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Synthesis of Modified Walnut Shell Biochar and Its Performance of Cadmium Adsorption

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Abstract

Biochar is a functional and environmentally friendly material mainly made from by-products of industrial and agricultural production as raw material, which is cracked at high temperatures and slow speeds. The preparation of biochar requires the thermochemical conversion of biomass in an oxygen-restricted environment. Different raw materials and preparation processes result in biochar with different internal structures and biofunctional groups, which often have different properties. Adsorption of heavy metal pollutants is one of the main research directions for biochar application, and there are still areas that can be improved in the current research for biochar for treating heavy metal wastewater. In this study, we take the treatment of cadmium-containing wastewater as an example, walnut shell biochar (WSBC) as a carrier, iron(VI) compounds as a modifying reagent, and test the performance of cadmium-containing wastewater treatment using simulated cadmium-containing wastewater by adjusting the pyrolysis process and modification method at the same time to find the optimal experimental scheme, and give a reasonable theoretical explanation in relation to the results of the characterization tests, such as SEM, FT-IR, and so on. The characterized results show that iron(VI) compound (K_2FeO_4)-modified WSBC has a significant ability to remove cadmium contamination in the wastewater (remove 96.62% of cadmium in 1 minute), and its structure is different from other iron compound-modified ones. The aim of this study is to improve the efficiency of cadmium adsorption by specific types of biochar, while realizing the whole process as environmentally friendly as possible.

Keywords

Biochar, Wastewater, Cadmium, Environmental Pollution, Walnut Shell

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1. Introduction

Over the past centuries, with the continuous expansion of human activities, humans have directly or indirectly emitted pollutants into the environment that exceed their self-purifying capacity, and these pollutants have adversely affected human survival and development, ecosystems, and habitats (Zhao et al., 2022). In the natural environment, many heavy metal elements, such as lead, cadmium, mercury and nickel, are difficult to naturally degrade and pose a threat to the ecosystem, resulting in heavy metal pollution. On the other hand, these heavy metal pollutants enter the organisms and accumulate through air, food and drinking water, and continue to enrich upward along the food chain, resulting in a more serious threat to human health (Cai et al., 2022).

Cadmium exists in nature mainly in the form of compounds, with high toxicity, difficult to degrade and can be enriched in living organisms and other characteristics. The International Agency for Research on Cancer (IARC) categorized cadmium as an A-class of carcinogens, once cadmium is in the human body to gather, will cause cadmium poisoning, mainly caused by kidney damage, bone damage and lung damage, etc., posing a greater risk of human health (Zhao et al., 2022), a typical representative of Japan's "Itai-Itai Disease". The main source of cadmium pollution is the wastewater of electroplating, mining, smelting, dyes, and batteries industries, so the treatment of cadmium in cadmium-containing wastewater is particularly important. From the point of view of methods, heavy metal wastewater treatment methods mainly include chemical precipitation, electrochemical method, adsorption method, ion exchange method and membrane separation method. Among them, the adsorption method has been increasingly emphasized by researchers due to the advantages of simple operation, low cost and high treatment efficiency (Cai et al., 2022; Deng et al., 2022).

Biochar is a functional and environmentally friendly material mainly made from by-products of industrial and agricultural production as raw materials and produced by slow pyrolysis at high temperatures, which is mainly composed of amorphous carbon, aromatic carbon and ash content. Preparation of biochar requires thermochemical conversion of biomass in an oxygen-limited environment (Zhao et al., 2022; Cai et al., 2022). Adsorption of heavy metal pollutants is currently one of the main research directions for biochar application, this is because biochar usually has a large specific surface area, a developed pore structure, and a rich set of functional groups, all of which can be used for the adsorption of heavy metal pollutants (Deng et al., 2022).

The current research on biochar for heavy metal wastewater treatment still has room for improvement. The main problems are the long retention time of biochar pyrolysis reaction, low absorption efficiency for cadmium-containing wastewater, and slow onset of action. In view of this, in this study, walnut shell biochar (WSBC) was used as a carrier, the modification process was separated from the preparation process, and a new type of modified biochar for cadmium-containing wastewater was finally prepared by adjusting the treatment process and modification method at the same time. In this study, WSBC produced under the conditions of pyrolysis temperature of 700˚C and retention time of 90 min was selected and modified using different modification reagents, and the modified biochar was used to treat simulated cadmium-containing wastewater, and the group with better efficiency was screened out according to the results of the ICP-MS test, and analyzed and interpreted together with the data of characterization, such as SEM, FT-IR, and so on. The experimental results showed that the use of potassium ferrate-modified WSBC has the advantages of fast onset, high efficiency (more than 96% of cadmium in simulated wastewater can be removed in 1 min of shock reaction), short pyrolysis retention time (retention time is only 90 min), and mild preparation conditions, which is in line with "whole-process environmental protection", and is in line with the advantages of the use of potassium ferricyanide and biochar alone. It is in line with the concept of "whole process environmental protection". The combination of high pyrolysis temperature and short pyrolysis retention time brings a relatively ideal biochar yield (the actual yield is around 44.1%), which is in line with the economic efficiency requirements of industrial production, and can be used to solve the problem of cadmium-containing wastewater treatment in industrial production.

2. Literature Review

Adsorption method as a cheap and efficient method for removing heavy metals from water is widely used in the purification of heavy metal-polluted wastewater, and at the same time, a literature review was made to analyze the direct and modified applications (Cai et al., 2022). Li et al. (2020) pointed out that if heavy metal pollutants are removed directly by biochar, there are problems such as the relatively low adsorption capacity and the poor adsorption selectivity. Zhang et al. (2023) used potassium permanganate modified coconut shell biochar (MCBC) as an adsorbent to investigate its removal performance and mechanism of Cd(II) and Ni(II), and pointed out that Cd(II) and Ni(II) were mainly attached to MCBC through surface adsorption and pore filling. Lai et al. (2022) also investigated the main adsorption pathways of Cd^{2+} on biochar can be categorized into ion exchange and precipitation, in which ion exchange is the main pathway for the adsorption of Cd^{2+} on low-temperature pyrolysis-prepared biochar, and precipitation has the highest proportion in the process of adsorption of Cd^{2+} on high-temperature pyrolysis-prepared biochar.

