In Situ Growth Synthesis of the CNTs@AC Hybrid Material for Efficient Nitrate-Nitrogen Adsorption

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ABSTRACT: Nitrate-nitrogen (NO₃⁻⁻N) is a common pollutant in aquatic environments and causes many environmental issues and health problems. This study successfully applied the activated AC@CNT composite synthesized by CNTs in-situ growth and post-treated by myristyltrimethylammonium bromide (MTAB) for NO₃⁻⁻N adsorption from wastewater. The results show that the highest NO₃⁻⁻N adsorption capacity of AC@CNTs-M was 14.59 mg·g⁻¹. The in-situ growth of CNTs gave a higher specific surface area and more mesoporous volume, while MTAB uniformly occupied part of the pore structure after the modification process. The AC@CNTs-M had more surface functional groups of hydroxyl and carboxyl, which are favorable for the adsorption of NO₃⁻⁻N. The NO₃⁻⁻N adsorption on AC@CNTs-M was best defined by the pseudo-second-order model, and the isothermal analysis shows that NO₃⁻⁻N adsorption is a multiple process with a maximum adsorption capacity of 27.07 mg·g⁻¹. All the results demonstrate the great potential of AC@CNTs-M for NO₃⁻⁻N adsorption from water, especially in acidic wastewater.

1. INTRODUCTION

Nitrate-nitrogen (NO₃⁻⁻N) is a common pollutant in aquatic environments. The growing concentration of water NO₃⁻⁻N has become an environmental issue of global concern because it can pose severe health risks and ecological imbalance, such as cancer, “blue baby syndrome”, and mutagenic. Therefore, it is necessary to take efficient measures to reduce the concentration of NO₃⁻⁻ in water. Traditional technologies, including biological nitrification-denitrification, chemical reduction, and physical adsorption are applied to remove NO₃⁻⁻N from water. Among them, the adsorption method is considered to be one of the most appropriate technologies because of its advantages of simple operation, low sludge production, and relatively low cost. Several porous materials such as clay, zeolite, nano-alumina, mesoporous silica, activated carbon (AC), and carbon nanotubes (CNTs) have been investigated for NO₃⁻⁻ removal from water. Although these adsorbents exhibit specific adsorption performance, their wide application is still subject to one or more problems, such as high preparation cost, low adsorption rate, poor regeneration performance, and so forth. Hence, rapid adsorption, low-cost, and promising renewability of the adsorbent need to be developed to improve the NO₃⁻⁻ adsorption.

AC is known to be a promising adsorbent for organic pollutants because of the large specific surface area (600–1400 m²·g⁻¹), high reactivity, and good stability, and it is commonly used to control gaseous pollutants. However, it generally shows a weak adsorption capacity for anions in water, and there are a few related studies. CNTs also have many of the advantages as mentioned above. Moreover, the ideal symmetrical structure lends CNTs unique properties, and the nano-channel structure can provide nano-space for reaction, so that it is possible to be applied in the environment protection field. Khani et al. used powder-activated carbon (PAC) and CNTs for removal of NO₃⁻⁻N from aqueous solution. The NO₃⁻⁻N capacity of CNTs (25 mmol·g⁻¹) was higher than that of PAC (10 mmol·g⁻¹), and it takes lesser reaction time to reach adsorption equilibrium. In contrast, it should be noted that the application of pure CNTs remains finite because of its high cost, potential biotoxicity, and agglomeration of CNTs in water treatment alone. For these purposes, using activated carbon—carbon nanotubes (AC@CNTs) composite will be a great choice.

There are some related reports of the carbon-CNTs hybrid materials. However, most of them were prepared by simple mechanical mixing by virtue of van der Waals, hydrogen bonding, or embedding. This typical post-treatment method...
easily destroys the wonderful properties of CNTs, and the stability is also low.\textsuperscript{22,25} Su et al.\textsuperscript{24} prepared carbon/nanofiber composites after the catalytic decomposition of a mixture of C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2} on the Fe/AC catalyst. In our previous study, we prepared the AC@CNTs hybrid by in-situ growth of CNTs on AC and applied it for low-temperature selective catalytic reduction of NO\textsubscript{x}.\textsuperscript{27} In contrast, it was found difficult for carbon materials to adsorb the NO\textsubscript{3}− ions because of their high solubility and stability in water.\textsuperscript{28,29} Therefore, a specific surface modification should be adopted to regulate its physicochemical properties to enhance the anion adsorption in aqueous media. Several studies have investigated the possibility of using surfactants post-treatment of materials to improve the NO\textsubscript{3}− adsorption.\textsuperscript{30,12,30} According to research,\textsuperscript{31} a quaternary ammonium salt cationic surfactant could increase the carbon surface positive charge, which favored the anion adsorption and enhanced its ion exchange capacity.

