH_4^+ using forestry waste.^{17,18} Several recent studies have focused on the adsorption of ammonium using activated carbon (AC).¹⁸ In addition to this, a few more carbon adsorbents, such as cellulose acetate membrane, AC derived from bacterial cellulose,¹⁸ and cellulose sulfate,¹⁹ have been used to address the NH_4^+ problem. To the best of our knowledge, none of the studies have in-depth discussed the use of carboxylated cellulose nanofibers (CNFs) for the remediation of NH_4^+ pollutants from real and simulated water, and have not provided a practical solution to tackle this problem sustainably. In this study, we have done a systematic in-depth study to apply the CNFs to remediate the NH_4^+ pollutant from the simulated and real water (from the aquaponic tank), followed by the development of a floatation remediation system (FRS) to ease the

handling and to provide the viability of the CNFs adsorbent system for all types of contaminated water sources.

Experimental section

Materials and instruments

TEMPO-oxidized cellulose nanofibers extracted from the forest biomass with a concentration of 1.04 wt% and a carboxylate (COO^-) content of 1.15 mmol g^{-1} were procured from the University of Maine. Analytical ammonium nitrate (ACS reagent, 99%) and sodium bicarbonate (ACS reagent, $\geq 99.7\%$) were purchased from Sigma-Aldrich. Sodium hydroxide (ACS reagent, $\geq 97.0\%$) pellets and hydrochloric acid (ACS grade, 36.5–38%) were purchased from Fisher Scientific. An ammonium ion-selective electrode was used to measure the concentration of NH_4^+ . The following instruments were used in this study.

Fourier transform infrared spectrometry (FTIR): A ThermoFisher instrument (ThermoFisher Scientific, U.S.A.) was used to record the FTIR spectra in transmission mode, between 4000 to 450 cm^{-1} . A total of 12 scans were taken per sample with a resolution of 4 cm^{-1} . The solid samples were recorded in attenuated total reflectance (ATR) mode.

The JEOL 7500F ultra-high-resolution scanning electron microscope, equipped with a cold-field emission emitter, was used to examine the morphology of CNFs. Zeta potential measurements on CNFs samples were performed using MÜtek™ PCD-06, Particle Charge Detector.

Preparation of ammonium solutions

A 5000 ppm NH_4^+ stock solution was prepared by dissolving 22.22 g of NH_4NO_3 in 1 L of deionized water. Serial dilutions were made to range from 5000 to 5 ppm for use in adsorption studies.

Preparation of cellulose nanofibers (CNFs) suspension

CNFs suspension was prepared using commercial TEMPO-oxidized CNFs gel at an initial concentration of 1.04% (wt%) with carboxylate (COO^-) content of 1.15 mmol g^{-1} . The CNFs were diluted to 0.5% (wt%) by adding deionized water under continuous stirring. The suspension was homogenized to ensure an even distribution of the nanofibers. This CNF's suspension was used as an adsorbent for the NH_4^+ adsorption experiments.

Remediation studies using simulated water

The concentration of active NH_4^+ in the solution was determined using an ion-selective electrode. For the adsorption capacity experiments, 5 mL of CNFs suspension was mixed with 5 mL of NH_4^+ solution (prepared from ammonium nitrate) in a test tube. In this study, NH_4^+ concentration is reported as parts per million (ppm) of NH_4^+ to maintain consistency with other studies that may employ different NH_4^+ salts. However, the specific NH_4^+ salt used is noted to account for any potential counter-ion effects.



For all experiments except the time study, the solution was stirred for 1 minute and then incubated at room temperature for 24 hours. After incubation, the samples were filtered using a syringe filter with a 0.22 μm pore size, showing effective separation. The filtrate was then analyzed for NH_4^+ concentration using an ion-selective electrode. To ensure that the syringe material did not contribute to NH_4^+ adsorption during the experiment, a control test was conducted. A solution of NH_4^+ with an initial concentration of 500 ppm was prepared and passed through the syringe without any additional materials or treatments inside. The difference in concentration was negligible, confirming that the syringe material did not significantly interfere with the adsorption of NH_4^+ .

pH study

To study the effect of pH on adsorption capacity, the pH of the NH_4^+ was adjusted to the desired levels using dilute sodium hydroxide or hydrochloric acid. After pH adjustment, the solutions were mixed with a 0.5% CNFs suspension at a 1 : 1 ratio. The mixtures were then incubated at room temperature for 24 hours.

