Eurasia Journal of Science and Technology
Print ISSN: 2663-1024
Online ISSN: 2663-1016
DOI: https://doi.org/10.61784/ejst3144

PREPARATION OF BIOCHAR FROM WASTE NUTSHELLS AND ITS APPLICATION IN NITROGEN-CONTAINING WASTEWATER TREATMENT

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Abstract: Due to their unique pore structures and physicochemical properties, agricultural nutshell wastes serve as ideal precursors for the preparation of biomass biochar. However, traditional nutshell-derived biochars exhibit limitations in adsorption selectivity and capacity, showing poor removal efficiency for nitrate and nitrite nitrogen from rural domestic wastewater. In this study, walnut shells were used as feedstock to prepare pristine biochar via carbonization and physical activation. Subsequently, the biochar was modified through oscillatory impregnation with acid, alkali, and Fe^{3+} loading. The effects of modification conditions, adsorbent dosage, and adsorption time on the removal efficiency of the target nitrogen pollutants were investigated. The results indicated that the biochar achieved the optimal removal efficiency for the target nitrogen pollutants under the following conditions: a carbonization temperature of 700°C, Fe^{3+} modification, an Fe^{3+} loading ratio of 20%, an adsorbent dosage of 2.0 g, and an adsorption time of 60 min. Featuring simple operation and controllable costs, this process achieves the dual goals of "high-value utilization of waste" and "water pollution control".
Keywords: Nutshell biochar; Agricultural waste; Iron modification; Nitrogen pollutants

1 INTRODUCTION

As typical agricultural and forestry waste, nutshells possess three major characteristics: natural porosity, mechanical stability, and biodegradability. This not only avoids the high energy consumption of synthetic materials but also compensates for the functional limitations of single biomass components [1-2]. The surface functional groups of traditional shell biochar are predominantly inert, exhibiting limited variety and a lack of active sites, which leads to poor adsorption selectivity and limited capacity for organic pollutants in wastewater. However, through modification processes such as acid or alkali impregnation and high-temperature activation, the quantity and distribution of oxygen-containing functional groups (e.g., carboxyl and hydroxyl groups) on the biochar surface can be directionally regulated, and the pore structure can be simultaneously optimized. This significantly enhances the targeted adsorption capacity for specific pollutants and broadens the application scope of biochar in practical water treatment scenarios [3-6].

Iron ions can introduce numerous active adsorption sites onto the carrier surface, strengthening the targeted capture of pollutants through complexation and ion exchange, thereby improving the adsorption capacity of the material. Furthermore, relying on the large specific surface area of iron oxides/hydroxides, they can enhance the physicochemical synergistic adsorption effect on organic pollutants, perfectly meeting the requirements for advanced wastewater treatment [7-10].

This study aims to address the low removal efficiency of traditional biochars for nitrogenous pollutants in wastewater. The material was optimized through acid, alkali, and iron-loading modification methods. The effects of carbonization temperature, modification method, iron loading ratio, adsorption time, and adsorbent dosage on the removal efficiency of nitrogenous pollutants were systematically investigated. This research can provide a theoretical basis and technical support for the treatment of nitrogen-containing wastewater, promoting the synergistic development of solid waste resource utilization and water environment governance.

2 MATERIALS AND METHODS

2.1 Materials

SX2-2.5-10 Muffle Furnace (Shanghai Dute Scientific Instrument Co., Ltd.); CIC-D100IC Ion Chromatography Analyzer (Qingdao Shenghan Chromatography Technology Co., Ltd.); SHA-BA Water Bath Constant Temperature Oscillator (Changzhou Runhua Electric Appliance Co., Ltd.); DHG-9030A Drying Oven (Dongguan Huoman Technology Co., Ltd.); JP- 100S Ultrasonic Cleaning Instrument (Shenzhen Jiemeng Cleaning Equipment Co., Ltd.).

Sulfuric acid, oxalic acid, sodium hydroxide, ferric chloride, potassium nitrate, sodium nitrite, and anhydrous ethanol, all of analytical reagent (AR) grade.

