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The Improvement Effects of Different Treatment Methods of Soil Wastewater Washing on Environmental Pollution

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Abstract: This paper focus on how to treat the wastewater after soil washing since water pollution is a severe threat to the water security of China. Ca $(OH)_2$ and two kinds of biochars (biochar and $ZnCl_2$ modified biochar) were tested to treat the waste $FeCl_3$ washing effluent. Two kinds of biochars (biochar and $ZnCl_2$-modified biochar) were prepared from maize straws. Soil samples were collected near a smelter for adsorption experiments. ICP-OES was used to determine the concentration of metal ions in the samples, as well as calculating their adsorption capacity and removal rate. As to $Ca(OH)_2$ treatment, the maximum removal rates of Cd, Pb, Cu, and Zn could exceed 99%, and the concentrations of Cd, Pb, Cu, and Zn in solution could reduce to 0.08, 0.018, 0.15, 0.44 mg/dm^3, respectively. However, both of the two biochars had relatively low removal rates compared with Ca $(OH)_2$ treatment. The wastewater shows significantly lower environmental implications after the two treatments, and the lime precipitation method has better effects than biochar adsorption. The activated carbon adsorption method discussed can significantly improve the environmental pollution caused by soil washing wastewater, which is suitable for environmental treatment projects.

Keywords: soil washing; wastewater treatment; heavy metal contamination; environmental implications; biochar

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1. Introduction

Soil heavy metal pollution has been a severe problem, along with economic growth and rapid industrialization. According to a report by the Chinese government made in 2014, about 13% of farmland soils were polluted by heavy metals metalloids [1] in the soil survey. Heavy metals in soil can pose an enormous threat to the environment and human health, as their ability in poisoning plants and bioaccumulation [2]. Therefore, a large body of research in the remediation of heavy metal polluted soil has been conducted. The physical repair technology, chemical repair technology, biological repair technology, and joint repair technology are roughly summarized [3–6]. Soil washing was one of the most effective means among the different treatments of the heavy metal polluted soil. $FeCl_3$ is a popular soil washing leachate [7], and it has already been applied in some countries to remediate soil contaminated by certain heavy metals, such as Cd and Pb [8,9].

Though soil washing can remove heavy metals in soil with high efficiency, the waste soil washing effluents would be a new hazardous to the environment, as the washing effluents contain high amounts of heavy metals after washing. Soil washing can generate a great deal of wastewater [10,11]. How to handle the wastewater is a severe problem when using soil washing to remediate heavy metal polluted soils. Conventional methods to treat soil washing leachate are electrochemical treatment [12], chemical precipitation [11], adsorption by biochar (BC), and photocatalytic degradation [13]. However, treatments, like electrochemical and photocatalytic degradation, usually need complicated devices or costly material. Moreover, the polluted soils are usually located in countries or suburbs, far away from sewage treatment plants, which means the washing effluents must be treated on-site and inexpensively with simple equipment. Therefore, chemical precipitation and adsorption progress are more available in treating waste soil washing effluents.

During the process of chemical precipitation, the chemical reagents could form hard soluble complexes with heavy metal ions; thus, the complexes precipitates can be separated from the water by precipitation or filtration, and the treated water can be discharged or reused [14]. Traditional chemical precipitation, such as hydroxide precipitation, sulfide precipitation, and ferrite precipitation, are widely used in industry [15]. As to hydroxide precipitation, alkaline materials are added to control the pH of the solution, and the undissolved hydroxide precipitation was generated to be separated from the water [16]. Lime is most commonly used to treat the sewage contained with heavy metal ions for its advantages of convenience and economic operation [17]. Many studies [8,17,18] have found that lime had an excellent removal capacity for metal ions.

The pyrolysis of biomass materials produces BC under low temperatures and limited oxygen conditions. With ample surface area and strong adsorption [14], BC adsorbing has also received significant attention, and is popularly used during the treatment of industrial wastewater [19]. A previous study found that maize BC has a better immobilizing effect than corn straw, wheat straw, or cotton straw during the remediation of Pb and Cd in soil [20–22]. Experiments have proved that $ZnCl_2$ modified BC had a good effect in increasing low-cost carbon surface area [23,24].

