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Study on the effect of corn cob biochar on the performance of constructed rapid infiltration systems

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Abstract. The corn cob biochar (CCB600) was prepared at 600℃ with wasted corn cob as raw material. The modified corn cob biochar (CCB600-M) was prepared by modifying CCB600 with hydrochloric acid and ultrasonic. CCB600 and CCB600-M were added into constructed rapid infiltration (CRI) systems respectively as one of the filter materials, and their effect on wastewater treatment performance was investigated. The results showed that the average removal rates of COD, NH4+-N and TP in CRI reactor with adding CCB600-M were respectively 4.8%, 6.1% and 18.2% higher than those with adding CCB600, and respectively 9.3%, 11.4% and 39.7% higher than those without adding any biochars. The modified corn cob biochar was a new type of filter materials with excellent performance and low price, which can effectively improve the wastewater treatment performance of CRI systems.

1. Introduction

In recent years, the problem of water pollution is becoming more and more serious. To solve the problem of water pollution, it is necessary to explore efficient, low cost and environment-friendly wastewater treatment technologies [1]. The constructed rapid infiltration (CRI) system is a new type of ecological wastewater treatment technology, which is based on traditional soil infiltration technology, uses natural or artificial materials with better infiltration performance to replace soil as filter material, and realizes pollutant removal by means of adsorption, interception and biodegradation. The hydraulic load of CRI technology can reach 0.5~1.2 m/d or even higher, which has more advantages than traditional soil infiltration technology. The CRI technology is especially suitable for the treatment of domestic sewage, polluted surface water and rural scattered sewage in small and medium-sized cities, which has a broad application prospect [2]. The research and development of new filter materials that can effectively improve the performance of wastewater treatment has become a hotspot in the way of popularization and application of CRI technology.

At present, the preparation of biochar from wasted biomass as adsorption materials for heavy metals, ammonia nitrogen and organic pollutants is increasing [3]. Biochar has a large specific surface area, developed pore structure and excellent adsorption performance. It has the advantages of high efficiency and low cost and can be used to return to the field after adsorption saturation to improve the soil quality [4]. The annual output of corn in China is as high as 200 million tons. If the corn cob can not be used reasonably after being abandoned, it will cause serious waste of resources and environmental pollution. The preparation of biochar from wasted corn cob can not only reduce environmental pollution, but also realize the reuse of waste. However, there is little research on the application of corn cob biochar as filter material in CRI systems.

Therefore, corn cob was used as raw material to prepare biochar and modified biochar in this study. The structural characteristics of corn cob biochar before and after modification were investigated, and the enhancement effect of corn cob biochar as filter material on the treatment performance of CRI systems was explored, which could provide theoretical basis for the application of corn cob biochar in wastewater treatment and a new method for utilization of agricultural wasted biomass.

2. Materials and Methods

2.1 Preparation and modification of biochar

2.1.1 Preparation of biochar

Wash and dry the wasted corn cob, smash it through 80 mesh sieve, take a appropriate amount of it into the crucible, cover it and put it into the muffle furnace, heat it to 600℃ with a temperature gradient of 23 ℃/min under the condition of anoxia, and then keep the temperature constant for 3 hours. After cooling to room temperature, pass it through 80 mesh sieve, clean and dry at 105℃ after

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filtration. The prepared corn cob biochar was labeled as CCB600.

2.1.2 Modification of biochar

Take a proper amount of CCB600 to a 250 mL conical flask, add 1.0 mol/L hydrochloric acid in the proportion of 10 mL hydrochloric acid/1g CCB600, and modify it in the ultrasonic generator with 560 W power for 1 hour. After cleaning to neutral, dry at 105℃ after filtering. The modified corn cob biochar was prepared and labeled as CCB600-M.

2.2 Reactors and operation conditions

Fig.1 shows the diagrammatic sketch of CRI reactors.

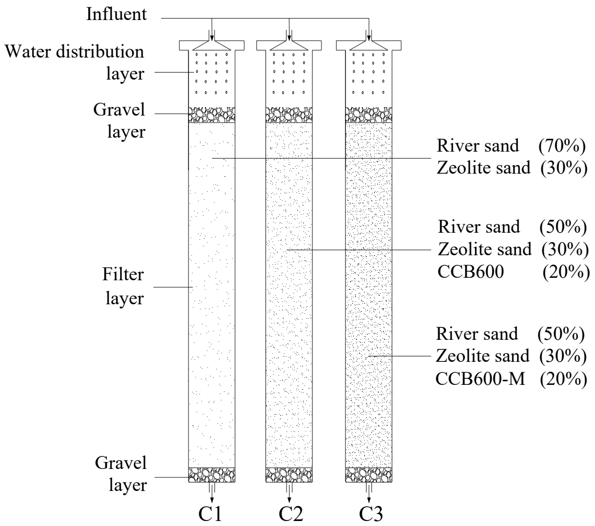


Figure 1. The diagrammatic sketch of CRI reactors.