2.2 Methods

2.2.1 Carbonization and physical activation process of biomass activated carbon

The pretreated raw materials were placed in a crucible, sealed with a lid, and tightly wrapped with tin foil. The crucible was then placed in a muffle furnace and heated to 500°C, 600°C, and 700°C at a heating rate of 3-5°C/min for carbonization, respectively. After generating the preliminary carbonized materials, they were calcined at a constant temperature for 2 hours. Upon completion of calcination, the muffle furnace was allowed to cool naturally to below 100°C before the biochar was taken out. The obtained biochar was ground and passed through a 100-mesh sieve to yield a uniform and fine physically activated biochar product for subsequent use.

2.2.2 Preparation of acid, alkali, and iron-loaded modified biochar via impregnation method

Equal amounts of the prepared physically activated nutshell biochar were added into 1 mol/L oxalic acid solution and 1 mol/L sodium hydroxide solution, respectively. The mixtures were placed in a constant-temperature water bath shaker and oscillated at 150 r/min for 24 h at room temperature. Afterward, the biochars were repeatedly rinsed with deionized water until the filtrate became neutral, followed by drying in an oven, sealed storage, and set aside for later use.

Chemical modification for metal loading was conducted using the oscillatory impregnation method to prepare iron-loaded modified biochar from the physically activated biochar [11]. A 1 mol/L ferric chloride solution was prepared. Based on the preset iron loading mass ratios of 10%, 20%, 30%, and 50%, the Erlenmeyer flasks containing the mixed systems were placed in a constant-temperature water bath shaker. The oscillation speed was set to 150 r/min, and the reaction lasted for 24 hours. After the reaction, the biochar was washed with deionized water, dried, and hermetically stored in a desiccator to provide standardized samples for subsequent adsorption performance experiments.

2.2.3 Treatment efficiency of modified biochar for nitrogen-containing wastewater

To investigate the differences in the treatment efficiency of modified activated carbons for nitrogen-containing wastewater, the mixed simulated wastewater was configured with a nitrate nitrogen concentration of 20 mg/L and a nitrite nitrogen concentration of 8 mg/L. The modified biochars were prepared by carbonizing the biomass materials at 500°C, 600°C, and 700°C, followed by acid modification, alkali modification, or iron-loading modification. The iron loading ratios for the iron-modified biochars were set at 10%, 20%, 30%, and 50%; the adsorption times were set at 0, 5, 10, 20, 30, 60, and 120 min; and the adsorbent dosages were set at 0.2, 0.5, 1.0, 1.5, and 2.0 g.

2.3 Analytical Methods

The concentration of nitrate nitrogen and nitrite nitrogen was determined using an ion chromatograph, and the removal rate was calculated using following formula to analyze the impact of different influencing factors on the treatment efficiency of simulated wastewater.

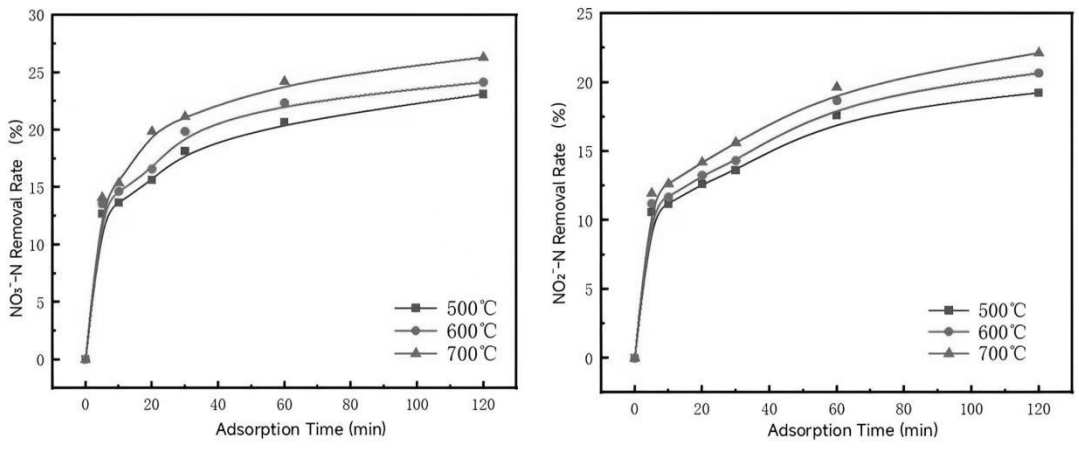
$$\eta=\frac{c_0-c}{c_0}\times 100\% \quad (1)$$

Where η is the removal efficiency of the modified activated carbon; c_0 and c represent the pollutant concentrations (mg/L) before and after adsorption by the modified activated carbon, respectively.