In this study, the AC@CNTs hybrid has been synthesized by in-situ growth method and applied for NO\textsubscript{3}− removal from wastewater. The AC@CNTs material was controllably modified using myristyltrimethylammonium bromide (MTAB). The organic cation group was grafted onto the hybrid structure of AC@CNTs to increase the AC@CNTs adsorption performance for NO\textsubscript{3}− in water, so as to expand its application in the field of wastewater treatment. Based on the best sample chosen, the effect of operating parameters like adsorbent dosage, contact time, temperature, pH, and NO\textsubscript{3}− initial concentration on adsorption was investigated. Finally, the kinetic and isotherm studies were carried out to get more reaction details.

2. RESULTS AND DISCUSSION

2.1. Preparation and Adsorption Performance of AC@CNTs. The preparation of AC@CNTs was optimized using the orthogonal experiment method. The nickel catalyst content, CNTs growth temperature (T), period time (t), and methane flow rate (Q) were discussed on the basis of the NO\textsubscript{3}− adsorption performance. As shown in Table 1, the NO\textsubscript{3}− adsorption capacity of the selected pure AC was 1.22 mg g\textsuperscript{−1}, which is low but comparable to that of the related materials used in the previous studies.\textsuperscript{32,33} Based on the findings of the orthogonal experiment, the in-situ growth of the CNTs on AC influenced the adsorption properties of the composites differently. Most AC@CNTs composites showed NO\textsubscript{3}− adsorption efficiency improvement because of CNT growth, while 8 out of 25 AC@CNTs samples (32%) still had a lower adsorption capability than pure AC. The range analysis shows the influence of CNT in-situ growth conditions on the NO\textsubscript{3}− adsorption in the order: period time > nickel catalyst content > methane flow rate > CNTs growth temperature. The maximum capacity of 4.25 mg g\textsuperscript{−1} was obtained at the condition of 8% nickel loading ratio, 873 K of pyrolysis temperature, 75 min of growth time, and 50 mL min\textsuperscript{−1} of methane supply. Therefore, the sample prepared under the above condition, with the relative best efficiency of NO\textsubscript{3}− removal, was used in the following study.

As shown in Table 1, the adsorption capacity of AC@CNTs for NO\textsubscript{3}− is still low. To improve the adsorption performance, the surface modification of samples with MTAB surfactant was applied. Figure 1a shows the impact of MTAB modification on the NO\textsubscript{3}− adsorption of AC and AC@CNTs before and after MTAB pre-treatment. The AC presented the worst adsorption performance of NO\textsubscript{3}−. Its adsorption capacity was just 1.22 mg g\textsuperscript{−1} at a temperature of 25 °C and AC dosage of 1.0 g L\textsuperscript{−1}. Compared to AC, the adsorption performance of AC-M increased by 0.72 to 1.94 mg g\textsuperscript{−1} under the same operating conditions. The MTAB modification improved the adsorption performance of AC@CNTs even more. The NO\textsubscript{3}− adsorption capacity of AC@CNTs-M peaked at 14.59 mg g\textsuperscript{−1}, which is 3.4 times that of the unmodified AC@CNTs (4.25 mg g\textsuperscript{−1}). The strengthened adsorption performance of the AC@CNTs-M is because of the fact that the MTAB treatment, which not only increased the surface functional groups but also changed the charge on the material surface, enhanced the classical adsorption between the adsorbent and the anion, and increased the anion exchange capacity on the activated carbon surface, and thus contributed to the adsorption of NO\textsubscript{3}−.\textsuperscript{34} The effect of MTAB concentration for AC@CNTs pre-treatment on the adsorption performance was also investigated to assign the optimum surfactant concentration. Figure 1b shows the adsorption capacity of AC@CNTs as a function of the MTAB concentration. The result shows that the adsorption of AC@CNTs-M modified in different MTAB concentrations

