Preparation of sheep manure biochar and its enhancement effect on wastewater treatment performance of CRI systems

Jiao Chen¹², Shuxin Li¹, Qin Huang¹, Haolin Liu¹, Jieyu Sun¹, Ying Zhang¹, Yixin Lu¹²³,*

¹School of Materials and Environmental Engineering, Chengdu Technological University, Chengdu 611730, China
²State Environmental Protection Key Laboratory of Synergetic Control and Joint Remediation for Soil & Water Pollution, Chengdu 610059, China
³Haitian Water Group Co., Ltd., Chengdu 610200, China

Abstract: Sheep manure biochar (SMB550) was prepared by limited oxygen pyrolysis at 550°C and applied to constructed rapid infiltration (CRI) systems. The structural characteristics of SMB550 were tested and its effect on the wastewater treatment performance of CRI systems was investigated. The results showed that SMB550 had a large specific surface area, abundant pore structure and rich functional groups, showing a good adsorption potential. Using SMB550 as one of the filter material of CRI system, the average removal rates of COD, NH₄⁺-N and TP were respectively 9.3%, 8.6% and 34.9% higher than those of the blank group, which enhanced the treatment performance of CRI systems for wastewater. As a new type of filter material, SMB550 had a good application prospect in the field of wastewater treatment.

Key words: CRI systems; sheep manure; biochar; wastewater treatment.

1. Introduction

As a kind of eco-friendly wastewater treatment technology, the constructed rapid infiltration (CRI) system has attracted more and more attention in recent years, and has broad application prospects in the treatment of urban domestic sewage and polluted surface water [1,2]. This technology is different from the traditional soil infiltration system. It uses natural or artificial filter materials with better infiltration performance to replace the soil for filling, so as to obtain higher hydraulic load [3]. This technology mainly relies on the adsorption, interception and microbial degradation of the filter material to remove pollutants from wastewater, so the filter material is the key functional component of the technology, and the appropriate filter material structure is essential to improve the wastewater treatment performance of CRI systems. Biochar is a carbonate substance produced by pyrolysis of biomass residue under the condition of anoxic and high temperature. In general, it has the advantages of large specific surface area, simple preparation process, low cost and good adsorption potential [4]. Recently, the application of biochar in the treatment of organic matter, nitrogen, phosphorus and other pollutants in water is increasing [5-7]. At present, the traditional CRI systems mostly used river sand, zeolite sand and marble sand as the filter material, while the research of using biochar as the filter material was rarely reported.

Therefore, this study used waste sheep manure as raw material to prepare biochar, and applied it to CRI systems to investigate the variations of wastewater treatment performance before and after the addition of biochar, so as to provide a new filter material for CRI systems and explore a new way for resource utilization of wasted sheep manure.

2. Materials and Methods

2.1 Preparation of sheep manure biochar

Wasted sheep manure was taken from a sheep farm. After being dried, crushed and sieved for 60 mesh, put a proper amount of sheep manure powder into the crucible, covered it and put it into the muffle furnace, heated it to 550°C at a heating rate of 20°C/min, and then kept it at a constant temperature for 3 hours.

After cooling to room temperature, added 1.0 mol/L hydrochloric acid with the solid-liquid ratio (m/V) of 1:20, shaken at room temperature for 3 times, 30 minutes each time, and the frequency of vibration was 150 r/min. After cleaning to neutral and drying in an oven at 105°C, sheep manure biochar (SMB550) was successfully prepared [8].

* Corresponding author: yxlu61@163.com
2.2 Experimental reactors and operation conditions

Two CRI reactors (CRI1 and CRI2) were used in this study, all of which were made of polyvinyl chloride. Fig. 1 shows the device diagram of CRI reactors. The column height and inner diameter were 120 cm and 7 cm respectively, and the filter material was 100 cm high. CRI1 reactor adopted river sand, zeolite sand and marble sand with the particle size of 0.5~1.0 mm uniformly mixed by volume ratio of 5:3:2 as filter material, and CRI2 reactor adopted river sand, zeolite sand, marble sand and SMB550 evenly mixed by volume ratio of 5:3:1:1 as filter material. A layer of gravel with a particle size of 5~10 mm was laid on the top and bottom of the filter material respectively as a buffer layer and a supporting layer. The wastewater was evenly distributed via drip infiltration, the wastewater inflow was controlled by metering pump, and the inflow time was controlled by relay. During the experiment, the controlled temperature was $(25 \pm 5)$ $^\circ$C, running for 2 cycles every day, each cycle running for 12 hours, in which the flooding and drying time were 3 hours and 9 hours respectively, and the hydraulic load was 1.0 m/d.

2.3 Influent quality and inoculated sludge

The wastewater used in the experiment was taken from the domestic sewage of a college student apartment in Chengdu. The influent COD, NH$_4^+$-N and TP concentrations were 212.6~285.8 mg/L, 38.5~50.6 mg/L and 3.6~4.9 mg/L respectively, and the pH was 6.5~7.9. The inoculated sludge was taken from the secondary sedimentation tank of a wastewater treatment plant in Chengdu.

2.4 Analysis items and methods

The ash content of SMB550 was determined by muffle furnace (SG-XL1200, China). The content of C, H, N and O was determined by element analyzer (VARIO EL cube, Germany).

The specific surface area, total pore volume and pore size distribution were determined by specific surface area analyzer (NOVA4000e, USA). The surface morphology of SMB550 was characterized by field emission scanning electron microscope (ZEISS SUPRA40, Germany). The surface functional groups were determined by FT-IR spectroscopy (FT-IR Spectrum100, USA). The analysis method of COD, NH$_4^+$-N and TP concentration referred to Water and Wastewater Monitoring and Analysis Methods (4th Edition, China).