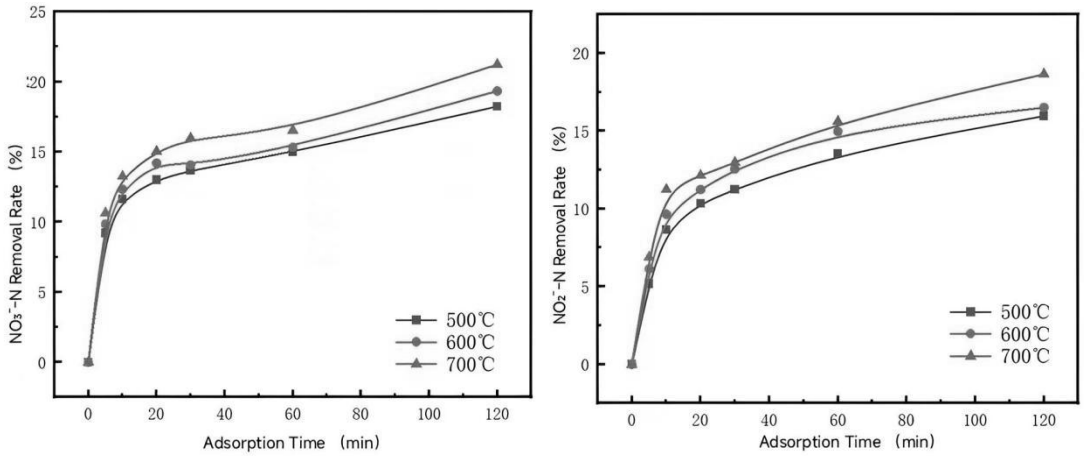
3 RESULTS AND DISCUSSION

3.1 Effects of Different Modification Conditions on the Adsorption Performance of Biochar

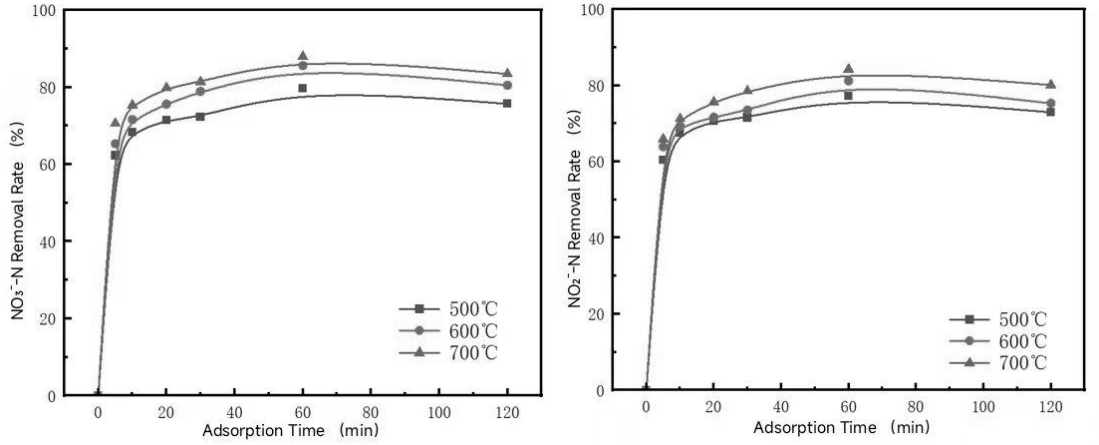
For each sample, 0.5 g was placed into 100 mL of simulated wastewater and oscillated in a constant-temperature shaker at 150 r/min, aiming to systematically evaluate the influence of different preparation conditions on the adsorption performance of the biochar.