2.1. Raw Materials

In terms of raw materials for the preparation of biochar, the main choices are as follows: waste polymers, such as polyethylene and polyester (Ma et al., 2022); and agricultural production waste, such as straw, peanut shells, tea stems, walnut shells, etc. (Sanchez-Hernandez et al., 2021; Oh & Seo, 2019). Cai et al. (2022) found that it is also feasible to prepare biochar by high temperature pyrolysis using marine plant-based wastes such as algae, doped with alginate or components with hydroxyapatite structure, such as lobster shells and crab shells. Meanwhile, the biochar obtained by pyrolyzing straw had a stronger adsorption capacity for heavy metals Pb^{2+} and Cd^{2+} at relatively high temperatures (Yang et al., 2023), but further studies need to be done on the retention time of the pyrolysis process.

2.2. Pyrolysis Parameters

Regarding the selection of pyrolysis temperature of biochar, Lai et al. (2022) studied biochar prepared by pyrolysis of rice straw as raw material, and found that the Cd^{2+} adsorption on rice straw-based biochar generated at a pyrolysis temperature of 700˚C was in accordance with the quasi-secondary kinetics and Langmuir model, and compared with that of 300˚C and 500˚C, it had a larger specific surface area and a better adsorption effect of Cd^{2+}. In addition, the use of potassium salts in the pyrolysis process can improve the yield of biochar due to the escape behavior of the potassium salts loaded on the surface with the pyrolysis process, and the loss is negatively correlated with the increment of biochar. Potassium contained in walnut shells is richer than normal leaves and straw, and can even be used as a potassium fertilizer. Therefore, in this study, we chose walnut shells as the raw material for the preparation of biochar, and chose high-temperature pyrolysis (not less than 700˚C) to prepare biochar.

In addition to the pyrolysis temperature, there are two other parameters to be considered in the study of pyrolysis, one being the rate of temperature increase and the other being the retention time, which is divided into the retention time in the low-temperature zone and the retention time when the pyrolysis temperature is reached. The retention time is divided into retention time in the low-temperature zone and retention time when the pyrolysis temperature is reached, which are referred to as "low-temperature retention time" and "pyrolysis retention time", respectively, for the convenience of presentation. Chen et al. (2020) took straw biochar as the research object and found that a higher heating rate would easily lead to an increasing rate of thermal weight loss, which eventually led to a decrease in the biochar yield. Haykiri-Acma and Yaman (2009) also found that an increase in the heating rate would lead to a decrease in the biochar yield in the study of hazelnut shell biochar. He attributed this to the fact that the faster the heating rate, the shorter the retention time at low temperature, resulting in insufficient time for the organic macromolecules in the feedstock to decompose and reorganize, and not enough thermally stable solids could be generated. The insufficient amount of thermally stable solids will lead to the decomposition of biochar in the high temperature zone, which in turn affects the yield. In the preparation of biochar from rice straw, corn straw and walnut shells. The inflection point temperature for the yield of pyrolyzed biochar from walnut shells, i.e. the pyrolysis temperature was around 411˚C (Ma, 2020). When higher than this temperature, the efficiency ratio of biochar output and input started to decrease. Based on the above conclusions, in this study, a tube furnace was used to pyrolyze walnut shells to prepare biochar, and the heating rate was controlled at 10˚C/min and protected by nitrogen gas throughout the process in order to maximize the yield inflection temperature and avoid excessive decomposition in WSBC.

2.3. Modification Reagents

As a common biochar modification reagent, potassium permanganate belongs to strong oxidizing reagents and high valence heavy metal salts, which can change the surface structure of biochar and increase the specific surface area and pore volume (Zhang et al., 2023). Besides potassium permanganate, potassium hydroxide and phosphoric acid are also common modifying reagents, and some biochar modified by iron-based reagents have significant advantages in the treatment of Cd^{2+} containing wastewater (Li, 2021; Liu et al., 2019). Li (2021) found that corn straw biochar loaded with n-FeOOH had a high specific surface area. Compared with the pre-loading, the specific surface area of corn straw biochar loaded with n-FeOOH increased by 42 times, the pore volume increased by 10 times, and the removal rate of Cd(II) at a concentration of 150 - 300 mg/L was maintained at more than 70%.

In summary, in this study, potassium pertechnetate, potassium permanganate, potassium hydroxide and phosphoric acid were selected as the modification reagents to modify walnut shell biochar, respectively, and unmodified walnut shell biochar was added as a blank group, and simulated wastewater experiments and ICP-MS means were used to test the performance of various biochars for treating cadmium-containing wastewater, and give a reasonable explanation in combination with the characterization data, such as SEM and FT-IR.

3. Materials and Methods

3.1. Materials

Raw biochar was prepared by walnut shell through slow pyrolysis. The walnut particles were ground to below 2 mm and pyrolyzed at 700˚C under an atmosphere of N_2 for 1 h. Elements and functional groups in the biochar were determined by XRD (PHILIPS X'Pert MPD) and FT-IR (Thermo Nicolet Corporation Nicolet 8700). Potassium permanganate ($KMnO_4$), phosphoric acid (H_3PO_4), and cadmium (II) chloride hemi(pentahydrate) ($CdCl_2·2.5H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium ferrate (K_2FeO_4) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd.