Time study

Additionally, a study assessed the adsorption capacity over different incubation times ranging from 0.5 to 48 hours using an initial NH_4^+ concentration of 500 ppm. The NH_4^+ concentration in the filtrate was measured at each time point to evaluate the effect of contact time on adsorption efficiency.

Remediation studies using real water

The contaminated water was collected from the real fish tank located in the Greenhouse Facility at Western Michigan University's Department of Biology. The water was collected directly from the tank before it passed through the *in situ* filtration. The NH_4^+ concentration before and after adsorption using a CNFs suspension was determined using an NH_4^+ test kit, followed by quantitative measurement using UV-adsorption. The details are mentioned in the SI.

Floc separation procedure

The floc term refers to the gel material that forms when CNFs interact with NH_4^+ impurities, causing the suspended CNF

fibers to clump together into a lumpy gel. The separation of the floc was performed in the following steps. A 5 mL suspension of 0.5 wt% CNFs having COO^- groups was mixed with 5 mL of NH_4^+ solution prepared from NH_4NO_3 for simulated water testing at different concentrations from 5000 to 5 ppm (SI) in a test tube. In contrast, the water collected from the fish tank contained its own NH_4^+ impurities (SI). The solution was gently shaken for 1 minute and then incubated at room temperature for 24 hours to neutralize the charges and initiate the aggregation of CNFs and adsorbed NH_4^+ into flocs. For separation, the flocs were filtered through a vacuum filtration system equipped with a 0.45 μm membrane filter (Fig. 1). The retained flocs on the membrane were oven-dried and analyzed for further characterization.

Results and discussion

Chemical and morphological properties

The FTIR analysis (Fig. 2A), conducted at the dry stage, reveals significant changes in the functional groups of CNFs after exposure to NH_4^+ , confirming ion exchange as the dominant interaction mechanism. The broad O–H stretching peak around 3338 cm^{-1} in CNFs exhibits slight shifts and intensity reductions, which can be attributed to overall hydrogen bonding alteration due to the interaction of NH_4^+ ions. A notable decrease in the intensity of the ($-\text{COO}^-$) stretching peak near 1599 cm^{-1} in CNFs suggests the involvement of $-\text{COO}^-$ groups in the binding with NH_4^+ ions. Additionally, in the floc sample containing CNFs + NH_4^+ , the emergence or intensification of a peak around 1578 cm^{-1} in the N–H bending vibration provides direct evidence of NH_4^+ binding to the CNFs. The C–O stretching peak at approximately 1176 cm^{-1} in CNFs also shows changes in intensity and position, indicative of interactions between NH_4^+ and ester or carboxyl groups on the CNFs structure. These spectral changes collectively validate that NH_4^+ ions are adsorbed onto CNFs through an ionic interaction process between the carboxylate and ammonium groups (Fig. 2B), followed by changes in the hydrogen bonding in CNFs as evident by the changes in the O–H stretching vibration at 3338 cm^{-1} .²⁰ The observations emphasize the crucial role of the carboxyl and hydroxyl groups in facilitating effective NH_4^+ adsorption, making CNFs a promising material for wastewater remediation.^{21–28} FTIR analysis

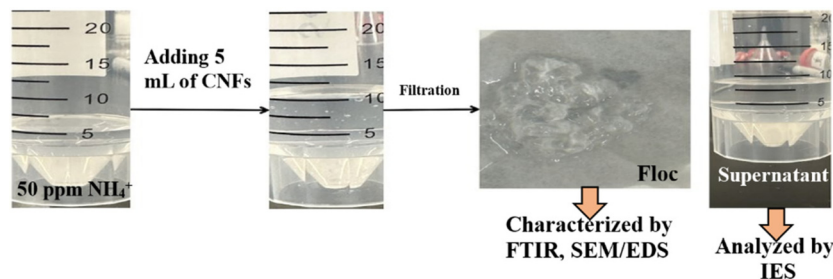


Fig. 1 Demonstration of floc preparation and separation of supernatant from the floc for further characterization.