| sample | nickel catalyst content (%) | T (K) | t (min) | Q (mL·min\textsuperscript{−1}) | q (mg·g\textsuperscript{−1}) |
|--------|----------------------------|-------|---------|-------------------------------|----------------------------|
| 1      | 5                          | 773   | 30      | 10                            | 1.22                       |
| 2      | 5                          | 823   | 45      | 20                            | 0.89                       |
| 3      | 5                          | 873   | 60      | 30                            | 1.22                       |
| 4      | 5                          | 923   | 75      | 40                            | 1.32                       |
| 5      | 5                          | 973   | 90      | 50                            | 1.29                       |
| 6      | 8                          | 773   | 45      | 30                            | 2.72                       |
| 7      | 8                          | 823   | 60      | 50                            | 2.76                       |
| 8      | 8                          | 873   | 75      | 50                            | 4.25                       |
| 9      | 8                          | 923   | 90      | 10                            | 0.94                       |
| 10     | 8                          | 973   | 30      | 10                            | 0.94                       |
| 11     | 10                         | 773   | 60      | 50                            | 3.93                       |
| 12     | 10                         | 823   | 75      | 10                            | 1.19                       |
| 13     | 10                         | 873   | 90      | 20                            | 3.80                       |
| 14     | 10                         | 923   | 30      | 30                            | 1.08                       |
| 15     | 10                         | 973   | 45      | 40                            | 1.00                       |
| 16     | 12                         | 773   | 75      | 20                            | 2.03                       |
| 17     | 12                         | 823   | 90      | 30                            | 0.65                       |
| 18     | 12                         | 873   | 30      | 40                            | 1.87                       |
| 19     | 12                         | 923   | 60      | 50                            | 1.13                       |
| 20     | 12                         | 973   | 45      | 10                            | 2.62                       |
| 21     | 15                         | 773   | 90      | 40                            | 1.95                       |
| 22     | 15                         | 823   | 30      | 50                            | 2.47                       |
| 23     | 15                         | 873   | 45      | 10                            | 1.59                       |
| 24     | 15                         | 923   | 60      | 20                            | 2.81                       |
| 25     | 15                         | 973   | 75      | 30                            | 1.76                       |

| K1j    | 0.390                      | 0.656 | 0.464   | 0.462                        |
| K2j    | 0.642                      | 0.480 | 0.450   | 0.594                        |
| K3j    | 0.620                      | 0.696 | 0.724   | 0.458                        |
| K4j    | 0.494                      | 0.450 | 0.598   | 0.522                        |
| K5j    | 0.600                      | 0.464 | 0.510   | 0.710                        |
| range  | 0.252                      | 0.246 | 0.274   | 0.252                        |

**q** is adsorption capacity at the equilibrium (mg·g\textsuperscript{−1}); order is primary and secondary order.
is different. With the increase of MTAB concentration, the equilibrium adsorption capacity of AC@CNTs-M showed a tendency to first increase and then decrease. The optimal adsorption capacity reached up to 14.59 mg·g⁻¹ at the 10 mmol·L⁻¹ concentration of MTAB. The potential explanation for this is the critical micelle concentration (CMC) of cationic surfactant, which affects its solubility in water.35,36 However, the formation of micelle was observed in MTAB when initial concentrations reach their maximum CMC values, which were not conducive to the diffusion of nitrate ions in AC@CNTs because of their large size. When the concentration of MTAB continually increased, its equilibrium adsorption capacity began to decrease.

Figure 1c shows the adsorption capacity variation with the modification temperature at 10 mmol·L⁻¹ MTAB. When the temperature ≤80 °C, the increased MTAB modification temperature showed a promoting effect on the NO₃⁻N adsorption. The AC@CNTs-M had the optimum adsorption capacity of 14.59 mg·g⁻¹ at 80 °C. The increase in adsorption capacity with rising temperature is related to many factors. The temperature rise will accelerate the thermal motion of the molecules, which is not conducive to the aggregation behavior of the surfactants. In addition, the loose micelle structure limits the entry of the surfactant and produces a higher CMC value.37

Along with the rise of modification temperature, the hydration of the surfactant decreased steadily, leading to an increase in the hydrophobic quality of the MTAB surfactant. In addition, more MTABs may be loaded onto AC@CNTs resulting in more adsorbent hydrophilic surface groups that increase the adsorption performance of NO₃⁻N. It can be concluded that the ion surfactant no longer exists as a single molecule and forms multiple micelles as the temperature rises to the Krafft point of the surfactant, resulting in a decrease in the adsorption capacity.

2.2. Characterization of Adsorbents. The SEM images at different amplitudes are shown in Figure 2. Figure 2a shows there are numerous macro-channel structures of virgin AC. Compared to virgin AC, as shown in Figure 2b, several CNTs are distributed on the surface of AC, indicating the success of CNTs in-situ growth. This will be discussed in conjunction with BET characterization later. Figure 2c,d shows the AC and AC@CNTs treated by MTAB modification (AC-M and AC@
It can be seen that the surface of the modified AC-M is relatively smooth (Figure 2c). This might be due to the MTAB treatment that washed away the surface impurities. The morphology features of AC@CNTs may also prove this when the CNTs are ignored. Both AC@CNTs and AC@CNTs-M show identical morphology based on the SEM images, demonstrating that MTAB functionalization did not alter the morphology of AC@CNTs (Figure 2d). In addition, the growth of CNTs was found to center on the macro-channel of AC, verified by the CNTs’ distribution both on the internal and external surfaces.