(a) Acid-modified biochar



(b) Alkali-modified biochar



(c) Iron-modified biochar

Figure 1 Removal Rates of Nitrate and Nitrite by Biochars under Different Modification Conditions

The adsorption removal efficiencies of the modified biochars for nitrate nitrogen and nitrite nitrogen in the simulated wastewater are shown in Figure 1. Figures 1(a) and 1(b) illustrate the variations in the removal rates of nitrate nitrogen and nitrite nitrogen by the acid-modified biochars and alkali-modified biochars prepared at 500°C, 600°C, and 700°C, respectively. Both the acid-modified biochars and alkali-modified biochars exhibited a consistent temporal pattern: regardless of the carbonization temperature, the highest adsorption removal rates for both nitrate and nitrite nitrogen were achieved at an adsorption time of 120 min, with the biochars prepared at 700°C demonstrating the optimal removal performance. Theoretically, acid modification enhances the adsorption of cationic pollutants by introducing negatively charged groups such as carboxyl and hydroxyl groups; in contrast, alkali modification focuses on expanding the mesoporous structure of the biochar, improving the diffusion efficiency of pollutants within the pores, and optimizing the adsorption performance for macromolecular organic matter [12-15]. However, the experimental results revealed that the overall removal rates of the acid-modified biochars and alkali-modified biochars for nitrogen pollutants in the simulated wastewater were relatively low, ranging only from 12.8% to 27.3%. This indicates that modification with acid or alkali alone has a limited adsorption effect on such nitrogen pollutants, which may be restricted by the number of surface active sites following modification or the adaptability of the adsorption mechanisms with different categories of pollutants [12].

The results for the iron-modified biochars are shown in Figure 1(c). Unlike the temporal pattern observed for the acid-modified biochars and alkali-modified biochars, the adsorption performance of the iron-modified biochars gradually improved with increasing adsorption time within the first 0–60 min, reaching an optimum at 60 min. This is attributed to the larger specific surface area, highly developed pore structure, and abundant active adsorption sites on the surface of the iron-modified biochar, which endow it with a robust adsorption capacity. Furthermore, in the initial stage of adsorption, there was a significant concentration difference of nitrogen pollutants between the solution and the interior of the biochar. Benefiting from the synergistic effect between the diffusion driven by the concentration gradient and the surface active adsorption sites, the adsorption process was further enhanced [13].

However, with the prolongation of adsorption time, the removal rates of the iron-modified biochars for nitrate and nitrite nitrogen slightly decreased. This phenomenon can be attributed to two core factors: First, the active sites on the iron-modified biochar surface approached saturation within 60 min, and further extension of time did not increase the adsorption capacity; instead, it shifted the adsorption-desorption equilibrium, leading to the desorption of pollutant ions.

Second, the redox reactions between the iron active sites and the nitrogen pollutants reached equilibrium within a short period, and prolonged reaction times might trigger various side reactions, such as the leaching of iron ions, which consequently weakened the adsorption performance.

Similar to the acid-modified biochars and alkali-modified biochars, the iron-loaded modified biochar also exhibited the optimal removal rate for nitrogen in the simulated wastewater at a carbonization temperature of 700°C, with a removal rate exceeding 62.6%. Studies have shown that this phenomenon occurs because, at excessively low carbonization temperatures, the pyrolysis of cellulose and hemicellulose in the walnut shells is insufficient. Side reactions, such as the reduction of lignin and the decomposition of reaction intermediates, cause mass loss, resulting in a lower biochar yield and underdeveloped pore structures. In contrast, at 700°C, cellulose and hemicellulose can undergo relatively sufficient pyrolysis to release volatiles, while lignin simultaneously undergoes moderate degradation and polycondensation reactions. This process promotes the formation and development of the biochar pore structure, thereby yielding a biochar with a higher specific surface area and an abundant porous structure [14].