Fig. 2 (A) FTIR of CNFs and floc (CNFs and NH_4^+), (B) schematic of the mechanism of CNFs and NH_4^+ interaction.

(Fig. 3) was further supported by the morphological changes that occurred before and after the NH_4^+ interactions on CNFs.

The morphological analysis conducted *via* SEM/EDS reveals significant structural changes in CNFs as the concentration of NH_4^+ varies. One hundred fibers were selected from each image, and their dimensions were measured using ImageJ software to ensure statistical reliability. Pristine CNFs (Fig. 3A and Fig. S1 in SI) exhibited a maximum fiber diameter between 15.4 and 18.1 nm. However, after exposure to 5 ppm

NH_4^+ (Fig. 3B and Fig. S1 in SI), the range increased to 19.7–22.8 nm, indicating swelling of the individual fibers. Notably, when the CNFs were further exposed to a higher concentration of 5000 ppm NH_4^+ (Fig. 3C and Fig. S1 in SI), the range increased to 21.3 and 24.8 nm, demonstrating substantial structural changes due to the intake of NH_4^+ . The swelling of individual cellulose fibers illustrates the mechanism of NH_4^+ removal, which can be explained by (i) an ion-exchange mechanism: the size of the NH_4^+ ion is 140 pm, which is



Fig. 3 SEM images of CNFs at different NH_4^+ concentrations, (A) CNFs; (B) CNFs + NH_4^+ (5 ppm); (C) CNFs + NH_4^+ (5000 ppm); (D) A, B, C respective EDS spectra.



larger than that of Na (95 pm) or H (0.208 nm). The Na^+ or H^+ is associated with the carboxyl ($-\text{COO}^-$) groups on the CNFs. During the interaction of CNFs and NH_4^+ ions for remediation, the increase in fiber diameter indicates the NH_4^+ ions replacement with the CNF's carboxyl counterions. These results are consistent with the FTIR results, further supporting ion exchange and indicating ionic interactions. This ion exchange corresponds to the absorption phenomenon. Hence, different isotherm models, as presented in the adsorption studies section, are used to analyze the adsorption efficiency of CNF fibers. (ii) Absorption: Typically, the CNF's fiber width is between 4 and 6 nm. Here, the CNFs we have used have a maximum diameter between 15.4 and 18.1 nm, indicating that CNFs still retain a layered structure, which may have led to the absorption of impurities on the CNFs. The EDS analysis (Fig. 3D) depicts significant changes in the elemental composition of CNFs before and after NH_4^+ adsorption. Initially, the pristine CNFs sample (Fig. 3D) contains 7.9 wt% of sodium (Na), with no detectable nitrogen (N) present. After exposure to 5 ppm NH_4^+ (Fig. 3D), the wt% of Na decreases to 3.4 wt%, while nitrogen appears at 21.9 wt%, indicating the successful adsorption of NH_4^+ ions onto the CNF's surface. This trend changes at 5000 ppm NH_4^+ (Fig. 3D), where Na increases to 10.1 wt%, and nitrogen decreases to 17.7 wt%. This indicates that at a higher concentration of NH_4^+ , absorption is more dominant than ion exchange. To confirm these results further, elemental analysis is recommended. The indication of nitrogen in the elemental composition strongly supports the intake of NH_4^+ , highlighting CNF's effectiveness as an adsorbent for NH_4^+ removal in wastewater treatment. We have also performed zeta potential measurements to investigate the change in surface charges of CNFs upon interaction with different NH_4^+ impurities. The results indicate that the surface charge of CNFs at a concentration of 0.0125 w% showed a charge of $-418.5 \mu\text{g L}^{-1}$. When 5 ppm NH_4^+ was added, the charge decreased to $-283.8 \mu\text{g L}^{-1}$, and further addition of 250 ppm NH_4^+ reduced the surface charge to $-222.6 \mu\text{g L}^{-1}$. This trend

of decreasing the surface charge of CNFs with an increase in ammonium concentration further evidences the presence of ionic interactions between these two functionalities.