Textural properties of AC, AC-M, AC@CNTs, and AC@CNTs-M have been characterized using the standard N$_2$ adsorption–desorption test, and the isotherms are presented in Figure 3a. According to the IUPAC classification, all four samples are observed to have typical type-I isotherms accompanying the H4 hysteresis loop, suggesting they were microporous materials even though the CNTs are commonly mesopore structure materials. The BET surface area ($S_{\text{BET}}$) and single-point adsorption total pore volume of AC were about 453 m$^2$·g$^{-1}$ and 0.209 cm$^3$·g$^{-1}$, respectively. The $S_{\text{BET}}$ of AC@CNTs was 543 m$^2$·g$^{-1}$, 19.9% higher than that of pure AC. The structure of CNTs contributes to the increased $S_{\text{BET}}$ and higher pore volume of AC@CNTs (0.286 cm$^3$·g$^{-1}$). The giant hysteresis loop at $P/P_0 > 0.3$ means the AC@CNTs had more a mesoporous structure. Its mesopore volume was 0.119 cm$^3$·g$^{-1}$, 3.3 times higher than that of AC. After the MTAB modification, it can be seen that the N$_2$ adsorption capacity was substantially reduced, the $S_{\text{BET}}$ of AC-M and AC@CNTs-M were 183 and 286 m$^2$·g$^{-1}$, respectively, only 51.7 and 52.7% of AC and AC@CNTs, respectively. Figure 3b shows the pore diameter distribution. It can be seen that the CNTs’ in-situ growth blocked some micropores of AC, and alternatively, there was a more mesoporous structure because of the CNTs. This is consistent with the data listed in Table 2. The introduction of the surfactant filled part of the pore structure after MTAB modification, while the samples still showed similar distribution of pore size, suggesting that the modification process is uniform and thorough. Compared with AC, the pore structure blocking of AC@CNTs by MTAB modification is minor. This is because the CNTs had a comparatively larger pore size, and the average pore diameter is apparent.

Fourier transform infrared spectroscopy (FTIR), a structural spectroscopic technique analytic method, was used in this study to characterize the bonding structure of atoms and vibrations in molecules. As shown in Figure 4a, for the virgin AC, the band at approximately 3436 cm$^{-1}$ is ascribable to the $\nu$(O–H) stretching vibrations in hydroxyl groups, the two bands at 2921 and 2850 cm$^{-1}$ were attributed to the $\nu_{as}$(C–

Table 2. Specific Surface Area and Pore Structure Properties of Adsorbents

| samples      | total | micro | total | micro | meso | pore diameter (nm) |
|--------------|-------|-------|-------|-------|------|--------------------|
| AC           | 453   | 375   | 0.209 | 0.173 | 0.036 | 1.84               |
| AC-M         | 183   | 139   | 0.087 | 0.064 | 0.023 | 1.90               |
| AC@CNTs      | 543   | 351   | 0.286 | 0.167 | 0.119 | 2.11               |
| AC@CNTs-M    | 286   | 174   | 0.150 | 0.083 | 0.067 | 2.10               |

Figure 3. Nitrogen adsorption–desorption isotherms (a) and pore diameter distribution (b) of AC, AC-M, AC@CNTs, and AC@CNTs-M samples.

Figure 4. FTIR spectra of the (a) AC, (b) AC@CNTs, (c) AC@CNTs-M, and (d) AC@CNTs-M after.
H) and $\nu$ (C–H) of methyl and methylene, respectively, the C=O bond was assigned to the carboxyl group was seen as the peak at about 1716 cm$^{-1}$, the $\nu$ (C=O) stretching vibrations located at 1562 cm$^{-1}$, and the band due to $\delta$ (C–H) vibrations appeared at 1383 cm$^{-1}$. At 1177 and 1133 cm$^{-1}$, bands attributed to C–H, C–C, or C–O bonds were observed. Similarly, the spectra of AC@CNTs in the range of 4000–2700 cm$^{-1}$ show dominant O–H, $\nu_{as}$ (C–H), and $\nu_{s}$ (C–H) peaks at 3436, 2921, and 2850 cm$^{-1}$, respectively, indicating the CNT in-situ growth did not significantly change the surface chemistry of AC. Nonetheless, some new bands on the AC@CNTs were detected. Features at 1454 cm$^{-1}$ attributed to MWCNT vibrational modes are apparent. The peak at 1629 cm$^{-1}$ indicates the stretching vibration of C=C bonds and/or C=O stretching vibration in aliphatic ketone, and the peak at 1706 cm$^{-1}$ indicates the formation of COO$^-$ groups. The overlapping bands centered at 1000–1200 cm$^{-1}$ are related to the C–O bond. Peaks present at 870 cm$^{-1}$ may be assigned to the $\delta/\gamma$ (C–H) bond.