Soil washing to remove heavy metals in soil has been reported by numerous researchers [8,10,25]. However, research about the treatment of waste washing effluents are relatively rare. Therefore, this article focuses on (1) adding $Ca(OH)_2$ to treat waste $FeCl_3$ washing effluent; (2) using BC and $ZnCl_2$ modified BC to treat the waste effluent; (3) investigating the applicability of the two treatments and to compare them based on their efficiency. Two kinds of BCs were prepared, and an electron microscope observed their microstructure. Soil samples near the smelter were collected, and the values of BCs for heavy metal adsorption in wastewater and environmental pollution control were explored through experiments.

2. Materials and Methods

2.1. BC Sample Preparation and Characterization

Two kinds of BCs (BC and $ZnCl_2$ modified BC) were prepared in the experiment, and they were all made by maize straws from Xinyang city in China. After washed with deionized water, we dried them at 100 °C for 10 h, then smashed and sieved them through a 1 mm sieve. BC was pyrolyzed in nitrogen at the temperature of 450 °C for 2 h in a ceramic pot. For the preparation of $ZnCl_2$-modified BC (ZnBC), the maize straw was immersed in $ZnCl_2$ 1 M solution for 24 h at room temperature, using a proportion of $ZnCl_2$ respect maize straw at a mass ratio equal to 1 [26]. Then, the modified BC was pyrolyzed in a ceramic tank filled with nitrogen at 450 °C for 2 h. The obtained materials were dried at 100 °C for 10 h and finally pyrolyzed with the same condition of BC. Both of the two BC samples were washed with deionized thoroughly until the pH of the supernatant was around 7. Next, the soil samples were dried and sieved through a 100 μm sieve. Then, the obtained BCs were added to the soil samples for experimentation.

The characteristics [26] of BC and ZnBC were tested as follows: an automatic Micromeritics measured pore characteristics ASAP2460 volumetric sorption analyzer (Micromeritics Instrument Corp., Norcross, GA, USA), and the microstructure and morphology were acquired by scanning-electron-microscopy (SEM) through Nova Nano SEM 230 (USA).

2.2. Soil Characteristics and the Soil Washing Effluents

The soil sample was collected near a smelter in Zhuzhou city, China, which had high contamination levels of Cd, Pb, Cu, and Zn. After collection, the soil was air-dried at room temperature and passed through a 2 mm sieve. We tested soil pH with a liquid–solid ratio of 1:2.5 [27], soil organic matter (SOM) after $K_2Cr_2O_7$ digestion [28], cation exchange capacity (CEC) through $BaCl_2$ displaced [29] soil texture [30] (Ball, 1964), and total soil Pb, Cu, Zn, and Cd contents by inductively coupled plasma–optical emission spectrometry (ICP–OES) after HNO_3–$HClO_4$–HF digestion [31]. The main physicochemical characteristics of the soil are shown in Table 1 (USDA).

Table 1. The main characteristics of the soil sample.

Variables/Properties and Units	Value
Clay (%)	32.81 ± 0.04
Silt (%)	43.27 ± 3.43
Sand (%)	23.92 ± 3.48
pH	5.22 ± 0.03
SOM (%)	38.43 ± 0.59
CEC (cmol/kg)	20.50 ± 1.30
Fe (g/kg)	32.13 ± 3.18
Cd (mg/kg)	16.83 ± 0.22
Pb (mg/kg)	465.28 ± 2.36
Cu (mg/kg)	182.43 ± 2.25
Zn (mg/kg)	1178.35 ± 1.58

We placed six hundred grams of the soil sample to 2 L Pyrex beaker, then filled with 900 cm^3 of 0.1 M $FeCl_3$, so that the liquid to solid ratio was about 1:1.5 [32]. We stirred the mixture by a magnetic stir rod at a fast speed. After stirring for 1 h at room temperature, we centrifuged the soil suspensions by 100 cm^3 plastic bottles at 4000 rpm for 10 min. The supernatant was then prepared for the next experiment after being filtered through a 0.45 µm membrane filter. The heavy metals concentrations (Cd, Pb, Cu, and Zn) in the waste washing water were analyzed by ICP–OES. The pH value of wastewater was 3.42, and the water quality monitoring results were shown in Table 2.

Table 2. Monitoring results of heavy metal contents in wastewater.

