Effect of Modified Pig Manure Biochar on the Sewage Treatment Performance of Biological Sand Filters

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Abstract. Biochar was prepared by pyrolysis of wasted pig manure at 700 ºC and modified by sulfuric acid and ultrasonic. The properties of pig manure biochar before and after modification were characterized. The modified pig manure biochar was added into the biological sand filter (BSF) to investigate its effect on the performance of sewage treatment. The results showed that the content of oxygen-containing functional groups, specific surface area and total pore volume of modified pig manure biochar were significantly increased. By mixing river sand and modified pig manure biochar evenly according to the volume ratio of 7:3 as the filter material of BSF, the average removal rate of COD, NH_4^+-N and TP increased by 10.6%, 11.4% and 31.9% respectively compared with that without adding any biochars, and the treatment performance of the BSF was significantly improved. The modified pig manure biochar could be used as a kind of filter material with low cost and excellent performance.

Keywords: Biochar; Pig Manure; Biological Sand Filter; Sewage Treatment.

1. Introduction

In recent years, the use of biochar for sewage treatment is increasing [1–3]. Biochar with large specific surface area, developed pore structure and excellent adsorption performance is considered as the most potential adsorbent [4]. However, at present, the researches on the adsorption effect of biochar mainly focused on the plant waste [5, 6], the researches on the preparation of biochar from animal manure were relatively less. With the rapid development of China's pig industry, there is an urgent need for new ways of resource utilization to solve the problem of pig manure pollution. If pig manure can be prepared into biochar, it will be a good way for the resource utilization of wasted pig manure.

Biological sand filter (BSF) is a kind of bio-reactor used for sewage treatment, which has the advantages of lower construction and operation cost, higher hydraulic load and less secondary pollution [7, 8]. It is especially suitable for the application in underdeveloped areas. In a BSF, river sand is usually used as filter material, and microorganisms are inoculated on the surface of filter material to form a stable biofilm. When sewage flows through the filter material, the pollutants in sewage are adsorbed or intercepted by the filter material, and then degraded by the microorganisms in the biofilm on the surface of filter material to realize the purification of sewage. When only river sand is used as the filter material, due to the limited adsorption capacity of sand for pollutants in sewage, the treatment effect of BSF cannot reach the best state. Developing new and efficient filter material is an important way to improve the treatment performance of BSF.

In view of this, this study selected wasted pig manure as raw material, prepared biochar and modified it, investigated the feasibility of using it as filter material of BSF. The purpose of this study is to provide theoretical basis for the application of pig manure biochar in the field of sewage treatment and provide a new efficient filter material for BSF.

2. Materials and Methods

2.1 Preparation and Modification of Pig Manure Biochar

Pig manure was taken from a pig farm and dried. The impurities in the pig manure were picked out. Then the pig manure was crushed and screened for 60 mesh. The pig manure powder was placed in the crucible, covered, put into the muffle furnace, heated to 700 ºC with a temperature gradient of 10 ºC/min under the condition of oxygen limitation, and then kept at a constant temperature for 150 min. The pyrolysis product was cooled to room temperature, grinded through 80 mesh sieves, washed with deionized water, filtered and dried at 105 ºC. Pig manure biochar was prepared after drying to constant weight and marked as $PMB_{N,700}$. Take a proper amount of $PMB_{N,700}$, add 1.0 g biochar to each 20 mL sulfuric acid solution in a conical flask of 250 mL, and modify it for 90 min under the ultrasonic power of 200 W. After that, the modified pig manure biochar, labeled $PMB_{M,700}$, was prepared by washing it repeatedly with deionized water to neutral and drying it at 105 ºC to constant weight [9].

2.2 Reactors and Operation Conditions

In this study, two biological sand filters (BSF1 and BSF2) were used. The structure of BSF1 and BSF2 is shown in Figure1. The height of the filter was 120 cm and the inner diameter was 14 cm. The sewage was distributed from the top of the filter and discharged from the bottom of the filter. From the top to the bottom, the filter was divided into water distribution area, buffer area, filter material area and support area. Their heights were 15 cm, 2.5 cm, 100 cm and 2.5 cm respectively. There was no filling in the water distribution area. Gravel with the particle size of 0.5~1.0 cm was used as filler for the buffer area and supporting area. River sand with the particle size of 0.2~0.5 mm was used as filler for the filter material area of BSF1. Uniformly mixed river sand and $PMB_{M,700}$ by volume ratio of 7:3 was used as filler for the filter material area of BSF2. Intermittent sewage inflow mode was used in this experiment. It was operated for 2 cycles every day. Each cycle included 3 hours of water inflow time and 9 hours of water falling time. The hydraulic load was 1.0 m/d. The ambient temperature during operation was (25±5) ºC.