Three CRI reactors were used in this study, numbered as C1, C2 and C3 in sequence, all of which were made of PVC, with column height, inner diameter and filter layer height of 150 cm, 7 cm and 120 cm respectively. The filter layer of C1 was composed of river sand and zeolite sand with the particle size of 0.5~1.0 mm uniformly mixed by volume ratio of 7:3. The filter layer of C2 was composed of river sand, zeolite sand and CCB600 evenly mixed by volume ratio of 5:3:2. The filter layer of C3 was composed of river sand, zeolite sand and CCB600-M evenly mixed by volume ratio of 5:3:2. A gravel layer was set above the filter layer for buffering, and a gravel layer was set below the filter layer for supporting. The thickness of the gravel layer was 5 cm.
The sprayer was used to distribute water evenly, and the metering pump and relay were used to control the influent quantity and time respectively. The ambient temperature was controlled at (25±5) ℃. The CRI reactors operated for two cycles a day. Each cycle consisted of flooding period and drying period. The flooding time was 4 hours, the drying time was 8 hours, and the hydraulic load was 1.0 m/d.

2.3 Wastewater quality and inoculated sludge

The domestic wastewater of farmer households was used as the influent wastewater. The influent COD, NH_4^+-N and TP concentration was 160.5~213.2 mg/L, 35.1~47.6 mg/L and 3.4~4.1 mg/L respectively, and the pH value was 6.8~8.1. The inoculated sludge used in this study was taken from the returned sludge from the secondary sedimentation tank of a wastewater treatment plant.

2.4 Analysis items and methods

2.4.1 Biochar analysis

The content of C, H, N and O was tested by the element analyzer (VARIO EL cube, Germany). The content of oxygen-containing acidic functional groups on the surface of biochar was determined by Boehm titration. The ash content was determined by the burning method (SG-XL1200, China). The specific surface area, total pore volume and average pore diameter were tested by the BET-N_2 method (NOVA4000e, USA). The surface morphology was observed by the SEM method (ZEISS SUPRA40, Germany).

2.4.2 Water quality analysis

The main monitored water quality indexes included COD, NH_4^+-N and TP. The analysis methods referred to *Water and Wastewater Monitoring and Analysis Methods* (4th Edition, China).

3. Results and Discussion

3.1 Structural characteristics of biochar

As can be seen from the results of elemental analysis showed in Fig. 2(a), the content of C in corn cob biochar was the highest. The contents of all elements after modification were increased, and the (N+O)/C of CCB600-M was higher than that of CCB600, indicating that the surface polarity of corn cob biochar after modification was improved [5].
As can be seen from Fig. 2(b), the content of oxygen-containing acidic functional groups in CCB600-M was 18.2 times higher than that in CCB600, among which carboxyl, lactone, phenolic hydroxyl and carbonyl were 25.5, 33.0, 22.7 and 6.0 times higher respectively. This is because some micropores on the surface of CCB600 were blocked by impurities that were difficult to be cleaned with water. With the chemical dissolution of these impurities by hydrochloric acid and the strong shear force generated by ultrasonic cavitation effect, the insoluble substances were dispersed in hydrochloric acid solution. As a result, the oxygen-containing acidic functional groups blocked on the pore surface were exposed and their concentrations increased.
According to the results of BET analysis, the specific surface area, total pore volume and average pore diameter of CCB600 were 12.58 m^2/g, 0.0317 cm^3/g and 5.546 nm respectively. After modification, the specific surface area, total pore volume and average pore diameter of CCB were

increased to 106.93 m^2/g, 0.1028 cm^3/g and 12.855 nm respectively. Therefore, the specific surface area of CCB600-M was 7.5 times higher than that of CCB600. The total pore volume and average pore size of CCB600-M were also significantly increased. The ash content of CCB600-M was only 3.02%, which was 62.3% lower than that of CCB600. This was due to the effect of "hydrochloric acid + ultrasonic" modification on demineralization and ash removal. The removal of ash would be conducive to open the blocked pores on the surface of biochar, and the original smaller pores would be oxidized and expanded by hydrochloric acid. Therefore, the number of pores increased significantly.