3. Results and Discussion

3.1 Structural characteristics of SMB550

The productivity of SMB550 was 48.71%, indicating that the mass loss of the preparation process of SMB550 was appropriate. The component contents of SMB550 were shown in Fig.2. In terms of element composition and atomic ratio, SMB550 contained a large number of C, and H/C<0.6, O/C<2.0, reflecting that SMB550 had a high biochemical stability [9].

According to BET analysis results, the specific surface area, total pore volume and average pore diameter of SMB550 were 105.61 m$^2$/g, 0.107 cm$^3$/g and 8.64 nm respectively. It indicated that SMB550 had a large specific surface area, total pore volume and average pore diameter. According to the SEM results as shown in Fig.3, the surface of SMB550 was rough and it also had a large number of micro pores, which was conducive to improving its adsorption capacity [8].
Fig. 3. Scanning electron microscope of SMB550.

(b)SEM of SMB550(×3000)

Fig. 4 shows the FT-IR spectra of SMB500. The peak at about 3400 cm⁻¹ belongs to the stretching vibration of —OH [10]. The absorption peak at 2919 cm⁻¹ belongs to the stretching vibration of C—H. The absorption peak at 1600 cm⁻¹ is attributed to the stretching vibration of C=C and C=O. The absorption peak at about 1100 cm⁻¹ is attributed to the stretching vibration of C—O. The absorption peak at 790 cm⁻¹ is attributed to the bending vibration of C—H on the aromatic ring [11]. These absorption peaks showed that SMB500 was rich in functional groups and had high aromaticity and stability [12]. These will be conducive to its adsorption of pollutants.

Fig. 4. The FT-IR spectra of SMB550.

3.2 Comparison of pollutant removal effect

Fig. 5 shows the effect of CRI systems on COD, NH₄⁺-N and TP removal before and after the addition of SMB550.

It can be seen from Fig. 5 that the effluent COD, NH₄⁺-N and TP concentrations of CRI1 were 26.1~41.3, 4.2~6.8 and 1.4~2.6 mg/L respectively. Compared with CRI1, the effluent COD, NH₄⁺-N and TP concentrations of CRI2 were significantly reduced, which were lower than 15.2, 2.3 and 0.78 mg/L respectively. The average removal rates of COD, NH₄⁺-N and TP were 96.3%, 97.1% and 87.8% respectively. Compared with CRI1, the average removal rates of COD, NH₄⁺-N and TP by CRI2 increased by 9.3%, 8.6% and 34.9% respectively. It can be seen that the removal efficiency of COD, NH₄⁺-N and TP by CRI system was significantly improved after adding SMB550. The addition of SMB550 had the strongest enhancement effect on the removal effect of TP in sewage.

3.3 Analysis of strengthening principle

The CRI system could realize natural reoxygenation and form aerobic area in the period of drying, while in the period of flooding, it was in the state of anoxic. Therefore, wastewater could experience aerobic and anoxic environment successively in the process of infiltration, which provided suitable living conditions for different types of microorganisms [13]. COD, N and P in the wastewater could be absorbed or retained by the filter material, and then transformed or decomposed through the microbial action on the surface of the filter material, so that the wastewater could be purified [3,13]. Therefore, the performance of filter material would directly affect the performance of CRI systems on wastewater treatment.

In this study, the CRI1 reactor used river sand, zeolite sand and marble sand as filter material, which had good treatment effect.
on COD and NH$_4^+$-N, but poor removal effect on TP. Because of the addition of SMB550 in the CRI2 reactor, the removal efficiency of COD and NH$_4^+$-N was further improved, and the removal efficiency of TP was greatly improved. There are three reasons for this result. Firstly, sheep manure biochar had a huge specific surface area, abundant pore structure and rich functional groups, which had good adsorption effect on COD, NH$_4^+$-N and TP, and could effectively absorb or intercept pollutants from wastewater [14]. Secondly, sheep manure biochar could be used as an excellent carrier of microorganisms, and its rough structure was more conducive to the adhesion and growth of microorganisms, accelerating the formation and stability of biofilm on the surface of filter material [15]. Thirdly, the particle size of sheep manure biochar was relatively small, which enriched the particle size distribution of filter materials in CRI systems. Reasonable particle size distribution could effectively improve the capacity of holding pollutants and the utilization rate of filter materials, which was conducive to improving the treatment efficiency of wastewater [16].

4. Conclusion
By adding sheep manure biochar to CRI systems, the average removal rates of COD, NH$_4^+$-N and TP were 9.3%, 8.6% and 34.9% respectively higher than those without adding sheep manure biochar. The huge specific surface area, abundant pore structure and rich functional groups of sheep manure biochar provided the basis for better adsorption of COD, N and P pollutants in wastewater, and greatly promoted their removal effect. Using sheep manure biochar as the filter material of CRI system could enhance the wastewater treatment performance efficiently.

Acknowledgments
This work was financially supported by Sichuan Science and Technology Program (No.2022YFG0307, 2022NSFSC0393), Open Fund of State Environmental Protection Key Laboratory of Synergetic Control and Joint Remediation for Soil & Water Pollution (No.GHBK-2021-004), Sichuan Higher Education Talent Training Quality and Teaching Reform Project from 2021 to 2023 (No.JG2021-1409), Young Seedling Program of Chengdu Technological University (No.QM2021003), and Laboratory Open Fund Project of Chengdu Technological University (No.2022CHZH04).

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