3.2. Pyrolysis Experiments

We placed 100 g of grounded walnut shells as raw materials in a crucible, then compacted and covered, placed in a tube furnace, and 20 sccm of nitrogen gas (20 cm^3/min) was introduced, and the tube furnace was heated up to 700˚C at a rate of 10˚C/min, and retained for 90 min when reached 700˚C. Later, the device was cooled down to room temperature naturally, which took about 70 min.

The tube furnace was opened and the resulting walnut shell biochar was removed and the mass of the product was weighed to be 44.1 g, so the yield was 44.1% calculated by Equation (1). The resulting biochar was ground and pulverized for subsequent experiments.

$$\text{Yield Rate} = \frac{m_{production}}{m_{raw\ materials}} \times 100\% \quad (1)$$

3.3. The Modification Experiment of Walnut Shell Biochar

3.3.1. K_2FeO_4-Modified Walnut Shell Biochar

1) Prepare 1 L of 0.1 M K_2FeO_4 solution as the modifying solution;

2) Weighing 3 g of walnut shell biochar into a large beaker, pouring in the modifying solution and continuously stirring the reaction for 6 h;

3) Pour the mixed solution obtained in 2) onto a 200-mesh filter sieve and filter it, wash the large beaker three times using distilled water, pour the washed liquid onto the same filter sieve and filter it, and finally wash the product on the filter sieve again repeatedly with distilled water until a total of about 1 L of distilled water was consumed;

4) Collect the product obtained in 3) in a small beaker and put it into an oven to dry at a constant temperature of 80˚C for 24 h, then get dry production of K_2FeO_4-modified walnut shell biochar.

3.3.2. $KMnO_4$-Modified Walnut Shell Biochar

1) Prepare 1 L of 0.1 M $KMnO_4$ solution as the modifying solution;

2) - 4) Same steps as 3.3.1's.

3.3.3. H_3PO_4-Modified Walnut Shell Biochar

1) Prepare 1 L of 0.1 M H_3PO_4 solution as the modifying solution. Since the actual percentage of phosphoric acid in the selected phosphoric acid is 85%, the actual preparation of 100 mL of 0.1 M phosphoric acid solution requires that 6.84 mL of this phosphoric acid be mixed with 93.16 mL of distilled water;

2) - 4) Same steps as 3.3.1's.

3.3.4. KOH-Modified Walnut Shell Biochar

1) Prepare 0.1 L of 0.1 M KOH solution as the modifying solution;

2) Weigh 2 g of walnut shell biochar into a large beaker, pour in the modified solution, and continuously stir the reaction for 6 h;

3) and 4) Same steps as 3.3.1's.

3.4. Modified Walnut Shell Biochar Cadmium Removal Performance Test

1) Prepare 1 L of 50 mg/L (by elemental mass of cadmium) $CdCl_2$ solution as cadmium-containing wastewater. The cadmium content in the simulated wastewater of the blank group was measured to be 49982.94 ppb, marked as c_{blank};

2) Mix 0.04 g of walnut shell biochar samples (unmodified, K_2FeO_4-modified, $KMnO_4$-modified, H_3PO_4-modified, KOH-modified) with 25 mL of cadmium-

containing wastewater, respectively, and loaded into 50 mL centrifugal tubes, which were passed through a shaking machine and shaken to react for 1, 5, 10, 30, 60, and 120 min. At the end of the shaking, the upper clear liquid was quickly extracted from the centrifuge tube and filtered to obtain the filtered clear liquid;

3) The filtrate in (2) was tested by ICP-MS to obtain the cadmium content and marked as $c_{residue}$, then calculate the removal rate of cadmium by Equation (2):

$$\text{Cadmium Removal Rate} = \frac{c_{blank} - c_{residue}}{c_{blank}} \times 100\% \tag{2}$$

3.5. Supplementary Experiments

3.5.1. $FeCl_3$-Modified Walnut Shell Biochar

1) Prepare 1 L of 0.1 M $FeCl_3$ solution as the modifying solution;

2 - 4) Same steps as 3.3.1's.

3.5.2. $FeSO_4$-Modified Walnut Shell Biochar

1) Prepare 1 L of 0.1 M $FeSO_4$ solution as the modifying solution;

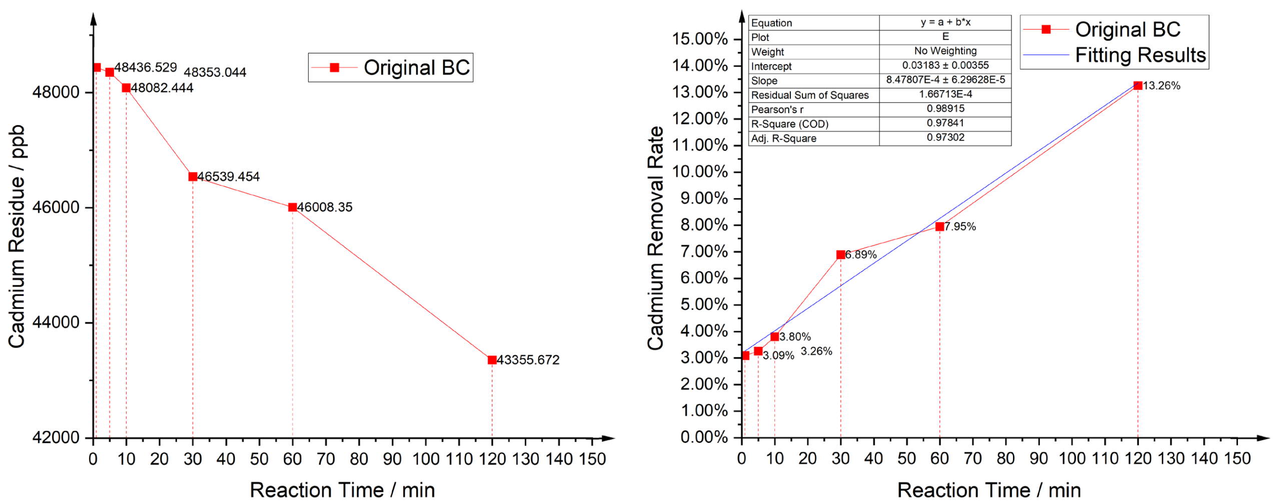
2 - 4) Same steps as 3.3.1's.