Metal Elements	Concentration ($mg \cdot L^{-1}$)
Fe	27.1
Mg	122.6
Mn	3.8
Cu	0.006
Zn	212.5
Pb	0.3
Cd	84.4

2.3. Heavy Metals Removal from the Washing Wastewater by $Ca(OH)_2$ Addition

Placed 40 cm^3 of the waste soil washing effluent (in Section 2.3.) in an Erlenmeyer flask, after adding a series concentrations of $Ca(OH)_2$ powder (0, 0.8, 1.6, 2.4, 3.2, 4.0, 4.8, 6.4, 8.0, 12.0, and 20.0 mg/dm^3), we equilibrated them on a shaker at the speed of 60 rpm for 1 h with a temperature of 25 °C [33]. We filtered the supernatants via a 0.45 µm membrane filter to measure the metals concentrations by ICP–OES. The pH values were acquired by HI 3221 pH meter.

2.4. Adsorption of Heavy Metals by BCs in the Wastewater

To achieved better experiment conditions, we used 0.2g BC and ZnBC to absorb Cu^{2+} with a volume of 100 cm^3 at a concentration of 100 mg/L, with vibration time of 4 h. Both BC and ZnBC reached their saturated adsorption after the 6th h.

To measure the adsorption abilities of BC and ZnBC, we added them at a concentration of 0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.5, and 1.0 g to 40 cm^3 wastewater in Erlenmeyer flasks. After shaking the mixture at 60 rpm at 25 °C for 6 h, we tested the metal concentrations of the suspensions as above.

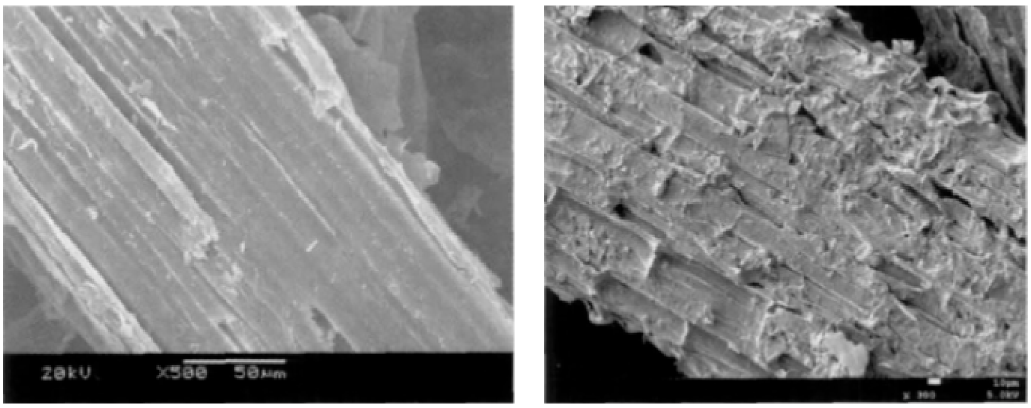
All experiments were performed in triplicates. Means and standard deviations were calculated with Microsoft Excel.

3. Results and Discussion

3.1. BC Characterization

3.1.1. SEM Analysis

The SEM images of BC and ZnBC are shown in Figure 1. The dark zones and light zones, are each referred to carbon structure and metal oxides [26]. As shown, BC had an ordered structure, contained porous morphology and some small particles on its surface [26]. After the modification by $ZnCl_2$, the original structure was broken, several metal oxides appeared on the carbon sheet. As a consequence, the surface area was increased compared to BC carbon.



(**a**) (**b**)

Figure 1. SEM images of BC and ZnBC: (**a**) BC, (**b**) ZnBC.

3.1.2. BET Analysis

The Brunauer–Emmett–Teller (BET) surface area and pore characters of the BC and ZnBC are listed in Table 3. After $ZnCl_2$ modified, BET surface area and total pore volume of the BC increased significantly, whereas average pore diameter showed minimal decrease: the BET surface area of ZnBC was increased from 59.21 to 780.23 m^2/g, thirteen folds more than BC; the total pore volume of ZnBC was increased by 350% compared to BC. A previous study [24] also found that $ZnCl_2$ modified carbon could increase C content in the proportion of the BC. As a consequence, the BET surface and the total pore volume of the BC were increased after activated by $ZnCl_2$. However, $ZnCl_2$ might promote the polymerization of tar-forming compounds or the retention of the tar-forming compounds in the pore structure, which would decrease the average pore diameter as a consequence [34].