Adsorption studies

pH study. In this study, the removal of NH_4^+ was significantly influenced by the solution's pH (Fig. 4A and Table S1 in SI), which affects the equilibrium between NH_4^+ and NH_3 . At lower pH values, NH_4^+ is the dominant species, which facilitates electrostatic attraction between the positively charged NH_4^+ and the negatively charged surface (COO^-) of CNFs, leading to higher adsorption efficiency. However, at pH 3, the removal efficiency was only 7%, despite NH_4^+ being the predominant species. This low removal efficiency can be attributed to the fact that at pH 3, the solution contains a high concentration of free H^+ ions. These H^+ ions compete with NH_4^+ for the active adsorption sites on the adsorbent surface. Since H^+ ions are more abundant, they preferentially occupy the available sites, further reducing the ability of NH_4^+ to be adsorbed. As a result, both electrostatic repulsion and competition for adsorption sites contribute to the low removal efficiency of NH_4^+ at this pH level.

As the pH increased from 3 to 7, the removal efficiency increased, reaching a peak of 98% at pH 7, corresponding to the highest concentration of NH_4^+ and a favorable interaction between the adsorbent surface and the NH_4^+ . Beyond pH 7, the removal efficiency plateaued at around 85% and slightly decreased due to the deprotonation of NH_4^+ to NH_3 , which is neutral and, therefore, less effectively adsorbed onto the adsorbent surface. Additionally, the adsorbent surface began to turn non-ionic (COONa), which decreased the number of COO^- groups available for interaction with NH_4^+ , further reducing the removal efficiency. However, at pH 9, it still maintained a removal efficiency of 85%.

Effect of adsorbate dose. The influence of CNFs dosage on NH_4^+ removal efficiency (Fig. 4B and Table S2 in SI) reveals a notable trend: as the CNFs weight percentage increases, the



Fig. 4 (A) Effect of initial pH on the removal efficiency of NH_4^+ ; (B) effect of adsorbent dose on NH_4^+ removal.



removal efficiency significantly improves, peaking at approximately 78.4% with a 1% CNFs dosage. Notably, no pH adjustment was done for this experiment. This enhancement is attributed to the rise in active adsorption sites that accompany a higher amount of CNFs, facilitating a more effective capture and removal of NH_4^+ from the solution. An increased CNFs dosage results in a larger surface area, providing more binding opportunities for NH_4^+ and enhancing adsorption and absorption performance. However, it is essential to note that while the removal efficiency increases with higher CNFs dosages, the equilibrium adsorption capacity (Q_e) exhibits a decreasing trend (Fig. 5A). The calculations for Q_e and equilibrium concentration (C_e) are presented in SI, Table S3. For instance, at a 0.25% CNFs concentration, the removal efficiency is only 34.4%, but the Q_e is relatively high at 67.6 mg g^{-1} (Table S2, SI). As the CNF dosage increases to 1.0%, the removal efficiency rises to 78.4% while Q_e decreases. This behavior occurs because, with higher CNF dosage, there are more active

adsorption sites than NH_4^+ in the solution, resulting in under-utilization of the available sites. Consequently, the amount of NH_4^+ adsorbed per unit weight of CNFs (Q_e) decreases despite the overall improvement in removal efficiency.

It is also important to emphasize that the increase in removal efficiency begins to stabilize at higher CNF concentrations, as outlined in Fig. 4B and Table S2 of the SI. This indicates that, beyond a certain point, the efficiency is not simply limited by the number of available active sites. Instead, factors such as site saturation, diffusion limitations, and potential agglomeration of CNFs at elevated concentrations can influence effectiveness by reducing the available surface area for interaction. Therefore, after the 1.0% dosage, further increases in CNFs are unlikely to yield significant improvements in removal efficiency, underscoring the importance of optimizing the dosage to achieve excellent results.

