Fabrication of low-moisture density bamboo charcoal moving biofilm reactor and removal performance in domestic sewage treatment

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ABSTRACT

In this paper, bamboo charcoal as raw material, low-density bamboo charcoal was prepared by modification with the potassium hydroxide activation. The results of scanning electron microscopy (SEM), specific surface area, and aperture analysis (Brunauer–Emmett–Teller–Barrett–Joyner–Halenda), and Fourier transform infrared (FT-IR) showed the total pore volume of bamboo charcoal increased, the wet density decreased after modification. Low-moisture density bamboo charcoal was used as a suspended biological carrier in a moving bed biofilm reactor (MBBR) to treat simulated domestic sewage. The removal effects of chemical oxygen demand (COD), ammonia nitrogen, total nitrogen (TN), and total phosphorous (TP) were systematically studied. Results showed the low-moisture density bamboo charcoal suspension bio-carrier takes good fluidization state and outstanding removal effect. For simulated domestic sewage with an influent COD mass concentration of 200 mg/L, the optimized MBBR process conditions are as the gas–water ratio of 100:1 (volume ratio), the filling rate for bamboo charcoal of 15%, and 4 h of hydraulic retention. After MBBR treatment, the effluent COD, ammonia nitrogen, and removal rates of TN and TP were 83%, 77%, 48%, and 57%, respectively.

Keywords: Bamboo charcoal; Wet density; Low humidity; Bio-carrier; Movable bed biofilm reactor (MBBR)

1. Introduction

With the continuous developments of human society and industry, living environment is suffering more and more severe damages. The shortage of global water resources is one of the major crises that human beings are facing [1,2]. The continuous increase in the discharge of industrial wastewater and domestic sewage has caused the water bodies to be continuously deteriorated [3]. Facing the problem of water pollution, water treatment technology is also improving, and innovative methods are being created; among them, biofilm wastewater treatment has received much attention. Moving bed biofilm reactor (MBBR) is a new type of high-efficiency and low-energy consumption composite biological wastewater treatment system device, which is based on the biofilm method and the advantages of the traditional activated sludge treatment. It has been widely applied in fields such as advanced treatment in small sewage treatment plants, transformation, and upgrading of original overload activated sludge system, treatment of agricultural water pollution, and industrial wastewater [4–8]. However, sewage treatment by biomass material lacks intensive attention.

Bamboo charcoal has massive pores, high mechanical strength, and outstanding adsorption performance [9,10]. After modification, the bamboo charcoal specific surface area is increased, and its performance in water treatment was significantly enhanced, which can be a high-performance filler of MBBR, acting as an excellent carrier for the growth
of microorganisms [11]. In this study, simulated sewage was used as the influent, and naturally-derived low-humidity density bamboo charcoal was fabricated as the MBBR suspended filler for sewage treatment. The removal efficiencies of chemical oxygen demand (COD), ammonia nitrogen, total nitrogen (TN), and total phosphorus (TP) under different gas–water ratio, bamboo charcoal filling rate, hydraulic remain time (HRT), and COD influent concentration were systematically studied to explore the optimum process conditions, aiming to further improve theoretical basis for preparation and application of modified bamboo charcoal as a biological carrier in water treatment.

2. Experimental

2.1. Materials

Bamboo charcoal was fired (220°C, 1 h) from 3 y-old *Phyllostachys pubescens* bamboo, produced in Ningbo, Zhejiang, China. The bamboo charcoal with low density was soaked in purified water until its density was higher than 1 kg/m³ (at room temperature 24°C), so it was ready for a filler after its wet density reached an equilibrium. The mixed strains powder was purchased from Eurovix S.r.l. Biomass company, Germany. Potassium hydroxide, high purity nitrogen, glucose, potassium dihydrogen phosphate, ammonium chloride, silver sulfate, mercury sulfate, potassium dichromate, concentrated sulfuric acid, Nessler’s reagent, potassium sodium tartrate, sodium hydroxide, potassium persulfate, ascorbic acid, ammonium molybdate, potassium nitrate, hydrochloric acid, aniline, potassium bisulfite, anhydrous sodium carbonate, sodium nitrite, ammonia sulfamate, and N-(1-naphthyl) ethylenediamine hydrochloride. All reagents in the experiment are analytical pure, produced by McLean Shanghai Biochemical Technology Co. Moreover, the water used in the experimental is deionized.