Table 3. The BET surface area and pore characters of the samples.

Sample.	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter (nm)
BC	59.21	0.17	2.60
ZnBC	780.23	0.59	2.57

3.2. Heavy Metals Removal by $Ca(OH)_2$ Addition

The influence of lime dosage on the heavy metal removal rates is shown in Figure 2. Since $FeCl_3$ is a weakly alkaline salt, it could generate a large number of H^+ in the washing solution. When Ca $(OH)_2$ was put into the wastewater, OH^- would neutralize the free H^+ in the water firstly. After that, the pH of the waste would increase along with the addition of Ca $(OH)_2$. The solution pH had a significant effect on the solubility of heavy metals. According to the research of [35], the hydroxide of metals would not be formed until the solution pH reached the "adsorption edge." Generally, the pH of the solution controls the degree of dissociation of acidic or basic compounds. When the pH reaches a specific range, these compounds will dissociate and thereby affect the adsorption of them. Makino et al. (2016) [11] found that the solubility product constant (Ksp) of Cd, Pb, Cu, and Zn were 2.8×10^{-14}, 1.1×10^{-20}, 1.9×10^{-20}, and 4×10^{-17}, respectively. The maximum removal rates of Cd, Pb, Cu, and Zn could exceed 99% when the pH was around 7, and the concentrations of Cd, Pb, Cu, and Zn in solution could reduce to 0.08, 0.018, 0.15, 0.44 mg/dm^3, respectively.

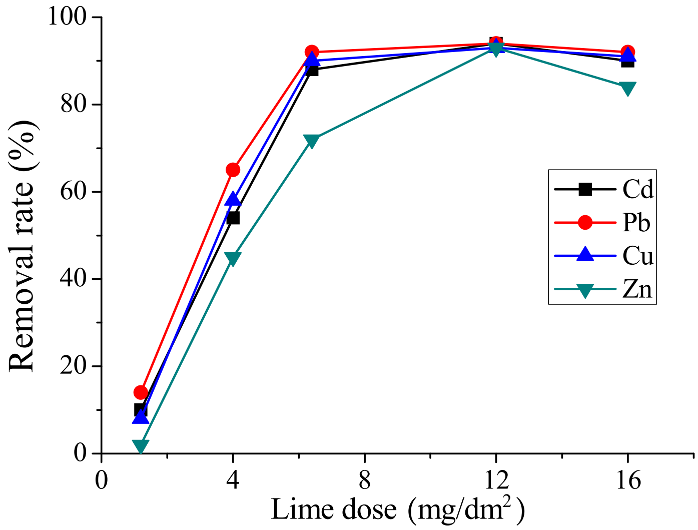


Figure 2. Influence of lime dosage on the heavy metal removal rates.

OH^- will react with the amino groups on the surface of the BC through hydrogen bonding; thus, the surface of the amino-modified BC presents negative charges. The effect of positive and negative charges is beneficial to the adsorption of Pb^{2+}. Due to the difference in the pH values of the aqueous solution, the existence of Pb and Cd ions are also different. If the pH value is less than 6, the chemical ions will exist in the form of free Pb^{2+}; if the pH value is greater than 6, the hydroxyl complex ions of Pb will be gradually generated and begin to precipitate. For Cd ions, if the pH value of the solution is less than 8, it will exist in the form of Cd^{2+} and a small amount of $CdOH^+$ ions; if the pH value is greater than 8, Cd precipitation will gradually occur.