4. Experiment Results and Analyses

4.1. Analysis of ICP-MS Test Results

4.1.1. Original Walnut Shell Biochar

The cadmium residue in the original walnut shell biochar (Original WSBC) treated wastewater ranged from 43355.672 ppb - 48436.529 ppb, and the calculated cadmium removal rate was found to be in the range of 3.09% - 13.26% as shown in Figure 1(a) and Figure 1(b). The results of this study showed that the cadmium removal rate was in the range of 3.09% - 13.26% for each minute of reaction time. Linear fitting of the cadmium removal rate image showed that the



(a) (b)

Figure 1. (a) Cadmium residue versus reaction time in the original biochar group; (b) Cadmium removal rate versus reaction time in the original biochar group.

cadmium removal rate increased by about 0.085 percentage points for every 1 min increase in the reaction time, $R^2 = 97.8\%$.

4.1.2. K_2FeO_4-Modified Walnut Shell Biochar

The cadmium residue in the wastewater treated with K_2FeO_4-modified WSBC was in the range of 43.810 ppb - 1690.107 ppb. The removal of cadmium was calculated to be as high as 96.61% - 99.91%. The results are shown in Figure 2(a) and Figure 2(b). Linear fitting of the cadmium removal images shows that for every 1 minute increase in reaction time, the cadmium removal rate increases by about 0.023 percentage points, $R^2 = 67.5\%$.

4.1.3. H_3PO_4-Modified Walnut Shell Biochar

The cadmium residue in the wastewater treated with H_3PO_4-modified WSBC ranged from 47722.256 ppb - 51100.932 ppb. Three of the points (5 min, 10 min, 30 min) had higher values than the blank group (49982.94 ppb) as shown in Figure 3. It is hypothesized that the reason for this is that the biochar itself contains traces of cadmium, and under the phosphoric acid modification condition, the cadmium in the biochar enters into the solution in the form of cadmium salts, which in turn leads to higher ICP-MS test results than those of the blank group. And with the time, the cadmium element in the solution was gradually absorbed by the H_3PO_4-modified WSBC, and finally the cadmium element in the solution reached 47722.256 ppb at 120 min. In view of the irregular situation of cadmium absorption, the group does not do the cadmium removal rate versus reaction time images.

4.1.4. KOH-Modified Walnut Shell Biochar

The cadmium residue in the wastewater treated with KOH-modified WSBC was in the range of 45935.038 ppb - 48158.519 ppb, and calculations showed that the cadmium removal rate was around 3.70% - 8.10%, as shown in Figure 4(a) and

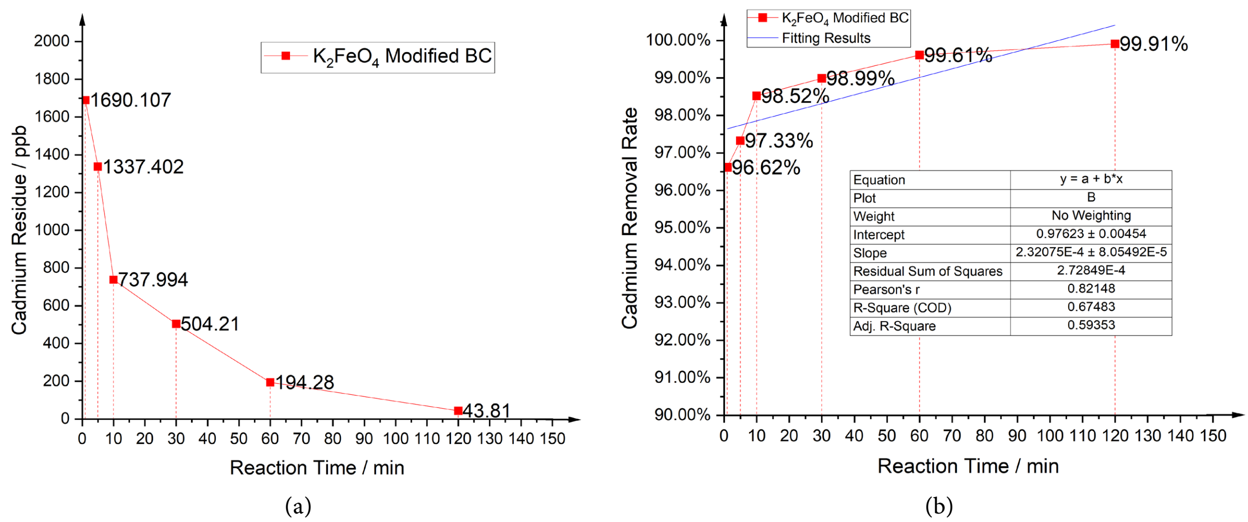


Figure 2. (a) Cadmium residue versus reaction time in the K_2FeO_4-modified biochar group; (b) Cadmium removal rate versus reaction time in the K_2FeO_4-modified biochar group.