After MTAB modification, as seen in Figure 4c, the peak attributed to $\nu$ (C=O) stretching vibration bonds from the carboxyl (COOH) group shifted to a higher wavenumber (1727 cm$^{-1}$). The peak at about 1128 cm$^{-1}$ became stronger and broader, indicating more C–O bonds on the AC@CNTs-M surface because of the functionalization by MTAB surfactant. The amount of carboxyl (COOH) groups increased by modifying the surfactant to boost the water affinity of adsorbent and, ultimately, to increase the adsorption capacity of NO$_3^-$-N. The FTIR spectrum of AC@CNTs-M after application for NO$_3^-$-N adsorption is shown in Figure 4d. The occurrence of a new peak at 1524 cm$^{-1}$ was attributed to the $\nu_{as}$ (C–O) bond. Moreover, the chemical adsorption also occurred between the NO$_3^-$-N and C–O. It is worthy to note that the absorption bands at 1000–1600 cm$^{-1}$ were reinforced and slightly shifted after the modification and adsorption process, suggesting that the functional groups have interacted with the surfactant MTAB and NO$_3^-$-N ions. No other distinct change in the IR test has been observed, which reveals that the adsorption of NO$_3^-$-N by AC@CNTs-M is accompanied by electrostatic interactions.

The XPS analysis was applied to learn more details about surface components and the elements of the AC@CNTs-M before and after NO$_3^-$-N adsorption, which are important for the identification of the mechanism of NO$_3^-$-N adsorption. The XPS full-scan spectra of the AC@CNTs-M-fresh and AC@CNTs-M-after are shown in Figure 5a. Both of them had the C 1s, O 1s, N 1s peaks, and the strength of the peaks was different because of the application of adsorption. The high-resolution C 1s XPS spectrum is shown in Figure 5b. Three peaks at 284.6, 285.6, and 289.2 eV can be attributed to C=C, C–C, and O–C=O, respectively. The peaks present at 870 cm$^{-1}$ may be assigned to the $\delta/\gamma$ (C–H) bond.

The O 1s spectra in Figure 5c had two analytical peaks. The peaks at 530.4 and 532.2 eV corresponded to C=O groups of ketone, carbonyl, and lactone. The peaks at 532.7 and 533.2 eV belonged to C–O groups. The binding energies were increased up to 0.8, and 0.5 eV, which is because of the combination of N and C. The N 1s spectra in Figure 5d shows the N 1s spectra, and the peaks at 399.3, 399.4, 402.9, and 402.7 eV correlated

Figure 5. XPS spectra of the adsorbents (a) full-scan spectra; (b) C 1s spectra; (c) O 1s spectra; (d) N 1s spectra.

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with C–N' and −NH'/N' = C (positively charged nitrogen atom). These peaks are slightly shifted (0.1–0.2 eV), suggesting a new chemical bond formation on the surface. The new peak at 406.2 eV of AC@CNTs-M after NO₃⁻–N adsorption is indicated by the NO₃⁻. The surface components based on the XPS study are the proof (Table 3) that there was 18.8% C–NO₃⁻–N on the surface of AC@CNTs-M.

Table 3. Relative Surface Atomic Ratios AC@CNTs-M-Before and After NO₃⁻–N Adsorption

| atoms | bond type | AC@CNTs-M-fresh | AC@CNTs-M-after |
|-------|-----------|-----------------|-----------------|
| O     | C=O       | 530.4 52.8      | 531.2 37.9      |
|       | C–O       | 532.2 47.2      | 532.7 62.1      |
| N     | −C–N–     | 399.9 75.1      | 399.4 69.6      |
|       | −NH'/N'–C | 402.9 24.9      | 402.7 12.6      |
|       | C–NO₃⁻–N | 406.2 18.8      |                 |

2.3. Adsorption Kinetics and Isotherm. To establish the relationship between the adsorption capacity and adsorption rate, the Langmuir and Freundlich models were used to describe the results. The adsorption was carried out at the initial pH (6.6), NO₃⁻–N = 100 mg L⁻¹, and 25 °C, and the experimental and fitting results are illustrated in Figure 6a. Table 5 shows that the 1/n of AC@CNTs is greater than that of AC@CNTs-M (1/n = 0.49) and also reveals that the NO₃⁻–N is easier to adsorb on AC@CNTs-M compared with AC@CNTs. The Freundlich model, however, fits better for AC@CNTs-M. The R² values for the Freundlich and Langmuir models were 0.9746 and 0.9447, respectively. Both models’ high R² values indicate that the NO₃⁻–N adsorption on AC@CNTs-M have multiple processes. The new species found in the FTIR and XPS analysis are the second-order and pseudo-first-order models were well matched to the experimental data, even though the pseudo-first-order was relatively better. Their R² values were 0.98 and 0.97, respectively. The estimated qe values for the pseudo-first-order and pseudo-second-order kinetic model were, respectively, 14.03 and 17.39 mg g⁻¹.
and the surface charge of the adsorbent. In the current study, capacities of 4.25 and 14.59 mg AC@CNTs and AC@CNTs-M got the best adsorption shown in Figure 7a, the ability to adsorb nitrates remained decreased after 1.0 g concentration of the adsorbate. Thereby, adsorption capacity active sites were available for nitrate adsorption than the initial. Generally, the more the adsorbent was added, the more the adsorption was restricted when the pH was lower than 9 and the adsorption was evaluated, and the results are shown in Figure 7.