3.2 Effect of Fe/C Loading Ratio on the Adsorption Performance of Biochar

In this study, based on the optimal carbonization temperature of 700°C, a concentration gradient of Fe/C loading ratios of 10%, 20%, 30%, and 50% was designed to determine the optimal Fe/C loading ratio. As shown in Figure 2, the four different loading ratios had a limited overall impact on the removal efficiencies of the iron-modified biochars, which exhibited an initial increase followed by a decrease. At a Fe/C loading ratio of 20%, the iron-modified biochar achieved the optimal adsorption performance for nitrate and nitrite, with removal rates reaching up to 88.3% and 84.9%, respectively. However, as the loading ratio further increased, the removal efficiencies declined instead. An excessively high iron loading led to the over-accumulation of active sites, resulting in the formation of iron particle agglomerates that blocked the pore structure of the biochar and hindered the diffusion of pollutants towards the internal active sites [15].

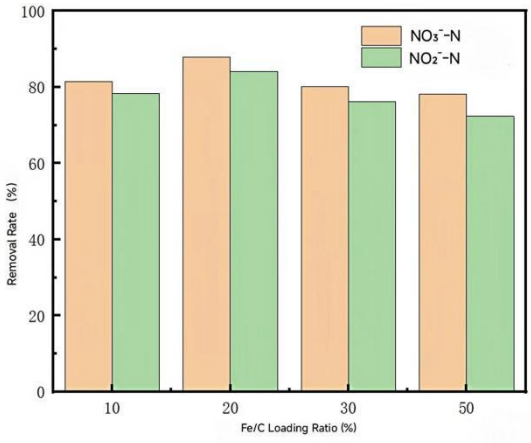


Figure 2 Effect of Fe/C Loading Ratio on the Adsorption Performance of Biochar

3.3 Effect of Dosage on the Adsorption Performance of Biochar

The removal efficiencies of the three modified biochars for nitrate and nitrite in wastewater at different dosages are shown in Figure 3. All three types of modified biochars exhibited a consistent dosage-dependent behavior: as the dosage gradually increased, the removal rates for nitrate and nitrite in the wastewater both showed an upward trend. This phenomenon can be attributed to the fact that an increased dosage directly expands the total number of active sites on the biochar while simultaneously increasing the collision probability between the biochar and pollutant particles. This enables biochars with different mesoporous structures to participate in the adsorption process, thereby enhancing the adsorption and removal performance. When the dosage reached a certain threshold, the growth rate of the removal rates tended to level off, indicating that the reaction was gradually approaching adsorption equilibrium.

Specifically, for the acid-modified biochar, the removal rates for nitrate nitrogen and nitrite nitrogen reached maxima of approximately 35.2% and 27.9%, respectively, at the optimal dosage of 2.0 g. The core mechanism of acid modification lies in introducing acidic functional groups, such as carboxyl groups, onto the biochar surface to achieve pollutant adsorption through ion exchange and hydrogen bonding. However, constrained by the types and quantities of these surface functional groups, the overall adsorption performance remains relatively limited [16-19].

For the alkali-modified biochar, at a dosage of 2.0 g, the maximum removal rates for nitrate nitrogen and nitrite nitrogen were 30.3% and 25.0%, respectively. Alkali modification alters the pore structure of the biochar, changing its pore size distribution and broadening the diffusion channels for pollutants. Concurrently, it generates certain alkaline sites on the surface. The synergistic effect of these two aspects enhances the removal capacity for specific substances. The varying removal efficiencies observed for different ions are hypothesized to be related to their physicochemical properties, such as charge characteristics and ionic radius.

The iron-modified biochar exhibited an exceptionally outstanding performance. At a dosage of 2.0 g, its removal rate for nitrate nitrogen and nitrite nitrogen reached 87.2% and 88.0%, respectively, significantly outperforming the acid-modified biochars and alkali-modified biochars. Iron modification introduces new active sites by loading iron onto the biochar surface, where multiple interactions, including complexation and redox reactions between iron ions and nitrogen pollutants, substantially enhancing the adsorption and removal efficiency of nitrogen pollutants.