Equilibrium adsorption capacity (Q_e) of CNFs. The effect of NH_4^+ concentration on the adsorption capacity of CNFs reveals a significant and compelling trend, as shown in Fig. 5A. As the initial concentration of NH_4^+ increases, the Q_e of CNFs shows a substantial rise. At lower concentrations, specifically within the 0 to 1000 mg L^{-1} range, Q_e experiences a sharp ascent, reaching approximately 120 mg g^{-1} . This notable increase suggests that many active sites on the CNF's surface are readily available for efficient adsorption. As the concentration increases from 1000 to 5000 mg L^{-1} , Q_e rises at a slower and more gradual pace, ultimately achieving a value of around 250 mg g^{-1} . This trend indicates that the active sites on the CNFs are progressively approaching saturation. The line on the graph in Fig. 5A represents a predicted trend that is relatively close to the experimental data, confirming the reliability of the results. This agreement not only reflects the reliability of the adsorption effect but also demonstrates the effectiveness and versatility of CNFs as an adsorbent agent. This alignment highlights the reliable nature of the adsorption behavior and underscores the exceptional performance and diverse abilities of CNFs as an effective adsorbent material. These findings demonstrate that CNFs are a highly effective medium for capturing NH_4^+ across a range of concentrations. Its impressive adsorption capacity diminishes only as the active sites near full occupancy. This behavior is characteristic of adsorption processes, where an initial solid driving force, resulting from electrostatic interactions, facilitates rapid molecular uptake *via* ion-exchange, which gradually slows as equilibrium is reached. Utilizing CNFs as an adsorbent presents a strategic and effective solution for efficiently removing NH_4^+ .

Adsorption isotherm. The adsorption behavior of NH_4^+ onto CNFs was investigated at various concentrations and analyzed using Langmuir and Freundlich isotherm models (Fig. 5A, B, Table 1, and Tables S3, S4 in SI). The Langmuir model revealed a maximum adsorption capacity (Q_m) of 303.03 mg g^{-1} , accompanied by a Langmuir constant (K_L) of 0.0033 L mg^{-1} , indicating a highly efficient monolayer adsorption process.²⁹ In contrast, the Freundlich model displayed a heterogeneity index (n) of 0.8211, suggesting a particularly favorable adsorption process on a heterogeneous surface, especially at lower

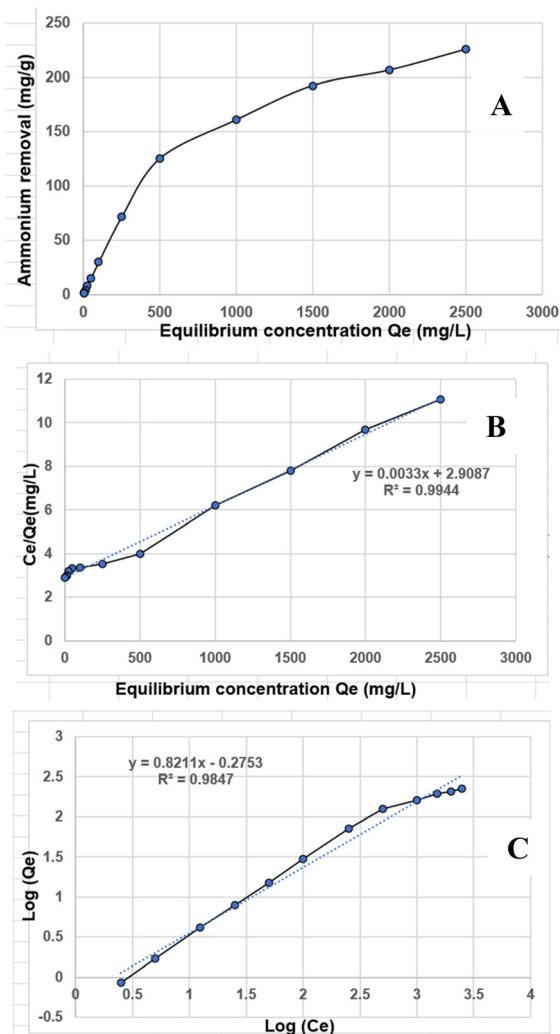


Fig. 5 (A) Relationship between NH_4^+ removal and equilibrium concentration; (B) Langmuir isotherm for NH_4^+ removal using CNFs; (C) Freundlich isotherm for NH_4^+ removal using CNFs.