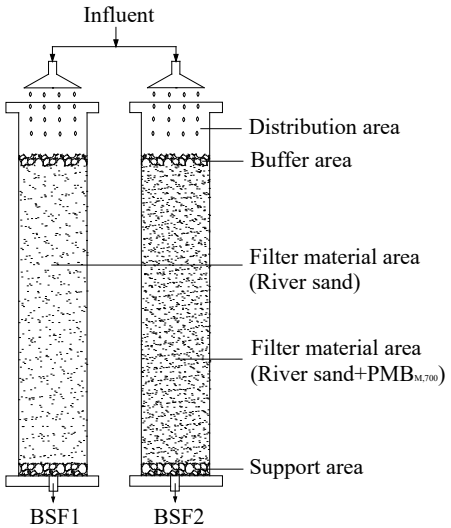


Figure 1. The schematic of biological sand filters

2.3 Sewage Quality and Inoculated Sludge

The domestic sewage to be treated was taken from a village community. The COD concentration of the influent was 181.3~247.5 mg/L, the NH_4^+-N concentration was 36.4~49.2 mg/L, the TP concentration was 3.7~4.5 mg/L, and the pH was 6.8~7.6. The inoculated sludge was taken from the sequencing batch reactor which was used for domestic sewage treatment in the laboratory of Chengdu Technological University and operated stably.

2.4 Analysis Methods

The C, H, N and O content of biochar was tested via the element analyzer (VARIO EL cube, Germany). The content of oxygen-containing functional groups was tested via the Boehm titration method. The specific surface area, pore volume and average pore diameter were tested via the BET-N_2 method (NOVA4000e, USA). The surface morphology of biochar was tested via the SEM method (ZEISS SUPRA40, Germany). The COD, NH_4^+-N and TP concentrations of sewage were respectively tested via potassium dichromate method, sodium reagent spectrophotometry and ammonium molybdate spectrophotometry.

3. Results and Discussion

3.1 Properties of Biochar

The element composition of pig manure biochar before and after modification is shown in Figure 2. In terms of element composition, the H/C of $PMB_{M,700}$ was lower than that of $PMB_{N,700}$, while the (N+O)/C of $PMB_{M,700}$ was higher than that of $PMB_{N,700}$, indicating that the modified pig manure biochar had higher aromaticity and polarity [10].