2.2. Instruments

OTL1200 tube furnace; HH-2 digital thermostatic water bath; KY-300DE numerical control ultrasonic cleaner; SHY-III circulating water vacuum pump; DHG9700-A air drying oven (digital display); BSA-2245 electronic balance; HP-250 full temperature shaking incubator; PHS-3C PH meter; BT1000-1000M peristaltic pump; ACO-2001 electromagnetic air compressor; AL32COD heater; YXXY-LS-50S11 automatic vertical electrothermal pressure steam sterilizer; YS100 trinocular microscope; 722N visible spectrophotometer UV751GD ultraviolet spectrophotometer; Avatar System 360A Fourier transform infrared spectrum (FT-IR) instrument; FEI Quanta 200 scanning electron microscopy (SEM); ASAP-2020 specific surface area and aperture analysis (Brunauer–Emmett–Teller–Barrett–Joyner–Halenda (BET-BJH)) instrument.

2.3. Preparation of low-moisture density bamboo charcoal

The low-density bamboo charcoal was prepared by potassium hydroxide activation. The bamboo charcoal (particle size 5,880–6,000 μm) was immersed in a 35% potassium hydroxide solution for 48 h. The mass ratio of potassium hydroxide to bamboo charcoal was 2:1; the environment temperature was set 70°C, followed by drying under 105°C. The dried impregnated mixture was laid flat in a crucible and placed into a quartz tube furnace. The tube furnace activated the impregnated bamboo charcoal under nitrogen protection at a heating rate of 10°C/min. The activation process was at a low temperature of 450°C for 60 min and at a high temperature of 900°C for 90 min. After completing modification and temperature in the furnace was resumed to room temperature, the prepared low-humidity bamboo charcoal was washed continuously with deionized water to neutrality (pH = 7), dried at 105°C, and finally stored in a dry box. The low-density bamboo charcoal was measured a wet density of 1.1291 g/cm³, and the wet density is reduced by 10%, as compared with untreated bamboo charcoal (wet density 1.2000–1.3000 g/cm³).

2.4. MBBR device

The MBBR water treatment system includes a water distribution bucket, a peristaltic pump, an air pump, a gas flow meter, an aerating disc, an MBBR main body, and an outlet screen. The effective volume of the water distribution bucket is 50 L, the total effective volume of the MBBR main body is 4 L with a 92 mm diameter ethylene propylene diene monomer (EPDM) rubber aeration disc, as shown in Fig. 1. The wastewater enters MBBR from the water inlet at the bottom of the device through a peristaltic pump and then flows out from the water outlet at the top after a certain period of reaction. The air passes through the air pump and enters from the bottom of the device with adjustment by the gas flowmeter. The air provides oxygen for microorganisms and power for the fluidization of the filler.

2.5. Sewage treatment

Table 1 illustrates the preparation method of simulated domestic sewage (50 L). The COD, ammonia nitrogen, TN, and TP were provided by glucose, ammonium chloride, and potassium dihydrogen phosphate, respectively, and the mass ratio of C, N, and P was 100:5:1.

The continuous flow biofilm culturing method was employed in this research [12], with flow rate 0.022 L/min,
the filling rate 10%, the air–water ratio (volume ratio) 60:1, the COD 200 mg/L, and 8 g bacteria powder. When the biofilm formation is stable, the microorganism adheres to the surface of low wet density bamboo charcoal and forms a biofilm. As the COD removal rate of effluent reaches 60%, this signifies biofilm starts up successfully. The species, structure, and activity of microorganisms were observed by microscope. The measured water quality indicators include COD, ammonia nitrogen, TP, and TN. For COD analysis, we referred to “determination of COD of water quality, rapid digestion spectrophotometry” (HJ/T399-2007) [11]. The analysis of ammonia nitrogen was Nessler’s reagent spectrophotometry, the TP analysis method was molybdenum antimony anti-spectrophotometry, and the TN analysis was alkaline potassium persulfate digestion UV spectrophotometry [13].