3.3. BC Sorption of Heavy Metals

Removal rates of heavy metals by BC and ZnBC in waste soil washing effluent were shown in Figure 3. After soil washing, the pH of the waste effluent was 2.41. ZnBC had better effects on the absorption of Cd, Pb, Cu, and Zn than BC. The removal rate of Cd, Pb, Cu, and Zn when treated with BC were 40.01%, 61.23%, 48.56%, and 33.27%, respectively. Compared with BC, Zn BC had much better adsorption capacity of metal ions in the wastewater, and the removal rates of Cd, Pb, Cu, and Zn were 93.18%, 99.23%, 95.44%, and 90.67%, respectively. According to previous research [36,37], sorption of the metal ion by BC is mainly influenced by BC surface chemistry and its surface area or by precipitation reactions. Therefore, pyrolytic temperature [38], surface chemistry [39] modification, and the solution pH [40] would exert a significant impact on the adsorption performance of BC. For example, some BCs had the maximum adsorption of metal ions when the solution pH value was around 5 [40–42]. In consequence, the high specific surface area of ZnBC was probably an important reason for its higher removal capacity, compared to BC. According to Section 3.1, the BET surface area of ZnBC is thirteen times larger than BC, which means there would be more adsorption sites available for the adsorption of heavy metals [43,44]. On the other side, the main existing form of Zn was Zn-OH on the surface of ZnBC after $ZnCl_2$ activated [24]. As a consequence, ions exchange could happen between Zn-OH and metal ions (Cd, Pb, and Cu). The ionic radius of Cd, Pb, Cu, and Zn were 0.97, 1.21, 0.70, and 0.74 nm [45], respectively; the average pore diameter of BC and ZnBC were 2.60 and 2.57 nm. So, the metal ions could fill in the micropores of both BCs. Therefore, $ZnCl_2$ modified BC possessed the practical value for removing metal ions in the waste washing effluent.

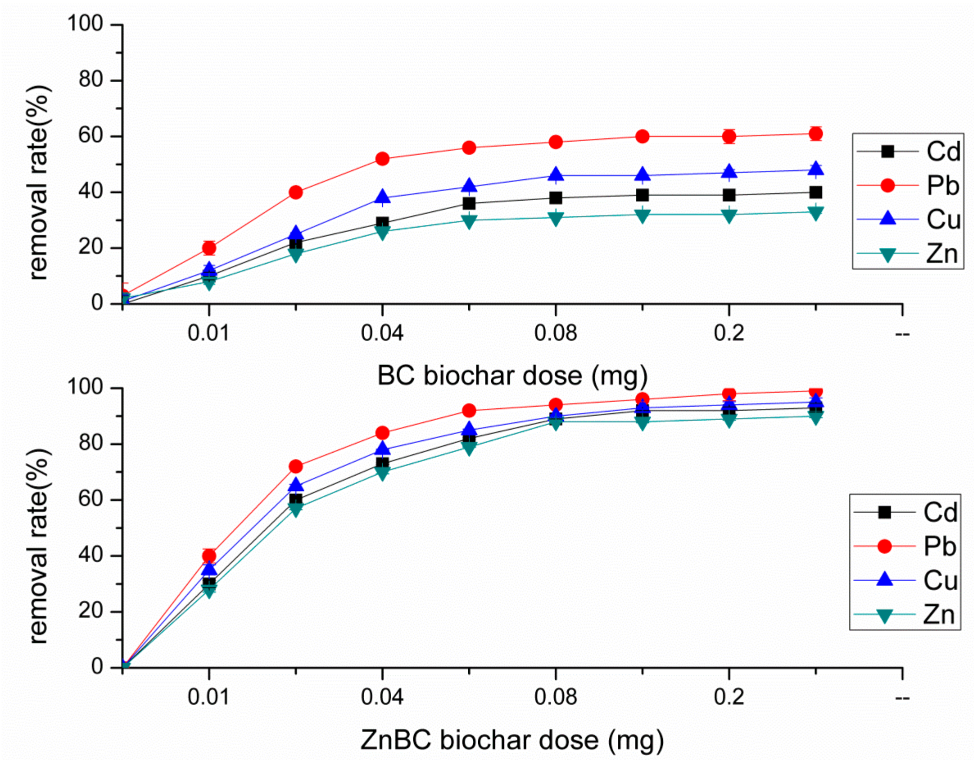
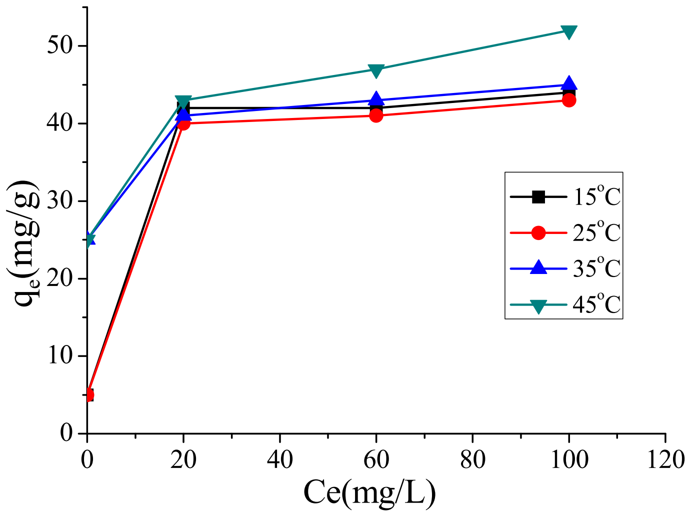
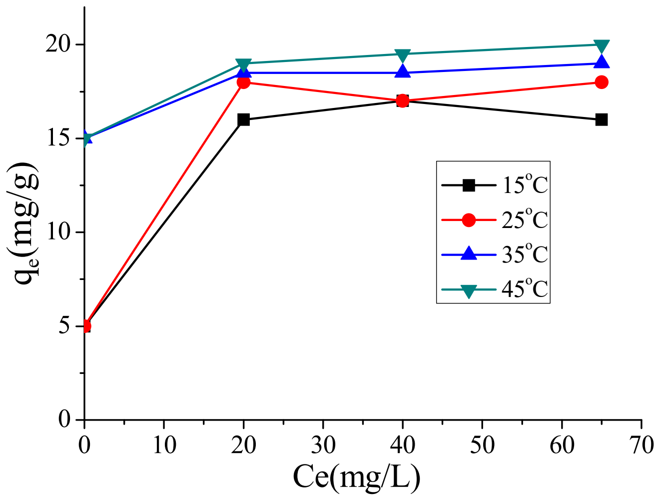