Table 1 Isotherm model parameters for NH_4^+ adsorption using CNFs

Isotherm model	Parameter	Value
Langmuir model	Maximum adsorption capacity (Q_{max})	303.03 mg g^{-1}
	Langmuir constant (K_L)	0.0033 L mg^{-1}
	R^2	0.9944
Freundlich model	Freundlich constant (K_F)	0.302 mg g^{-1} (L mg^{-1}) $^{1/n}$
	Heterogeneity index (n)	0.8206
	R^2	0.9847

NH_4^+ concentrations. The high R^2 values of 0.9944 for the Langmuir model and 0.9847 for the Freundlich model demonstrate an excellent fit for both models, emphasizing the involvement of adsorption (ion-exchange) and absorption (due to multilayered CNFs) in the removal of NH_4^+ using CNFs. The adsorption efficiency values in Tables S3 and S4 of the SI provide further insight into this mechanism. This suggests that at concentrations of 250 ppm and above, adsorption may be predominantly dominated by monolayer interactions due to the high concentration of impurities. In contrast, at lower concentrations (5–500 ppm), multilayered adsorption is a more pronounced mechanism, probably due to increased diffusion facilitated by lowered concentration of NH_4^+ impurities, reflecting the complex and adaptive surface chemistry of CNFs. The linearized Langmuir plot C_e/Q_e vs. C_e (Fig. 5B) showed a clear linear trend with an R^2 value of 0.9944, confirming the reliability of the Langmuir model in describing the adsorption behavior. On the other hand, the Freundlich model (Fig. 5C) offered valuable insights into adsorption at lower concentrations. It provided a heterogeneity index (n) of 0.8211 and a Freundlich constant (K_F) of 0.302 (L mg^{-1}) $^{(-1/n)}$, emphasizing the varied nature of the CNFs' surface. The Freundlich plot ($\log(Q_e)$ vs. $\log(C_e)$) also showed a strong fit with the experimental data, with an R^2 value of 0.9847. This model reflects the heterogeneous nature of the CNF's surface, where adsorption occurs at sites with varying affinities for NH_4^+ ions. The slope ($1/n$) suggests that the adsorption process is particularly favorable (with a nice fit) at lower NH_4^+ concentrations, where

multilayer adsorption and diverse interactions become significant. These results highlight the dual nature of NH_4^+ adsorption onto CNFs. These findings confirm the potential of CNFs as a robust and adaptable material for wastewater treatment and environmental remediation, capable of effectively responding to changing conditions and ion concentrations.

Adsorption kinetics. The adsorption kinetics of NH_4^+ removal using CNFs were evaluated using the Q_t vs. T and T/Q_t vs. T plots. The Q_t versus T plot (Fig. 6A and Tables S5 and S6 in the SI) shows that the adsorption capacity (Q_t) increases from 65 mg g^{-1} to $\sim 85 \text{ mg g}^{-1}$ within the first 24 hours. This rapid increase can be attributed to the high availability of active binding sites on CNFs at the initial stage, resulting in an efficient uptake of NH_4^+ . The peak, which occurs around 24 hours, marks a significant point, as the adsorption capacity begins to decline, dropping to approximately 60 mg g^{-1} by 48 hours. This reduction suggests potential desorption due to competitive inhibition among NH_4^+ . Notably, this peak marks the point at which the adsorption capacity reaches its maximum and begins to decline, indicating the saturation of active binding sites on CNFs. This may also be attributed to possible structural changes in CNFs or the re-equilibration of adsorbed ions back into the solution.

The T/Q_t versus T plot (Fig. 6B) was used to further assess the adsorption kinetics, fitting the pseudo-second-order model, which generally indicates chemisorption involving valence forces or covalent bonding. The high R^2 value of 0.9827 means that the adsorption process is well-described by this model. This suggests that the adsorption of NH_4^+ is rate-limited by the availability of active adsorption sites, following the pseudo-second-order kinetics.³⁰ The linear fit equation suggests a constant rate of 0.0163 g mg^{-1} hour, confirming the steady rate of the adsorption process. These findings align with previous studies, which indicate that nanocellulose materials, particularly CNFs, provide efficient active sites for NH_4^+ adsorption and can be described well using pseudo-second-order kinetics.³¹ The kinetic analysis confirms that CNFs hold significant promise for removing NH_4^+ from wastewater, with the initial stages of the adsorption process being

**Fig. 6** (A) Removal of NH_4^+ over time using CNFs; (B) Pseudo-second-order kinetics for NH_4^+ adsorption by CNFs.

particularly crucial. The potential of CNFs for wastewater treatment is a hopeful sign for the future of environmental science, although optimizing contact time is critical to maintaining high efficiency.