3. Results and discussion

3.1. Characterization of bamboo charcoal

Figs. 2 and 3 show the SEM images of bamboo charcoal before modification and after modification. Before modification, the particle structure is completed and the thickness is uniform, pores on the sieve plate are in a smaller amount, and the surface is relatively smooth. However, the modified bamboo charcoal structure is damaged to a certain extent, the thickness of the primary tissue is uneven, and there are penetrating damages between the vascular bundles and the vascular sieve plates. Additionally, slender cracks caused by high-temperature can be detected in SEM images. A lot of visible pores on the sieve plate, and surface areas are rough and uneven, showing wrinkles. There is a large number of microporous structures within these wrinkles, which lead to the decrease of wet density measured for bamboo charcoal [14,15].

Table 2 compares the BET-BJH results, and the FT-IR spectrum is shown in Fig. 4. In Table 2, the modification has significantly improved the specific surface area and pore

<table>
<thead>
<tr>
<th>COD (mg/L)</th>
<th>Glucose (g)</th>
<th>Ammonium chloride (g)</th>
<th>Potassium dihydrogen phosphate (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.69</td>
<td>0.96</td>
<td>0.22</td>
</tr>
<tr>
<td>200</td>
<td>9.37</td>
<td>1.91</td>
<td>0.44</td>
</tr>
<tr>
<td>400</td>
<td>18.74</td>
<td>3.82</td>
<td>0.88</td>
</tr>
<tr>
<td>600</td>
<td>28.14</td>
<td>5.73</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Fig. 2. SEM of bamboo charcoal at low magnification: (a) before and (b) after modification (×400).

Fig. 3. SEM of bamboo charcoal at high magnification: (a) before and (b) after modification (×5,000).
volume of bamboo charcoal. By comparing the specific surface area and micropore volume, micropores make a significant contribution to the increase of specific surface area and total pore volume [12]. The average pore diameter of the modified bamboo charcoal is slightly smaller than that of the untreated specimen (3.1575 nm). It is speculated that the generation of a large quantity of micropores also enlarges the original micropores, thereby increasing the average pore diameter and reducing the extent of decrement [12,16].

Fig. 4 shows the absorption peaks of bamboo charcoal before and after modification are basically the same, indicating the modification did not significantly generate new functional groups, but the heat treatment enhanced or weakened some specific peaks. The absorption peak of –OH at 3,435 cm–1 is significantly enhanced after modification, which corresponds to stretching vibration of –OH, indicating the hydroxyl and carboxyl groups are formed on the surface; the –CH2– antisymmetric stretching peak appears at 2,920 cm–1 [7,11]; the aromatics skeleton stretching vibration appears at 1,630 cm–1 [12]; the absorption peak at 1,420 cm–1 is significantly enhanced, which might result from the introduction of potassium to the surface of the material.

### 3.2. Biofilm formation

During biofilm start-up period, the CODs of inlet and outlet water were monitored (from 3rd day of initialization), as shown in Fig. 5. In the first 2 d of monitoring (i.e., 3rd–4th day), the removal rate of COD was less than 50%. With the continuing growth of biofilm, the removal rate of COD gradually increased, and removal rate of COD on 6th day became basically stable. On 8th day, the removal rate reached more than 60%. On 9th day, the COD of influent water was 215 mg/L, while the COD of effluent water was 77 mg/L, so the removal rate was 64%. The start-up of the bio-reactor membrane was effective.

The extent of film formation is evaluated by the growth of the microorganisms. Fig. 6 is the observation of the microbial phase during film start-up. On 2nd day, the number of observable microorganisms was inadequate, and the activity of the microorganisms was relatively low. On 5th day, a white biofilm had formed on the surface of the suspended filler. The ciliates and filamentous bacteria were clearly seen under microscope. On 9th day, a clearly dense microbial membrane was formed on the surface of the filler. Meanwhile, the removal rate of COD was over 60%. Under the microscope, we perceived a mixture of filamentous bacteria and various kinds of microorganisms, forming a complete dense microbial community [17,18]. The observation of microbial membrane also proved MBBR was started up successfully.