Figure 3. Removal rates of heavy metals by BC and ZnBC in waste soil washing effluent.

The equilibrium adsorption quantity qe of ZnBC adsorbing Cd^{2+} and Pb^{2+} with the equilibrium concentration Ce in the solution after adsorption equilibrium was plotted; the adsorption isotherms of ZnBC adsorbing Cd^{2+} and Pb^{2+} at different temperatures were obtained, as shown in Figure 4. Under the experimental conditions, when the equilibrium concentration was lower, the specific adsorption capacity of ZnBC for Cd^{2+} and Pb^{2+} increased sharply with the increase in the solution concentration, showing that the adsorbent had high adsorption capacity even at low concentrations. The specific adsorption capacity of the adsorbent for Cd^{2+} and Pb^{2+} generally increased with the increase in temperature, indicating that heating was beneficial to adsorption. Generally, increasing the temperature will increase the diffusion rate of adsorbate molecules in the outer boundary layer of the adsorbent. Second, temperature changes may affect the equilibrium adsorption capacity of the adsorbent. Figure 4 illustrated that the amount of adsorption increased with an increase in temperature. This change indicated that the reaction was endothermic.



(**a**) The adsorption isotherm of ZnBC to Pb^{2+}.



(**b**) The adsorption isotherm of ZnBC to Cd^{2+}.

Figure 4. Adsorption isotherms of ZnBC to Cd^{2+} and Pb^{2+} at different temperatures. (**a**) shows that under the same test conditions, the adsorption capacity will increase with the increase of temperature. (**b**) shows the increase of temperature will increase the diffusion rate of adsorbate molecules in the external boundary layer of adsorbent.

3.4. Comparison of $Ca(OH)_2$ and BC Treatment

Previous researchers (Chen et al., 2009 [17]; Chen et al., 2011 [40]; Makino et al., 2016 [11]) found that the formation of hydroxide metals or other complexes with metals had a significant influence on the removal of heavy metals, as they could precipitate from the water. Furthermore, our experiments indicated $Ca(OH)_2$ had a better effect in increasing solution pH than BCs (BC and ZnBC), which could be the main reason that $Ca(OH)_2$ had better removal rates of Cd, Pb, Cu, and Zn than above BCs during the treatment of waste $FeCl_3$ washing effluent. Though the solution pH was around 9 after