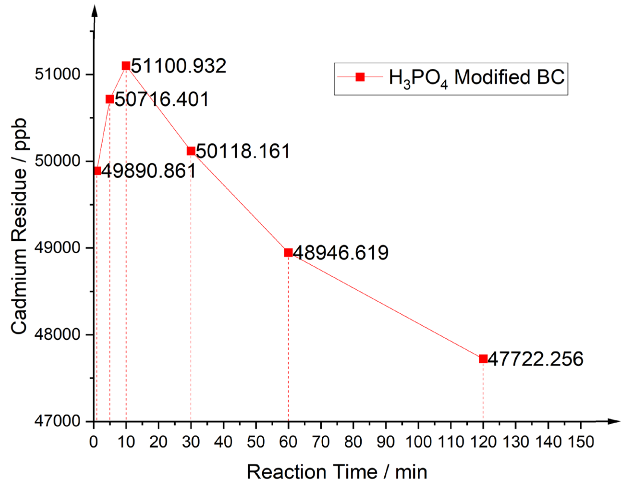
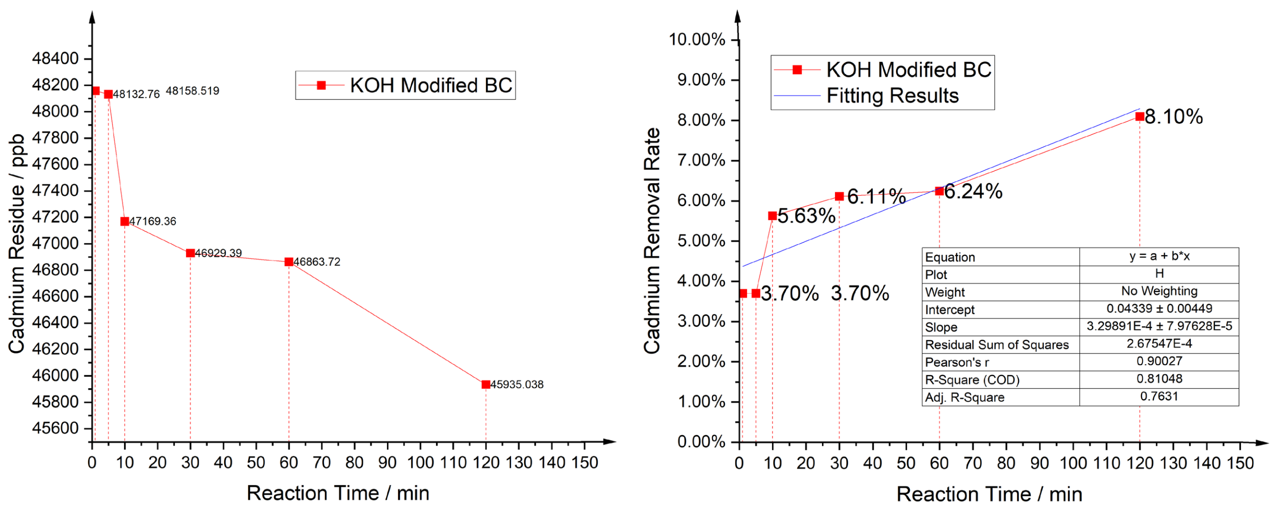


Figure 3. Cadmium residue versus reaction time in the H_3PO_4-modified biochar group.



(a) (b)

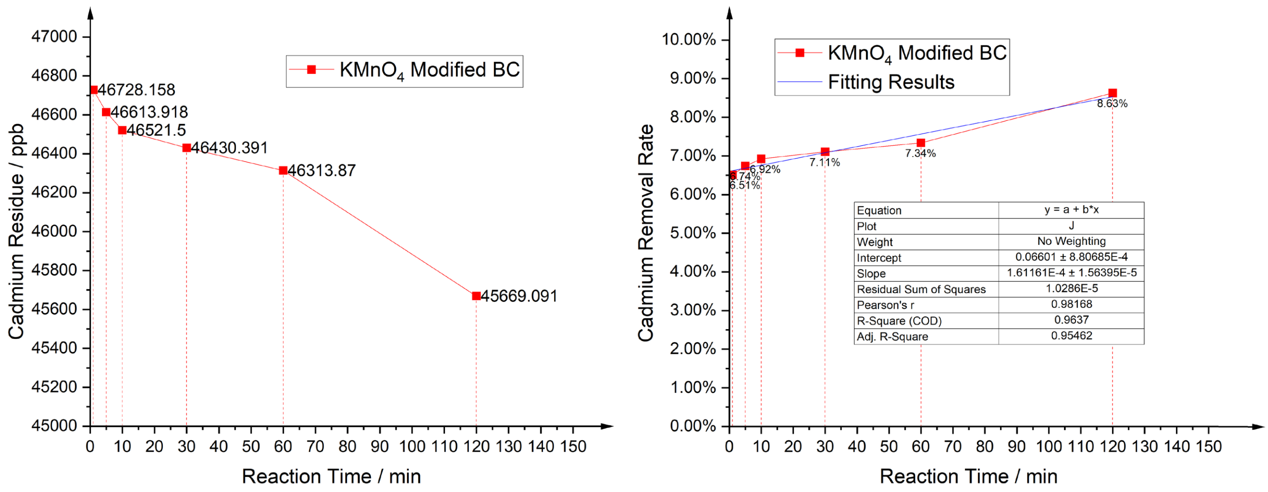
Figure 4. (a) Cadmium residue versus reaction time in the KOH-modified biochar group; (b) Cadmium removal rate versus reaction time in the KOH-modified biochar group.

Figure 4(b). Linear fitting of the cadmium removal rate image shows that for every 1 minute increase in reaction time, the cadmium removal rate increases by about 0.033 percentage points, R^2 = 81.0%.

4.1.5. $KMnO_4$-Modified Walnut Shell Biochar

The cadmium residue in the wastewater treated with $KMnO_4$-modified WSBC was calculated between 45669.091 ppb - 46728.158 ppb, which shows that the cadmium removal rate was in the range of 6.51% - 8.63%, as shown in Figure 5(a) and Figure 5(b). Linear fitting of the cadmium removal rate image showed that the cadmium removal rate increased by about 0.016 percentage points for every 1 minute increase in reaction time, R^2 = 96.4%.