### 3.3. Effect of air–water ratio on water treatment

In the experimental, the bamboo charcoal filling rate was 10%, the COD of influent water was 200 mg/L, and the HRT was 3h. The water treatment effect under different air–water ratios of 60:1, 80:1, 100:1, and 120:1 was investigated. The results are shown in Fig. 7. Under air–water ratio of 60:1, 80:1, 100:1, and 120:1, the average removal rates of COD, ammonia nitrogen, ammonia nitrogen, and TP were 67%, 68%, 70%, and 61%, respectively. The average removal rates were 31%, 33%, 41%, and 32%, respectively, and the average TN removal rates were 41%, 39%, 36%, and 21%, respectively. When the ratio of gas to water was 100:1, the removal rates of COD, ammonia nitrogen, and TP reached

### Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Specific surface area (m²/g)</th>
<th>Micropore specific surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micropore pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before modification</td>
<td>56.3123</td>
<td>30.3216</td>
<td>0.040072</td>
<td>0.016068</td>
<td>3.1575</td>
</tr>
<tr>
<td>After modification</td>
<td>403.6887</td>
<td>344.7866</td>
<td>0.224589</td>
<td>0.1890995</td>
<td>2.9524</td>
</tr>
</tbody>
</table>
Fig. 6. Microbial observation during biofilm formation: (a) 2nd day biological phase (×400), (b) 5th day biological phase (×500), (c) 9th day biological phase (×400), and (d) 5th day biofilm.

Fig. 7. Effect of air–water ratio on water treatment: (a) COD, (b) ammonia nitrogen, (c) TP, and (d) TN.
the highest value. With more active fluidization and contact between biofilm and wastewater in MBBR, it is beneficial for nitrous bacteria and nitrobacteria to fully oxidize ammonia nitrogen into nitrite or nitrate [19], and for the phosphate phagocytosis of polyphosphate bacteria.

When the ratio of air to water is 120:1, the excessive ratio of air to water intensifies the cutting effect of bubbles on biofilm. The mutual collision between the fillers also exacerbates the shedding of the biofilm. As a result, the removal rates of COD, ammonia nitrogen, and TP are significantly reduced. When the ratio of air–water is 60:1, the removal rate of TN is the highest. This may be caused by the poor fluidization state of the filler under low air–water ratio, and by the formation of an anoxic zone in inner parts of the accumulation zone [17,20]. Contrarily, it is advantageous for denitrifying bacteria to denitrify the nitrate produced by nitrification under anoxic conditions. In the meantime, each filler itself becomes a microreactor, forming a dissolved oxygen gradient state from the surface to the inside of particle [21,22]. Therefore, the purpose of simultaneous nitrification and denitrification on a single filler particle is achieved. Considering the removal effect of COD, ammonia nitrogen, TP, and TN, the best condition of the gas–water ratio is 100:1 in this study.

3.4. Effect of bamboo charcoal filling rates on water treatment

Under the conditions of air–water ratio 100:1, CODs of the influent 200 mg/L, and HRT 3 h, the water treatment effect under the filling rates of 10%, 15%, 20%, and 25% for bamboo charcoal with low wet density were investigated. In Fig. 8, with filling rates of 10%, 15%, 20%, and 25%, the average removal rates of COD were 70%, 72%, 74%, and 71%, the average removal rates of ammonia nitrogen were 67%, 73%, 69%, and 67%, the average removal rates of TP were 41%, 43%, 39%, and 35%, and the average removal rates of TN were 36%, 53%, 56%, and 46%, respectively. When the filling rate is 20%, the removal rates of COD and TN were the highest; when the filling rate is 15%, the removal rates of ammonia nitrogen and TP were the highest. The results could be explained by the more favorable microorganisms habitat introduced by the increase of filling rates [23]. Theoretically, the amount of microbial membrane would increase proportionally with higher filling rate. However, unnecessary high filling rate may affect the fluidization state for inner filler. Besides, the increase of the filling rate would also greatly improve the friction force [24,25] between fillers, thus increasing the chance of the fall-off for biofilm.

By the observation of fluidization state in MBBR, when the filling rates were 20% and 25%, the fluidization state of the fillers in MBBR gradually declines. When filling rate was 10%, the filler is entirely in aerobic condition, and this is not conducive to the formation of a dissolved oxygen gradient [26–28] on the surface of the filler and dramatically weakens the denitrification in MBBR. Considering the removal effect of COD, ammonia nitrogen, TP and TN and the economic benefit of fillers, the optimal filling rate is 15% here in this study.