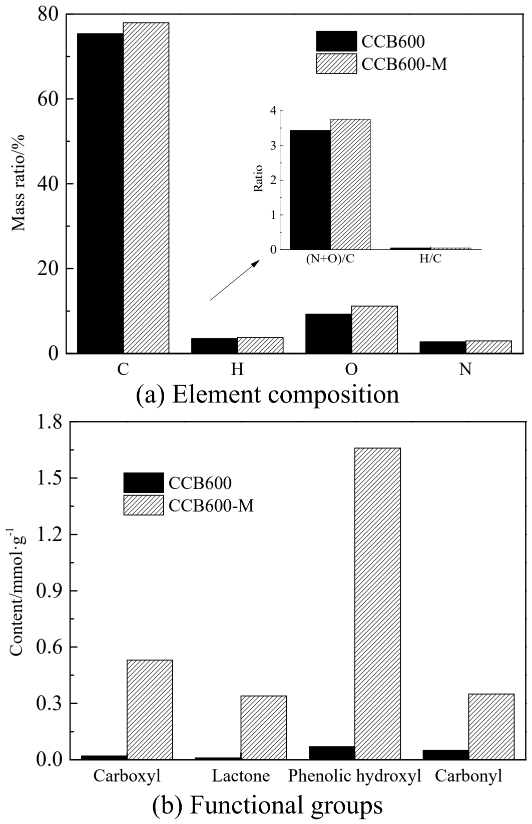


Figure 2. The element composition (a) and functional groups (b) of CCB600 and CCB600-M.

In addition, the cavitation of ultrasonic wave could make the energy density highly concentrated. The strong shear force generated could fracture the biochar and the number of massive fragments increased, which could be clearly seen from Fig. 3.

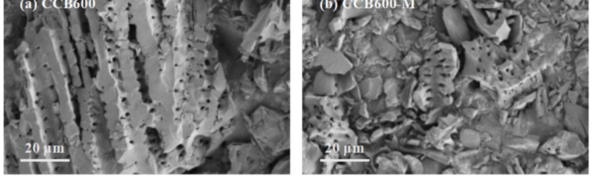
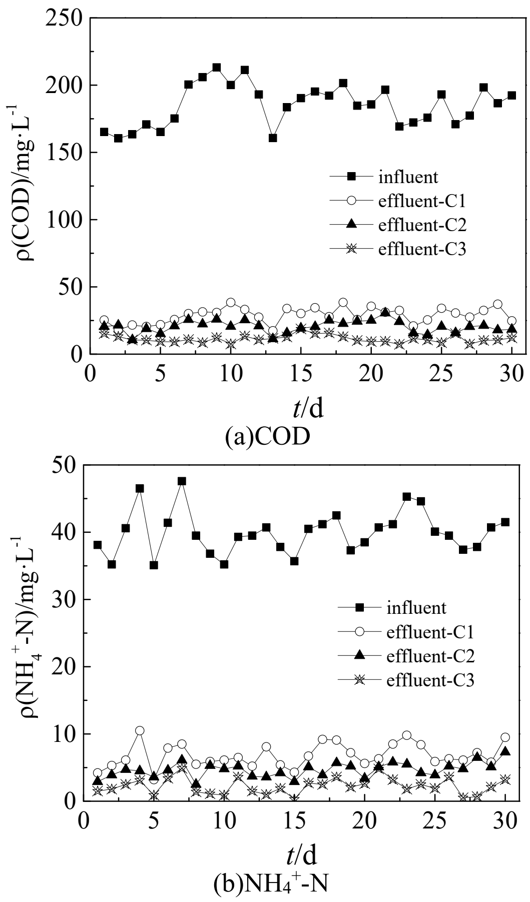


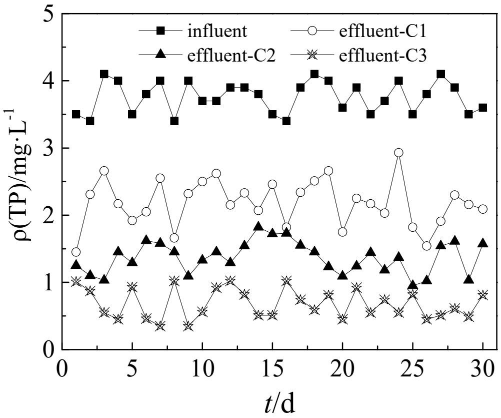
Figure 3. The SEM of CCB600 (a) and CCB600-M (b).