It is known from the literature that the adsorption of heavy metals in solution by biochar follows the process of "first fast and then slow" (Li, 2021; Ma, 2020):



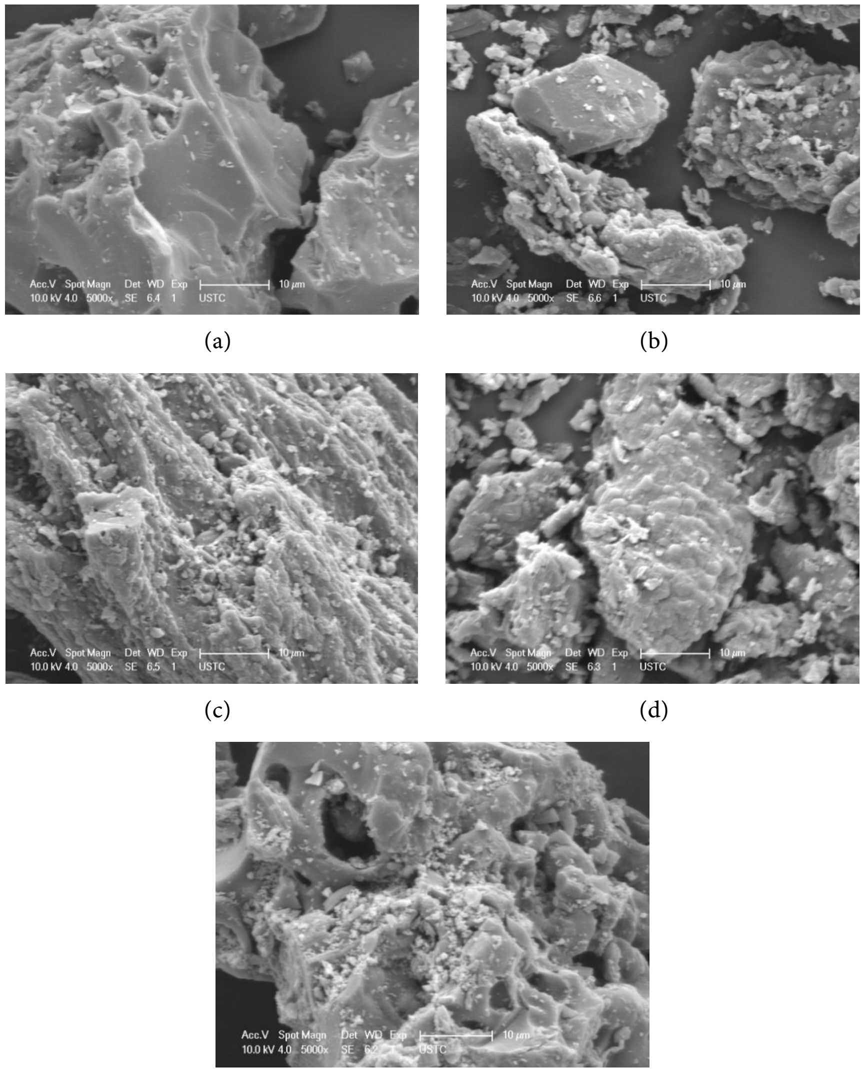
(a) (b)

Figure 5. (a) Cadmium residue versus reaction time in the $KMnO_4$-modified biochar group; (b) Cadmium removal rate versus reaction time in the $KMnO_4$-modified biochar group.

at the early stage of adsorption, the heavy metals in solution are adsorbed onto the surface of biochar, and the adsorption sites on the surface are occupied rapidly. In this process, the adsorption rate is fast, and the heavy metal ions in the solution decrease rapidly. In the five groups of experiments shown in this section, except for the $KMnO_4$-modified WSBC group and the H_3PO_4-modified WSBC group, all of them are generally consistent with this law, i.e. the content of cadmium in the solution decreases rapidly in the first 10 - 30 minutes of the reaction time. And after adsorption for a period of time, the remaining ions with lower concentration in the solution diffuse to the interior of the biochar and adsorb into the pore structure to be further removed, at which time the adsorption rate starts to decrease.

4.2. Analysis of SEM Characterization Results

Scanning electron microscopy (SEM) is a kind of microscopic characterization between transmission electron microscopy and optical microscopy, which can directly utilize the material properties of sample surface materials for microscopic imaging. We analyzed the SEM characterization images of unmodified WSBC and WSBC treated with four modifying reagents (shown in **Figures 6(a)-(e)**), and obtained the following conclusions: the surface of unmodified biochar particles was relatively flat, with fewer pores and cavities. After treatment with the modifying reagent, more pores and caves appeared on the surface of the biochar particles with higher specific surface area, which was often accompanied by the appearance of point-like bumps and layer-like stacking phenomena to further increase the specific surface area. The surface of the K_2FeO_4-modified WSBC produced a large number of pores and caves, and the particle scale was about 20 μm, which is the smallest scale among all the WSBCs. The smaller scale brings larger surface effect and greatly improves the reactivity of treating



(a) (b) (c) (d) (e)

Figure 6. (a) SEM characterization image of original WSBC; (b) SEM characterization image of K_2FeO_4-modified WSBC; (c) SEM characterization images of H_3PO_4-modified biochar; (d) SEM characterization image of KOH-modified WSBC; and (e) SEM characterization image of $KMnO_4$-modified WSBC (in sequential order).

cadmium-polluted wastewater, which is related to the fact that K_2FeO_4 containing +6-valent iron embodies stronger reactivity in the modification reaction.