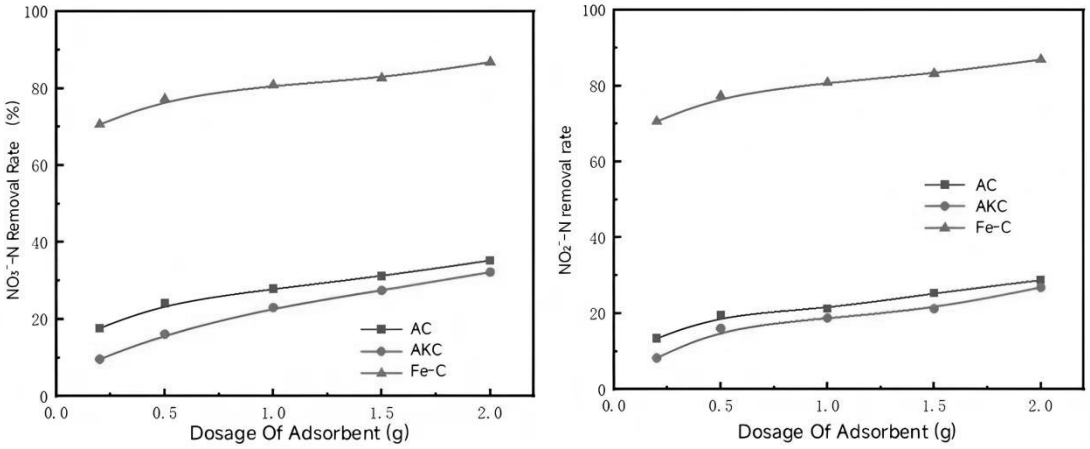


Figure 3 Effect of Dosage on the Adsorption Performance of Biochar

4 CONCLUSION

(1) Regarding the carbonization temperature for biochar preparation, the adsorption efficiencies of the acid-modified, alkali-modified, and iron-modified biochars for nitrate nitrogen and nitrite nitrogen in simulated wastewater were all optimal at 700°C.
(2) Regarding the modification conditions, the removal rate of the iron-modified biochar for nitrogen pollutants in wastewater exceeded 62.6%, whereas those of the acid-modified biochar and alkali-modified biochars were less than 27.3%. Thus, the treatment efficacy of the iron-modified biochar for nitrogen pollutants is significantly superior to that of the acid-modified biochar and alkali-modified biochars.
(3) In terms of the iron loading ratio for the modified biochar, the biochar with a 20% Fe/C loading ratio exhibited the optimal adsorption performance for nitrogen pollutants in wastewater, achieving a nitrate nitrogen removal rate of 88.3% and a nitrite nitrogen removal rate of 84.9%.
(4)In the context of adsorption performance, when the adsorption time was 120 min, the removal rates of the acid-modified biochars and alkali-modified biochars for nitrogen pollutants in wastewater were only 12.8%–27.3%. In contrast, the iron-modified biochar reached a maximum removal rate of 86.0% for nitrogen pollutants at just 60 min.
(5) For the biochar dosage, the optimal dosage for all three types of modified biochars was 2.0 g. Under this condition, the acid-modified biochars and alkali-modified biochars achieved removal rates of 35.2% and 30.3% for nitrate nitrogen, 27.9% and 25.0% for nitrite nitrogen in the simulated wastewater, respectively. Meanwhile, the iron-modified biochar achieved removal rates of 87.2% and 88.0% for nitrate nitrogen and nitrite nitrogen, respectively.
This study provides an efficient and eco-friendly technical pathway for the high-value utilization of biomass resources and the treatment of nitrogen-containing wastewater, demonstrating the application potential of iron-loaded modified biochar in practical water pollution remediation. It not only offers a feasible technical approach for the ecological treatment of water pollution and the recycling of agricultural solid waste, but also promotes the high-value utilization of agricultural and forestry by-products, thereby driving the development of a circular economy. Furthermore, upon process optimization, the production costs of biochar can be reduced, further enhancing its market competitiveness.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

FUNDING

This work was supported by the National Provincial College Students' Innovation and Entrepreneurship Training Program (202313242002) and the Scientific Research Project of the Hubei Provincial Department of Education (B2024317).

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