3.2 Wastewater treatment efficiency

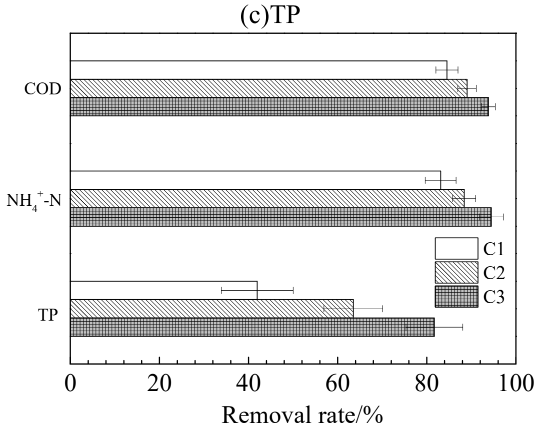
Fig.4 shows the removal efficiency of COD, NH_4^+-N and TP by C1, C2 and C3. It can be seen that under the same influent conditions, the average effluent COD concentrations of C1, C2 and C3 were 28.8 mg/L, 20.4 mg/L and 11.3 mg/L, respectively. The average COD removal rate of C3 was 93.8%, which was 4.8% and 9.3% higher than that of C2 and C1, respectively. The average concentrations of NH_4^+-N in the effluent of C1, C2 and C3 were 6.8 mg/L, 4.6 mg/L and 2.3 mg/L, respectively. The average removal rate of NH_4^+-N by C3 was 94.5%, which was 6.1% and 11.4% higher than that of C2 and C1, respectively. The average effluent TP concentrations of C1, C2 and C3 were 2.2 mg/L, 1.4 mg/L and 0.7 mg/L, respectively. The average TP removal rate of C3 was 81.7%, which was 18,2% and 39.7% higher than that of C2 and C1, respectively.

Therefore, the addition of corn cob biochar into CRI systems can greatly improve their wastewater treatment performance, especially the TP removal efficiency. In addition, the removal efficiency of COD, NH_4^+-N and TP in the CRI reactor with adding CCB600-M was better than that in the CRI reactor with adding CCB600 and the CRI reactor without adding any biochars. It can be seen that the modified corn cob biochar was more suitable as the filter material of CRI systems.





(c)TP



(d)Removal rate

Figure 4. Removal efficiency of COD, NH4+-N and TP by CRI reactors.

3.3 Strengthening mechanism analysis

According to the literature report, the CRI system had different oxygen environment at different heights, in which the upper part of the filter layer had a good aerobic environment and the lower part of the filter layer had a good anaerobic environment, which provided a good living environment for microorganism to remove pollutants from wastewater. The CRI system was a typical push flow bioreactor. In the process of infiltration from top to bottom, pollutants could be adsorbed or trapped on the filter particles, and then be decomposed or transformed by microorganism in the biofilm that attached to the surface of filter particles, so as to realize the purification of wastewater [6].

Both pollutants in wastewater and microorganism in biofilm need filter material as carriers. The composition of filter material directly affected the treatment efficiency of CRI systems. The filter material of CRI systems mostly adopted river sand or zeolite sand with good infiltration performance, which will help to increase the hydraulic load of the systems. However, the increase of hydraulic load will shorten the retention time of wastewater, resulting in the contact and reaction time of microorganism and pollutants were also shortened.

In this study, the addition of corn cob biochar improved the filter material structure of CRI systems. The corn cob biochar with good adsorption performance can provide the basis for improving the wastewater treatment performance of CRI systems. Compared with CCB600, CCB600-M contained more oxygen-containing acidic functional groups. The increase of oxygen-containing acidic functional groups can enhance the hydrophilicity and ion exchange capacity of biochars [7], providing the conditions for improving the adsorption performance of organic matter, nitrogen and phosphorus. In addition, the total pore volume, average pore diameter and fracture section of CCB600-M were higher than those of CCB600. The huge specific surface area and abundant pore structure provided more adsorption space for pollutants [8], and were also conducive to the adhesion of microorganism, so as to improve the removal effect of pollutants. As a result, the CRI reactor with adding CCB600-M as one of the filter materials had the highest removal rate of COD, NH_4^+-N and TP. The performance of the CRI reactor with adding CCB600 as one of the filter materials was not as good as C3, but it was still better than that without adding any corn cob biochars. Therefore, the modified corn cob biochar showed good application value as the filter material of CRI systems.

4. Conclusion

The modified corn cob biochar had a huge specific surface area, abundant pore structure and rich oxygen-containing acidic functional groups. When it was added to CRI systems, the adsorption performance of the filter material could be significantly improved. The average removal rates of COD, NH_4^+-N and TP could reach 93.8%, 94.5% and 81.7% respectively, which was 9.3%, 11.4% and 39.7% higher than those of the CRI system without adding any corn cob biochars. Modified corn cob biochar could be regarded as a new type of filter material for CRI systems and expand the application prospect of CRI technology in the field of wastewater treatment.

Acknowledgments

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