Fig. 8. Effect of filling rate on water treatment: (a) COD, (b) ammonia nitrogen, (c) TP, and (d) TN.
3.5. Impact of HRT on water treatment

The water treatment effect under the HRT of 2, 3, 4, and 5 h, respectively, was studied, with filler air–water ratio 100:1, the influent COD 200 mg/L, and filling rate of bamboo charcoal 15%.

From Fig. 9, it is found under HRTs of 2, 3, 4, and 5 h, the average removal rates of COD were 69%, 72%, 83%, and 85%, the average removal rates of ammonia nitrogen were 63%, 73%, 77%, and 79%, the average removal rates of TP were 40%, 43%, 48%, and 47%, and the average removal rates of TN were 52%, 53%, 57%, and 59%, respectively. If HRT was 5 h, the removal rates of COD, ammonia nitrogen, and TN reached the highest value. When HRT was 4 and 5 h, the removal rate of TP was almost identical, and both maintained at a relatively high level. It was suggested that the removal efficiency of MBBR increased with the growth of HRT, while the removal efficiency from 4 to 5 h only inclined slightly. Because when HRT reaches 4 h, the contact reaction of microorganisms and sewage is apparently sufficient, so further improvement of removal effect is limited. The optimal condition of HRT is set as 4 h, given removal effect and economic benefit of COD, ammonia nitrogen, TP, and TN.

3.6. Influence of influent concentration on water treatment

Based on above-mentioned experimental parameters, the air–water ratio of filler is set 100:1, HRT is 4 h, and the bamboo charcoal filling rate is 15%. The impact of influent COD on water treatment of 100, 200, 400, and 600 mg/L, respectively, were explored. Accordingly, the influent concentrations of nitrogen and phosphorus also changed.

The results are given in Fig. 10. Fig. 10 suggested that when the COD of influent water was 100, 200, 400, and 600 mg/L, respectively, the average removal rates of COD were 82%, 83%, 79%, and 58%, respectively, the average removal rates of ammonia nitrogen were 76%, 77%, 63%, and 61%, respectively, the average removal rates of ammonia nitrogen were 76%, 77%, 63%, and 61%, respectively, the average TP removal rates were 50%, 48%, 49%, and 44%, respectively, and the average TN removal rates were 44%, 57%, 56%, and 50%, respectively. The removal rates of COD, ammonia nitrogen, and TN were the most significant values with 200 mg/L COD. While dense COD concentration in influent provides more nutrients for the growth of microorganisms [29], the higher concentration of substrate affects the loading capacity for microorganisms, as a result of this, at 400 and 600 mg/L, the removal rates of COD, ammonia nitrogen, and TN fall down. However, the TP removal rate kept unchanged (≤400 mg/L), and decreased significantly at 600 mg/L. In general, with the increase of influent concentration, the growth rate of phosphorus accumulating bacteria would accelerate [30], but when the concentration is excessively high, the biological activity of phosphorus accumulating bacteria would be reduced. Considering the removal effect of COD, ammonia nitrogen, TP, and TN and the stability of effluent, the optimal condition of influent COD is 200 mg/L in this trial.

4. Conclusion

In this research, as a raw material, low-density bamboo charcoal was fabricated as the MBBR suspended biological
carrier by modification with potassium hydroxide activation. The purpose is to examine its feasibility and removal performance in simulated domestic sewage treatment, the removal effects of COD, ammonia nitrogen, TN, and TP under different impact factors were systematically studied. After modification, the pore structure of modified bamboo charcoal is more developed, total pore volume increases, and the wet density decreases. The test results showed the low-moisture density bamboo charcoal suspension microbial bio-carrier exhibits excellent fluidization performance and good removal effect. For simulated domestic sewage with an influent COD mass concentration of 200 mg/L, the optimized MBBR process parameters are 100:1 (volume ratio) gas–water ratio, 15% filling rate for bamboo charcoal, and 4 h of hydraulic retention time. The corresponding removal rates of COD, ammonia nitrogen, TN, and TP are 83%, 77%, 48%, and 57%, respectively. This work aims to provide a further theoretical basis for preparation and application for modified bamboo charcoal as an effective biological carrier in water treatment.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgments

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References