4.3. FT-IR Characterization Results and Analyses

4.3.1. Analysis of FT-IR Characterization Results of Original, KOH-Modified, $KMnO_4$-Modified, K_2FeO_4-Modified and H_3PO_4-Modified Walnut Shell Biochar

Fourier transform infrared spectroscopy (FT-IR) is a powerful tool to characterize the types of surface groups on organic matter. All five groups of biochar shown in Figure 7 showed absorption peaks near 3470 cm^{-1}, which was generated by the O-H absorption vibration in the hydroxyl group, due to the fact that after pyrolysis at high temperatures, part of the cellulose and lignin were retained,

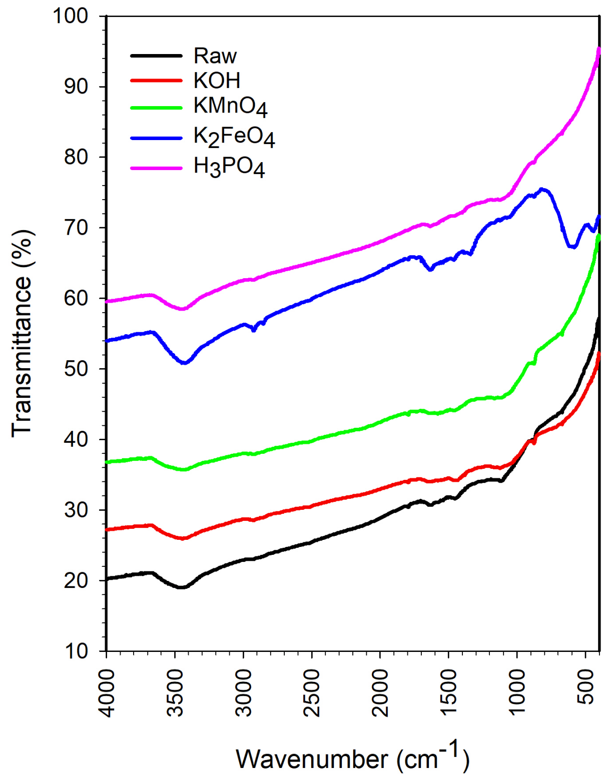


Figure 7. Five groups of WSBC FT-IR characterization test results. "Raw" refers to the original WSBC; "KOH" refers to KOH-modified WSBC; "$KMnO_4$" refers to $KMnO_4$-modified WSBC; "K_2FeO_4" refers to K_2FeO_4-modified WSBC; and "H_3PO_4" refers to H_3PO_4-modified WSBC.

which resulted in the presence of a large number of oxygen-containing groups on the surface of the biochar. In the K_2FeO_4-modified group (blue curve in Figure 7), new absorption characteristic peaks appeared near 650 cm^{-1} and 500 cm^{-1}, which were generated by the bending vibration of Fe-O and Fe-OH, respectively, indicating that the K_2FeO_4-modified experiments had achieved significant results, and the iron compounds were successfully loaded on the biochar, which might exist in the form of iron oxides or the hydrates of iron oxides; a new peak was observed at 2900 cm^{-1}, which was generated by the O-H absorption vibration in the hydroxyl group. The characteristic double peak was observed at 2900 cm^{-1} and another absorption peak was observed at 1650 cm^{-1} and 1300 cm^{-1}, respectively. The above two results indicate that the surface groups of WSBC complexed with iron, resulting in changes in the characteristic peaks of the groups.

4.3.2. Analysis of FT-IR Characterization Results of Original, K_2FeO_4-Modified, $FeSO_4$-Modified, and $FeCl_3$-Modified Walnut Shell Biochar

To make the conclusions of the above K_2FeO_4 modification experiments more robust, we designed supplementary experiments to modify WSBC using $FeSO_4$ and $FeCl_3$ as modification reagents and identify the types of groups they contain by FT-IR characterization tests, and the results are shown in Figure 8.

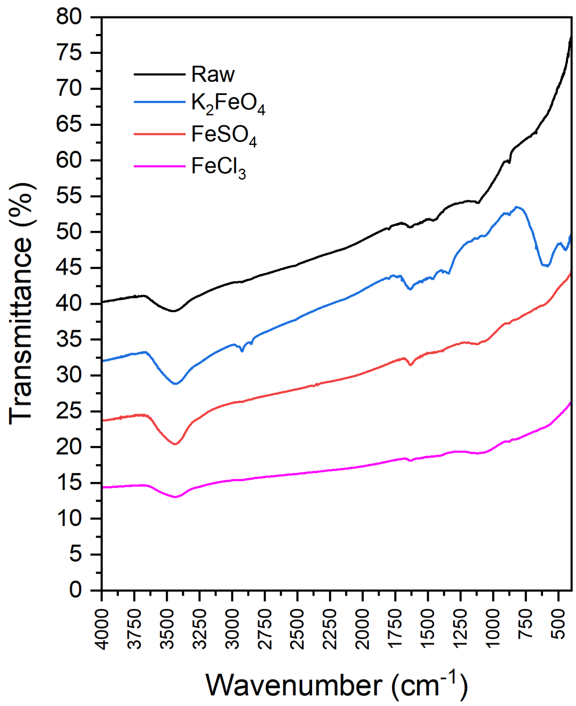


Figure 8. Four groups of WSBC FT-IR characterization test results. "Raw" refers to the original WSBC; "K_2FeO_4" refers to K_2FeO_4-modified WSBC; "$FeSO_4$" refers to $FeSO_4$-modified WSBC; and "$FeCl_3$" refers to $FeCl_3$-modified WSBC.