![Figure 7](https://dx.doi.org/10.1021/acsomega.0c00566)

**Figure 7.** Effect of adsorption conditions on NO$_3^-$-N. (a) Adsorbent dosage ($C_0 = 100$ mg L$^{-1}$, temperature = 25 °C, pH = 6.6); and (b) initial pH of simulated wastewater ($C_0 = 100$ mg L$^{-1}$, temperature = 25 °C, adsorbent’s dosage = 1 g L$^{-1}$).

### 2.4. Effect of Dosage and pH

The effect of adsorbent dose on nitrate adsorption performance was evaluated by adjusting the sorbent addition in the range of 0.5–4.0 g L$^{-1}$. As shown in Figure 7a, the ability to adsorb nitrates remained relatively stable initially at a dose of less than 1.0 mg g$^{-1}$. The AC@CNTs and AC@CNTs-M got the best adsorption capacities of 4.25 and 14.59 mg g$^{-1}$, respectively, at the 1 g·L$^{-1}$ adsorbent dosage. After that, the adsorption capacity gradually decreased. They were only 1.80 and 10.30 mg g$^{-1}$, respectively, when the dosage was increased up to 4.0 g·L$^{-1}$. Generally, the more the adsorbent was added, the more the active sites were available for nitrate adsorption than the initial concentration of the adsorbate. Thereby, adsorption capacity decreased after 1.0 g·L$^{-1}$ of dosage. The solution pH is also an important parameter that influences the NO$_3^-$-N adsorption process. It could affect the forms of ions in solution and the surface charge of the adsorbent. In the current study, the influence of pH varied from 3 to 11 on the NO$_3^-$-N adsorption was evaluated, and the results are shown in Figure 7b. For the pure AC, the improvement in adsorption efficiency was restricted when the pH was lower than 9 and the adsorption capacity ranged between 2.92 and 3.76 mg g$^{-1}$. As the pH increased to 11, the adsorption capacity greatly improved to 6.10 mg g$^{-1}$. In contrast to AC, the AC@CNTs and AC@CNTs-M showed better acidic adsorption ability. With the increase of pH, the adsorption capacity of AC@CNTs-M showed a decrease first and then it tended to stabilize to about 15 mg g$^{-1}$ when the pH was higher than 5. The higher pH effect of AC@CNTs was greater, and the adsorption capacity showed a clear decrease when the pH increased from 3 to 7. After that, like pure AC, it had a limited capacity for recovery. In the case of acidic conditions, the protons in the solution is more, and the adsorbent’s surface negative charge decreases. The positive charge increase could enhance the electrostatic attraction on the adsorbent surface and promotes the adsorption of NO$_3^-$-N. When the pH increases, the concentration of hydroxide radicals (OH$^-$) in the solution increases, and OH$^-$ will compete with NO$_3^-$ in the solution for adsorption, thereby hindering the adsorption of NO$_3^-$ by the adsorbent.

In order to evaluate the adsorption stability of AC@CNTs-M for nitrate, five cycles of adsorption-desorption experiments were carried out to investigate the effects of regeneration times on the adsorption capacity of the adsorbent. As can be observed in Figure 8, after five times generations, the adsorption capacity for nitrate was 64% of the initial adsorption capacity that is the AC@CNTs-M composites had better regeneration ability.

Table 6 compared the maximum NO$_3^-$-N adsorption capacity of AC@CNTs-M with other studies based on the Langmuir model simulation. It can be seen that the maximum adsorption capacity of AC@CNTs-M could go high up to 27.07 mg g$^{-1}$, which is much higher than most of the AC-based materials reported previously. Meanwhile, the NO$_3^-$-N adsorption rate of AC@CNTs-M is fast, and less equilibrium time is needed when the material is applied in the industrial scale. These results demonstrated that the AC@CNTs prepared by in-situ growth and post-modified by the MTAB surfactant is a promising adsorbent for a highly efficient and fast adsorption of NO$_3^-$-N from water, especially from acidic wastewater.