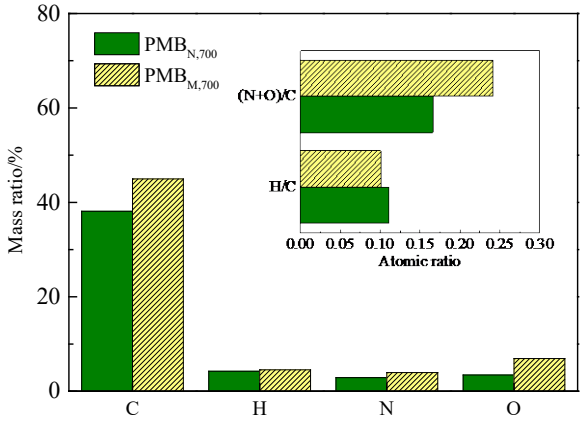


Figure 2. Elemental composition of $PMB_{N,700}$ and $PMB_{M,700}$

The content of oxygen-containing functional groups of $PMB_{N,700}$ and $PMB_{M,700}$ is shown in Figure 3. In terms of the content of oxygen-containing functional groups, the carboxyl, lactone and phenolic hydroxyl groups of $PMB_{M,700}$ were 5.8, 1.8 and 1.5 times higher than those of $PMB_{N,700}$ respectively. Before modification, some micropores on the surface of pig manure biochar were blocked by impurities that were hard to be washed away by water. After modification, the impurities blocked in micropores were dispersed under the strong shear force generated by ultrasonic cavitation effect and then dissolved in sulfuric acid solution. As a result, the carboxyl, lactone and phenolic hydroxyl groups blocked on the surface of micropores were exposed and their content increased. However, the carbonyl group on the surface of biochar may be oxidized by sulfuric acid to carboxyl group with more oxygen, so its concentration was reduced. The content of oxygen-containing functional groups of $PMB_{M,700}$ was 2.7 times that of $PMB_{N,700}$, indicating that the hydrophilicity and polarity of the modified pig manure biochar had been greatly improved [11].

The BET analysis results of pig manure biochars showed that the specific surface area, total pore volume and average pore diameter of $PMB_{M,700}$ were 46.25 m^2/g, 0.093 cm^3/g and 27.98 nm respectively, which were 5.1, 14.5 and 2.2 times higher than those of $PMB_{N,700}$. Analysis indicated that under the cooperation of sulfuric acid oxidation and ultrasonic cavitation, the original blocked pores were dredged to form a void structure, so the average pore diameter increased [9].

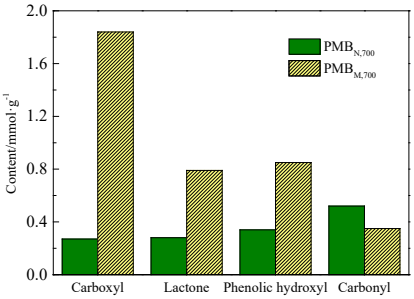


Figure 3. The content of oxygen-containing functional groups

The SEM analysis results are shown in Figure 4. According to the results of SEM analysis, the pore structure of $PMB_{M,700}$ was more developed, the number of mesopores and micropores per unit area was significantly increased, and the pore wall was thinner and more uneven. While the surface of $PMB_{N,700}$ was relatively smooth, and the pores on the surface were less, which was consistent with the results of BET analysis. The increase of the specific surface area of $PMB_{M,700}$ would be beneficial to the adsorption of pollutants [12].

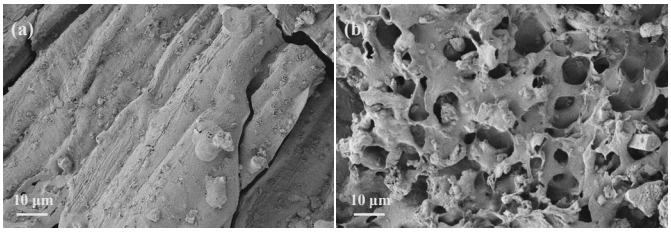


Figure 4. The SEM of (a) $PMB_{N,700}$ and (b) $PMB_{M,700}$

Above all, pig manure biochar modified by sulfuric acid and ultrasonic had higher aromaticity and polarity, more oxygen-containing functional groups, larger specific surface area and bigger total pore volume. Therefore, $PMB_{M,700}$ was selected as one of the filter materials to further investigate its effect on the sewage treatment performance of the BSF.