Comparative study. As mentioned earlier, biochar is a promising material to remove a wide range of impurities, including NH_4^+ . Hence, intensive practices have been deployed to increase their efficiency, as shown in Table 2. For example, Zhang *et al.*³³ have used sulfonation to enhance performance. Consequently, the study investigated the capacity of giant reed stalks to strengthen the production of biochar. Study results from Langmuir models determined that the combination of sulfonation and giant reed stalks improved the adsorption efficiency of biochar for NH_4^+ to 4.20–5.19 mg N g^{-1} . Liu and Zhang³⁵ improved their biochar by combining straw powder and soda residue in the co-pyrolysis process. Their findings indicated that industrial soda residue played a crucial role in enhancing the performance of biochar. In a separate study, Qin *et al.*³² investigated the effectiveness of biochar enhancement using bamboo in the ball milling process. The outcomes of batch adsorption models revealed the cost-efficiency and impeccable performance of the ball-milled bamboo biochar (BMBB) with Q_m of 29.9 mg g^{-1} . Khamkeaw *et al.*¹⁸ found that biochar obtained from bacterial cellulose exhibited an increased adsorption rate, with a maximum removal of ammonium ions at 30 °C ranging from 33.5 to 221.4 mg g^{-1} . Other vital materials, such as ion-exchange resin, have also been deployed to tackle the NH_4^+ impurities, for example, MIEX resin and pyridinium-type anion exchange resin have shown removal rates of 98% and 94%, respectively. A report showed the use of cellulose sulfate nanofibers with a maximum removal efficiency of 41.1 mg g^{-1} . Among these reported carbon materials, the CNFs presented in this study showed the maximum removal of 303.3 mg g^{-1} , due to their multilayer structure and surface chemistry, which fit both multilayer and monolayer adsorption models. This is a crucial study that opens up opportunities for applying various types of cellulose fibers to remediate global nutrient pollution.

Demonstration of the technical application of CNFs in a fish tank. The CNFs, like material, appeared in a suspension at a



Fig. 7 Demonstration of (A) FRS in contaminated water and (B) FRS design.

concentration of 0.5 wt%. Based on this study, CNFs can exhibit a maximum removal efficiency (Q_m) of 303.3 mg g^{-1} ; however, a significant challenge to adopting this material for technical applications is the handling, transportation, and recovery from the waste site. Hence, to overcome this problem, in collaboration with our Department of Fine Arts and Design at Western Michigan University, we have developed a flotation remediation system (FRS) as shown in Fig. 7, comprised of following parts: (i) dialysis tube to hold the adsorbent, more specifically, the CNFs-like suspension, (ii) the inlet opening and (iii) the wire gauzes to prevent the solid particles and creatures to prevent the strike with the dialysis tubing. In this study, the selected NH_4^+ impurity has a diameter of 1.5 Å, allowing these ions to travel through the dialysis tubing with a 5 kDa molecular weight cutoff. In contrast, when the same ions come into contact with the CNFs adsorbent, they do not escape back into the (bag) tubing due to the concentration gradient and the binding of NH_4^+ on polymeric CNFs. Due to electrostatic interactions and a concentration gradient, NH_4^+ continues to bind with the CNFs adsorbent until the saturation point is reached. We collected the contaminated fish water from a small aquarium (Fig. S2 and Table S7 in SI) and tested the NH_4^+ concentration before and after the remediation test. Table S7 in SI demonstrates the concentration of

Table 2 Comparative table depicting the NH_4^+ removal using different materials including CNFs

Modification	Removal efficiency	Ref.
Cellulose nanofibers (CNFs)	303 mg g^{-1}	This study
Ultrasonically activated forestry waste biochar	26.28 mg g^{-1}	17
Ball-milled biochar	22.9 mg g^{-1}	32
Sulfonated reed waste biochar	4.20–5.19 mg N g^{-1}	33
MgO-biochar composite	17.5 mg g^{-1}	34
Straw biochar modified by soda residue	3.87 mg g^{-1}	35
Reverse osmosis cellulose acetate membranes	98%	36
Bacterial cellulose activated carbon	33.5–221.4 mg g^{-1}	18
Nitro-oxidized cellulose nanofibers	22.7 mg g^{-1}	27
Cellulose sulfate nanofibers	41.1 mg g^{-1}	19
Crosslinked sulfonated polymer	87%	37
MIEX resin	98%	38
Pyridinium-type anion exchange resin	94.3%	39