$Ca(OH)_2$ treatment, the cleaned wastewater could help to neutralize the soil acidity caused by $FeCl_3$ washing [8], but the concentration of Cd, Pb, Cu, and Zn were 0.08, 0.018, 0.15, and 0.44 mg/dm^3, which exceed the values of Chinese effluent standards [46]. Therefore, the cleaned waste effluent could not be discharged into the soil or rivers nearby directly. Further treatments, such as the adsorption by activated carbon [47] and membrane filtration treatment [48,49] were needed to meet the effluent standards. Furthermore, the cleaned wastewater could not be reused to pair the $FeCl_3$ soil washing solution, unless there was enough HCl or other acid to neutralize the excess OH^- in the water. Some researchers found that the activated carbon had an excellent removal capacity of metal ions, some of them can remove nearly 100% metal ions in solution [48,50]. However, both BCs in our experiment had low removal rates of Cd, Pb, Cu, and Zn. Previous studies (Chen et al., 2013 [51]; Xu et al., 2020 [52]) found BC showed preferable adsorption capacity when the pH value was greater than 5, while the pH of the waste effluent was 2.41, which could be the main reason for the low performance of BC and ZnBC. As maize straws contain multiple complex chemical compositions, including cellulose, hemicellulose, lignin, and soluble sugar. These compositions can bind with heavy metal ion through hydrogen bonds or ion exchange, which could be influenced by pH. Therefore, BCs were in-suitable to treat waste $FeCl_3$ washing effluent directly. Since solution pH had a significant influence on the removal capacity of active carbon [40], the combination of $Ca(OH)_2$ and BC to treat waste effluent might achieve a better effect than just $Ca(OH)_2$ or BC treatment alone.

4. Discussion

Globally, the research on BC focuses on its applications in agricultural soil. However, reports on the chemical modification of BC, as well as the application of modified BC in treating heavy metals in wastewater, are rare. Therefore, a theoretical basis will be provided for the application of BC from the perspective of waste recycling and environmental remediation. Based on the application of BC in wastewater treatment, first, maize straws, a universal intercultural solid waste, were selected as the biomass raw materials to prepare and modify the BC adsorbent. Then, the adsorbent's adsorption performance to heavy metals was explored.

The prepared adsorbent ZnBC could adsorb different kinds of metal ions and completely treat low-concentration heavy metal-polluted wastewater. Since the magnetic BC adsorbs metal ions due to surface adsorption and surface activity, the active site on the surface is easy to be combined with positively charged metal ions [53]. Besides, the characterization analysis showed that magnetic BC had some unsaturated carbon bonds, carboxyl groups, hydroxyl groups, and other groups that were easily substituted with metal ions; they could bind to metal ions in the solution to remove the heavy metal pollutants in industrial wastewater. The experimental results showed that the hydroxide and sulfide precipitation method had a more significant impact on Zn^{2+} and Cd^{2+} in wastewater. Marshall et al. treated soybean and cotton husks with NaOH to improve their ability to adsorb Zn^{2+}, which was consistent with the results of this experiment [54,55]. In addition, a simple analysis of the possibility of the BC adsorption mechanism was carried out. The removal mechanism of heavy metals in aqueous solution by BC was more likely to be based on the co-precipitation of functional groups on the surface of BC.

5. Conclusions

Soil heavy metal pollution is a severe problem, along with economic growth and rapid industrialization. The ongoing food safety risk events push the security problems of agricultural products to an important issue and caused widespread social panic. Soil washing is an effective remedy to remove heavy metals, which is widely approved by the international community. However, how to treat the wastewater after soil washing is a significant social problem. In this paper, two simplified, highly efficient, cost-effective on-site methods—BC adsorption and lime precipitation method—had been investigated to treat washing wastewater containing Cd, Cu, Pb, and Zn. The washing wastewater was obtained from on-site soil washing with $FeCl_3$. The experiment revealed that these treatments could effectively remove all of the metals in the pretreated water, and the lime precipitation method has better effects than BC adsorption. During precipitation of metals ions with $Ca(OH)_2$, the maximum removal rates of Cd, Pb, Cu, and Zn could exceed 99%, and the corresponding concentrations of Cd, Pb, Cu, and Zn in solution could reduce to 0.08, 0.018, 0.15, and 0.44 mg/dm^3, respectively.

Because the actual environmental factors are more complicated, after some time (maybe several years, decades, or hundreds of years), various physical and chemical changes and biological reactions may exist. BC is common in water or soils, while the existing problems of aging and deterioration have to be considered. Therefore, limitations exist in the experimental process. In the future, it is necessary to carry out long-term tracking and monitoring of amino-modified BC to ensure its stable, functional applicability.

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