3.2 Removal Efficiency of Pollutants

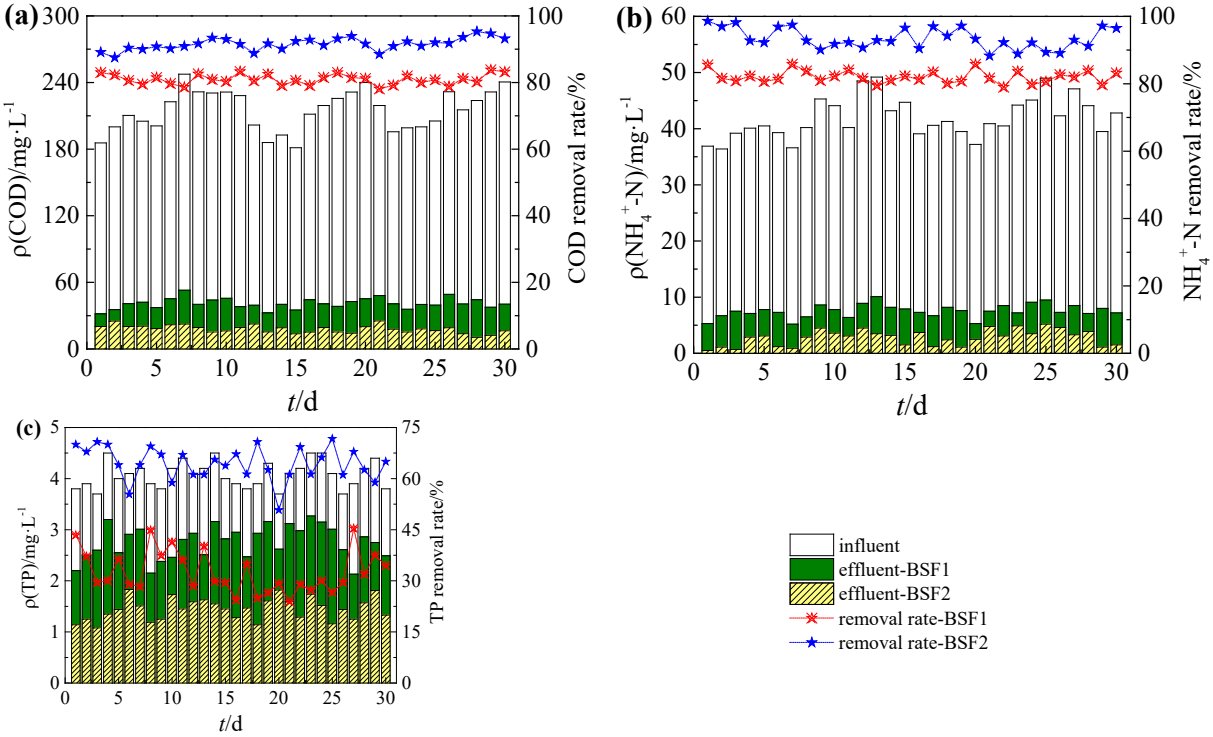


Figure 5. The removal efficiency of (a) COD, (b) NH_4^+-N and (c) TP

Figure 5 shows the difference of sewage treatment effect before and after adding $PMB_{M,700}$ into the BFS. It can be seen from Figure 5 that after adding $PMB_{M,700}$, the average removal rates of COD, NH_4^+-N and TP increased from 80.9% to 91.6%, 82.1% to 93.5% and 32.6% to 64.5% respectively. Compared with BSF1, the removal rates of COD, NH_4^+-N and TP by BSF2 increased by 10.6%, 11.4% and 31.9% respectively. Therefore, the addition of modified pig manure biochar can significantly improve the sewage treatment performance of the BSF.

3.3 Analysis of Enhancement Mechanism

With the good adsorption performance of $PMB_{M,700}$, pollutants in sewage can be absorbed and intercepted more efficiently in BSF, and more sufficient nutrients can be provided for microorganisms [13]. Additionally, $PMB_{M,700}$ can also be used as a good carrier of microorganisms to accelerate the formation of stable biofilm on the surface of filter materials and provide suitable conditions for efficient degradation of pollutants [14, 15]. Moreover, the particle size of $PMB_{M,700}$ was small, which can be used as a supplement to the pores between sand particles, so as to extend the infiltration process of sewage in the filter tank and further improve the treatment efficiency of sewage. The enhancement mechanism of modified pig manure biochar on BSF's wastewater treatment performance is shown in Figure 6.

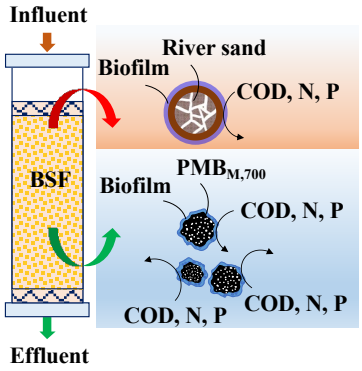


Figure 6. Schematic diagram of enhancement mechanism

4. Conclusion

The content of oxygen-containing functional groups, specific surface area and total pore volume of the pig manure biochar were significantly increased after the modification of sulfuric acid and ultrasonic. The average removal rates of COD, NH_4^+-N and TP were significantly improved after adding the modified pig manure biochar into the biological sand filter. The modified pig manure biochar can be considered as a promising filter material for the biological sand filter.

Acknowledgments

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