### Table 4. Parameters of the Pseudo-first Order and Pseudo-second Order Kinetic Models

| adsorbent     | $k_1$ (min$^{-1}$) | $q_e$ (mg·g$^{-1}$) | $R^2$ | $k_2$ (g·mg·min$^{-1}$) | $q_e$ (mg·g$^{-1}$) | $R^2$ |
|---------------|--------------------|---------------------|------|-------------------------|---------------------|------|
| AC@CNTs       | 0.24               | 3.63                | 0.6420 | 9.7 × 10$^{-2}$        | 3.79                | 0.7092 |
| AC@CNTs-M     | 0.01               | 14.03               | 0.9691 | 7.1 × 10$^{-4}$        | 17.39               | 0.9786 |

### Table 5. Parameters of Langmuir and Freundlich Isotherm Models of NO$_3^-$-N Adsorption

| adsorbent     | $q_m$ (mg·g$^{-1}$) | $K_L$ (L·mg$^{-1}$) | $R^2$ | $K_F$ (L·g$^{-1}$) | $1/n$ | $R^2$ |
|---------------|---------------------|--------------------|------|-------------------|-------|------|
| AC@CNTs       | 10.00               | 0.0040             | 0.7492 | 0.0260            | 1.00  | 0.7225 |
| AC@CNTs-M     | 27.07               | 0.0121             | 0.9447 | 1.5200            | 0.49  | 0.9746 |
The process of AC@CNTs-M resulted in a capacity of AC@CNTs-M of 14.59 mg·g⁻¹, which is greater than that of AC-M. Characterization results reveal that the growth of CNTs gives the AC@CNTs a greater specific surface area and more mesoporous volume, but MTAB surfactants uniformly occupy part of the pore structures after the modification process. The in-situ growth of CNTs provides AC@CNTs with more surface hydroxyl and carboxyl functional groups that are beneficial to the NO₃⁻ N adsorption. AC@CNTs-M demonstrated an excellent adsorption performance under acidic conditions because the increase of positive functional groups under acidic conditions favours the adsorption of NO₃⁻ N cations. The kinetic analysis reveals the NO₃⁻ N adsorption to follow the pseudo-second-order kinetics model. The adsorption isotherm of NO₃⁻ N adsorption was carried out in a constant-temperature shaker. The adsorption conditions were set as follows: adsorption temperature T = 25 °C, shaking speed of 150 rpm, and adsorption time of 6 h. After adsorption, the fluid was filtered with a 0.45 μm filter membrane, and then, the concentration of NO₃⁻ N was measured using ion chromatography (Thermal, ICS-600). The adsorption capacity or the amount of adsorbed NO₃⁻ N ions per mass of the adsorbents was calculated as follows:

\[ q_e = \frac{(C_0 - C_e)V}{w} \]  (1)

where \( q_e \) is the adsorption capacity of the adsorbent, \( C_0 \) is the initial NO₃⁻ N concentration (mg·L⁻¹), \( C_e \) is the equilibrium NO₃⁻ N concentration (mg·L⁻¹), \( V \) is the volume of NO₃⁻ N solution (L), and \( w \) is the mass of the dry adsorbents used (g).

In order to evaluate the regenerability of the AC@CNTs-M adsorbent, it was reused five times. The used AC@CNTs-M was ground into 30–40 mesh for use. The myristyltrimethylammonium bromide (MTAB, 99%), nitric acid (HNO₃, 99%), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99%), copper nitrate (Cu(NO₃)₂·3H₂O, 99%), and hydrochloric acid (HCl, 35–37%) were purchased from Chengdu Chron Chemical, and no further treatment was done prior to use.

### 4. Synthesis and Modification of AC@CNTs

A certain amount of commercial activated carbon was weighed, washed with deionized water, and then dried in an oven at 105 °C for 12 h. The washed AC was then completely immersed in 6% nitric acid for 24 h at 25 °C with a steady stirring of 150 rpm. Subsequently, the AC was filtered and washed with deionized water until the pH of the washed water showed no change, and then, it was further dried at 105 °C overnight. Ni-AC was prepared by wet-impregnation as described in the following: 10 g of activated carbon was added to the nickel nitrate solution and kept for 12 h. The impregnated samples were then slowly dried at 80 °C for 24 h. The dry samples were calcined for a certain time in a methane atmosphere to obtain AC@CNTs. MTAB was dissolved in deionized water to provide a solution with a concentration of 10 mmol·L⁻¹. AC and AC@CNTs were added to the prepared MTAB solution in an ultrasonic bath for 30 min and then heated slowly to 80 °C with constant stirring using a magnetic stirrer for 4 h to obtain functionalized AC-M and AC@CNTs-M. Also, the materials were washed using deionized water to a constant pH value. It was eventually dried for adsorption.