NH_4^+ from the fish tank, before and after testing with the CNFs in the dialysis tube using the FRS. We have filled 0.1 g (0.5 wt% CNFs in 20 mL) into the dialysis tubing with a 5 kDa molecular weight cutoff and dipped it in the contaminated water collected from the fish tank. We have done three individual tests using the same stock of contaminated water. The results indicated that the system could absorb 80–90% NH_4^+ from real fish tank water. Fig. S1 in the SI presents the aquaponic system from which the contaminated water was collected. Our focus was on performing remediation of NH_4^+ , so we measured the removal of NH_4^+ alone. The only problem we have noticed with this setup is the air gap that could be maintained in the tube while closing. The presence of this air gap allowed the water to move through the tubing along with NH_4^+ , resulting in dilutions of CNFs in the tube. Still, we have observed a negligible change in the absorption capacity. This demonstrated that dialysis tubing can be an effective option for technically utilizing nanofibers or similar adsorbent materials, such as powders or nanoparticles, to capture impurities in water.

Conclusions

In conclusion, this study provides a critical insight into the effectiveness of CNFs in adsorbing ammonium impurities from simulated and real contaminated water. CNFs with a negative surface charge, in the form of carboxylate groups, effectively removed ammonium impurities, achieving a maximum adsorption capacity of 303.3 mg g⁻¹. Additionally, the removal efficiency increased to 98% at a pH of 7, where the ammonium and ammonia both exist at equilibrium. The adsorption capacity of CNFs was evaluated under various conditions, including the amount of adsorbents, pH changes, time variations, and wastewater sources. The remediation experiment, conducted at an ammonium concentration of 500 ppm using a consistent amount of CNFs with 0.5 wt% under various conditions, provided more realistic results and demonstrated the versatility of CNFs in multiple situations. For example, 0.5 wt% of CNFs with 500 ppm ammonium, when mixed without pH alteration, showed a removal efficiency of 71.20%. In contrast, when the pH of the ammonium solution was altered, a 76.3% removal was observed at pH 5 with the same mixing conditions. The CNFs demonstrated the very high efficiency of 86.4–22.5% ammonium removal when tested against a range from 5 to 5000 ppm, respectively. CNFs are a layered structure with abundant negative surface charge, owing to ammonium removal *via* ion-exchange through the surficial functionality and multilayer adsorption through the layered structure. Therefore, the mechanism obeys both the Langmuir and the Freundlich isotherm models. In summary, CNFs are an eco-friendly, renewable, and sustainable material derived from abundant natural resources, offering tunable functionality and providing an attractive, scalable solution to various environmental remediation studies, with the added benefits of recycling and reusability as shown in this study.

Author contributions

EMAA, SCH, MAM, SM, ARR, JJK, PS, and MK designed the experiments. EMAA, SCH, SM, MAM, and JJK acquired and analyzed the data. The manuscript was compiled, written, and revised by PS, JS, AKS, WB, and SM. All authors gave approval to the final version of the manuscript.

Conflicts of interest

The authors declare that they have no conflict of interest.

Data availability

Data will be made available upon request from the authors. The Supplementary Information file includes Histograms for Figures 3A, B, and C. Effect of pH on ammonium removal efficiency and adsorption. Effect of CNFs dose on ammonium removal efficiency and adsorption capacity. Adsorption efficiency and experimental parameters for NH_4^+ removal using CNFs. Relationship between the values of Q_e and C_e . Effect of time on ammonium removal efficiency and adsorption capacity. Time-dependent adsorption and kinetic parameter values. The initial and final ammonium concentrations of real contaminated fish water tank samples using CNFs in the dilute bag of FRS for remediation. See DOI: <https://doi.org/10.1039/d5lp00201j>.

Acknowledgements

P. R. S. would like to thank the Start-up grant (2023–2026) from the Western Michigan University Department of Chemical and Paper Engineering.

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