By comparing the test results of the unmodified group and the K_2FeO_4-modified group, we found that the $FeCl_3$-modified group and the $FeSO_4$-modified group showed absorption peaks at 3300 - 3500 cm^{-1}, generated by the O-H absorption vibration in the hydroxyl group, and the absorption peaks were observed at 1650 cm^{-1}, which suggests that the functional groups of the WSBC may react with some metal ions in a complexing reaction, and there is a possibility that it is iron or ferrous ions (Fe^{3+} or Fe^{2+}); no new absorption peaks were observed near 650 cm^{-1} and 500 cm^{-1}, and no absorption peaks were observed at 2900 cm^{-1} and 1300 cm^{-1}, which indicates that iron is not loaded on the WSBC in the form of iron oxide compounds.

The above results support the conclusion of the SEM characterization test results in 4.3.1, that is, K_2FeO_4 containing +6-valent iron shows strong reactivity and oxidation in the modification reaction, and produces characteristic iron oxides loaded on WSBC, whereas the modification with other valence iron compounds ($FeCl_3$ containing +3-valent iron and $FeSO_4$ containing +2-valent iron in this case) does not have this effect.

4.4. Analysis of XRD Characterization Results

The X-ray diffraction (XRD) characterization test can be used to analyze and identify the surface phases of the samples. As shown in **Figure 9**, in this study, we analyzed all the iron compounds modified WSBC by XRD test and found that no sharp diffraction peaks could be obtained, indicating that all the modified

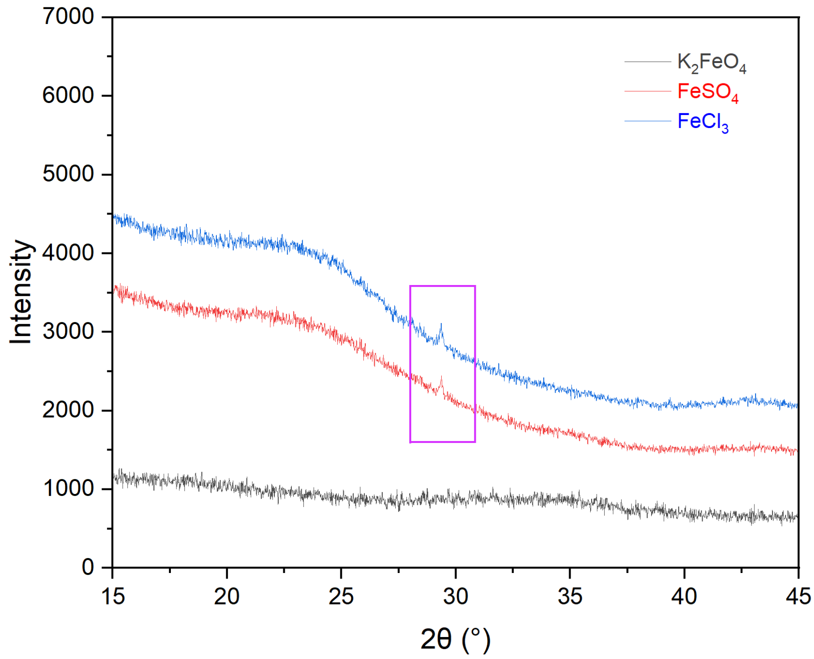


Figure 9. XRD characterization test results of three groups of iron compounds modified WSBC. In order to facilitate the observation of the significant peaks, the horizontal coordinates are taken as $15˚ \le 2\theta \le 45˚$.

biochar materials produced are amorphous materials. However, we found that both the $FeSO_4$-modified group and the $FeCl_3$-modified group showed a significant peak at about $2\theta = 30˚$ (as shown by the purple box in **Figure 9**), which is a characteristic peak of amorphous carbon (Li, 2021; Liu et al., 2019), while the K_2FeO_4 group did not. This finding suggests that K_2FeO_4, which is both reactive and oxidizing, altered the physical phase and morphological structure of the biochar in the modification experiments, causing it to fail to show the characteristic packet peak of amorphous carbon, thus supporting the conclusion in 4.3.1 and 4.3.2.

5. Conclusion

After a series of studies, the following conclusions were obtained in this study:

Walnut shell biochar (WSBC) modified with K_2FeO_4 can efficiently remove cadmium from contaminated water, and the removal rate of cadmium in simulated cadmium wastewater with 50 mg/L of cadmium was as high as 96.62% - 99.9%, with the onset of action time of 1 minute, and only 0.04 g of samples per 25 mL of simulated cadmium wastewater were needed to be added to the onset of action. Compared with no modification and other reagent modifications, the cadmium removal effect of K_2FeO_4-modified WSBC was outstanding. SEM characterization results showed that K_2FeO_4 modified the morphology of WSBC, which resulted in the reduction of the particle scale of the biochar to about 20 μm, with a stronger surface effect. FT-IR characterization results showed that the iron compounds were loaded on the biochar successfully and the iron compounds had reacted with the surface groups of the biochar, which is significantly different from the unmodified and other reagent-modified WSBCs. XRD characterization test results show that the K_2FeO_4-modified group has no significant peak at about $2\theta = 30^\circ$, which is a characteristic peak of amorphous carbon. It indicates that K_2FeO_4 has strong reactivity and oxidizability to change the physical phase and morphological structure of WSBC.

On the preparation of WSBC, we found that a yield of about 44.1% could be obtained under the conditions of a heating rate of 10˚C/min, a pyrolysis temperature of 700˚C, a residence time of 90 min, and a nitrogen flow rate of 20 sccm. The reason is that during the pyrolysis process, due to the longer residence time in the low-temperature zone and nitrogen protection throughout the process, enough heat-stable solids are generated during pyrolysis to try to avoid the conversion of solid products to pyrolysis liquid and pyrolysis gas that results in a better biochar yield.

K_2FeO_4-modified WSBC has a good treatment effect against cadmium in wastewater, with the function of deep purification and treatment of water resources, with significant practical value. It is also an effective way to utilize solid waste resources, which helps to realize the whole process of environmental protection.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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