### 4.4. Batch Adsorption

0.025 g of the adsorbents were accurately weighed and added to a 100 mL conical flask with 25 mL NO₃⁻ N containing solution (\( C_{NO_3^-} = 100 \) mg·L⁻¹). The adsorption reaction was carried out in a constant-temperature shaker. The adsorption conditions were set as follows: adsorption temperature T = 25 °C, shaking speed of 150 rpm, and adsorption time of 6 h. After adsorption, the fluid was filtered with a 0.45 μm filter membrane, and then, the concentration of NO₃⁻ N was measured using ion chromatography (Thermal, ICS-600). The adsorption capacity or the amount of adsorbed NO₃⁻ N ions per mass of the adsorbents was calculated as follows:

\[ q_e = \frac{(C_0 - C_e)V}{w} \]  (1)

| adsorbents | \( Q_m \) (mg·g⁻¹) | temperature (°C) | contact time (h) | pH | \[ NO_3^- \] | references |
|------------|-------------------|------------------|-----------------|----|----------|------------|
| AC@CNTs-M  | 27.07             | 25               | 6               | 6.6| 100      | this study |
| AC-2       | 21.51             | 25               | 2               | 7  | 40       | 29         |
| LGAC       | 10.44             | 25 ± 2           | 24              | 5  | 5–150    | 15         |
| AC-F400    | 8.68              |                  |                 |    |          |            |
| AC-10OG    | 11.16             | 25               | 24              | 0–186|      | 58         |
| AC-O₂-9OG  | 13.02             |                  |                 |    |          |            |
| AC-10ST    | 9.92              |                  |                 |    |          |            |
| GACs       | 1.7               | 25 ± 2           | 2               | 5.5| 5–200    | 28         |
| ZnCl₂-GACs | 10.2              |                  |                 |    |          |            |
sample was collected by filtration with a 0.45 μm filter membrane; then, it was regenerated using 0.01 M KOH and HCl solutions.

4.4. Adsorption Kinetic Study. The kinetic equilibrium studies have been conducted under the above established experimental conditions. The adsorption kinetic study was carried out by adding 0.025 g of adsorbents into conical flasks containing 25 mL NO3−-N solution with initial concentrations ranging from 40 to 150 mg·L−1. The reaction times were of 1, 3, 5, 10, 30, 60, 90, 120, 180, 240, and 360 min. The pseudo-first and pseudo-second-order kinetic models were used to fit the experimental data and to investigate the mechanism of adsorption and potential rate. These models are given below

\[ q_t = q_e(1 - e^{-kt}) \]  
(2)

\[ q_t = \frac{q_e^2 k_f t}{1 + q_e k_f t} \]  
(3)

where \( q_e \) is the adsorption capacity at contact time \( t \) (mg·g−1), \( q_t \) is the adsorptive capacity at equilibrium, \( t \) is the time (min), \( k_1 \) is the pseudo-first-order kinetic rate constant (min−1), and \( k_2 \) is the pseudo-second-order kinetic rate constant (g·mg−1·min−1).

4.5. Adsorption Isotherm Study. Similarly, an adsorption isotherm study was carried out under the same conditions as the adsorption kinetics operation. Different concentrations of NO3−-N solutions ranging from 40 to 150 mg·L−1 were added into the conical flasks with adsorbents that were accurately weighed. The series mixture were then stirred for 6 h at different reaction temperatures in the range of 25–55 °C. According to their equilibriums, the Langmuir and Freundlich models were used to provide an insight into their surface properties.

\[ q_e = \frac{q_m K_f C_e}{1 + K_f C_e} \]  
(4)

\[ q_e = K_f (C_e)^{1/n} \]  
(5)

where \( q_e \) is the adsorption capacity at the equilibrium (mg·g−1), \( q_m \) is the maximum adsorption capacity of the adsorbent (mg·g−1), \( K_f \) is the Langmuir constant (L·mg−1), which is related to the affinity of the binding site of the adsorbent, and \( C_e \) is the adsorbate concentration at equilibrium (mg·L−1).

\[ K_f (L·g^{-1}) \]  
(6)

where \( K_f \) (L·g−1) and \( n \) are model constants, \( K_f \) is related to the adsorption affinity of the adsorbent, and \( n \) indicates the adsorption process’s support.

4.6. Characterization of the Adsorbent. The scanning electron microscopy (SEM) images of AC, AC-M, AC@CNTs, and AC@CNTs-M were obtained on a JEOL JSM-7500F. The specific surface areas, total pore volume, and pore size distribution were determined by the Brunauer–Emmett–Teller (BET) method using the N2 adsorption–desorption technique with a Micromeritics ASAP 2460. Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700) was used to analyze the functional groups present in the adsorbent in the band of 400–3500 cm−1. The surface chemical state and elemental changes of adsorbents were investigated by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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