Purifying Aquaculture Wastewater by Ecological Carbon Fiber

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A new type of ecological carbon fiber is recently developed in order to increase the treatment efficiency of aquaculture wastewater. In this study, the key experimental parameters are investigated and optimized using the ecological carbon fiber, including the fiber density, the concentration of dissolved oxygen and hydraulic retention time. The performance of aquaculture wastewater treatment was evaluated by measuring the removal efficiencies of COD, ammonia-nitrogen, total phosphorus and turbidity. According to the results, the optimized parameters are obtained with the fiber density of 0.3 kg m^{-3} , the concentration of dissolved oxygen of 6 mg L^{-1} and the hydraulic retention time of 10 h corresponding to the concentrations of COD, ammonia-nitrogen, total phosphorus and turbidity reduced by 81, 63, 54 and 93 %, respectively, which indicates that the improvement of aquaculture wastewater quality by ecological carbon fiber was significant.

Key Words: Ecological carbon fiber, Aquaculture wastewater, Fiber density, COD, Hydraulic retention time.

INTRODUCTION

Reducing the negative impacts associated with aquaculture activities is essential to maintain the long-term sustainability of aquaculture industry^{1,2}, which acquires specific water quality^{3,4}. Considering the increasing use of recirculated aquaculture systems, the continuous supply could be threatened due to the limited water resources⁵ and low treatment efficiency^{6,7}. Therefore, in order to improve the performance of aquaculture wastewater treatment, new materials and techniques are developed and studied during decades⁸. Considering the specific requirements for aquaculture water, numerous technologies are used to improve the aquaculture wastewater treatment efficiency by, such as, solar⁹, elodea nuttallii¹⁰, water hyacinths¹¹, biological activated carbon¹², ozone¹³, water hyacinth (*Eichhornia crassipes*) and lettuce (*Pistia stratiotes*)¹⁴ recently, a new method is also reported by recirculating horizontal and vertical flow constructed wetlands¹⁵, which could be used for aquaculture wastewater.

However, this method requires natural wetlands. Fiber based methods have been widely applied^{6,16,17}. However, the performance of available fiber materials is still need to be improved according to Kuhn¹⁶ and Chiam and Sarbatly⁸ indicated that the new membrane-based and biofilm techniques with fiber material could be used to achieve higher treatment efficiency with relatively lower cost.

A new type of fiber, ecological carbon fiber, is developed by our team, composed of microfiber and ecological carbon

fiber material. A series of experiments were conducted, using the ecological carbon fiber, to investigate the aquaculture wastewater treatment and optimize the experimental parameters including the fiber densities, the concentration of dissolved oxygen and the hydraulic retention time (HRT). The performance of aquaculture wastewater purification was evaluated by measuring the removal concentrations of COD, ammonia-nitrogen, total phosphorus and turbidity.

EXPERIMENTAL

Experimental set-up and operating conditions: The principal components of the newly developed ecological carbon fiber are microfiber and ecological carbon. The surface area of microfiber, made of polyamide, is $70 \text{ m}^2 \text{ g}^{-1}$. The diameter and length of the fiber are 0.3 and 40 mm. The inner is PAN-wrapped fiber with a surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ and the diameter, length and beam space are 40, 1000 and 100 mm, respectively. The studied wastewater was obtained from Beijing Hong Yu aquaculture farm. The concentrations of COD and ammonia-nitrogen in the wastewater ranged from 130-150 and 1-2 mg L^{-1} , respectively. The concentration of total phosphorus was around 1 mg L^{-1} and the turbidity ranged from 150-180 mg L^{-1} . Water temperature and pH were maintained around 20°C and 8.

The experiments were carried out in 3 identical biological contact oxidation tanks with a dimension of $1 \text{ m} \times 0.8 \text{ m} \times 1.8 \text{ m}$ (length $\times$ width $\times$ height). The effective volume of the tank is 1.35 m^3 . The ecological carbon fiber was fixed by detachable

stainless steel frame for easy packing and cleaning. The wastewater from aquaculture farm through the outfall is raised by the pump to flow into the regulator tank and then, through the baffle into the primary sedimentation tank. When the water level is higher than H1, electronic floating valve stops automatically the lifting, resulting in the cutoff of the water. Adjustable peristaltic pump is used to modify the wastewater rate in the contact oxidation tank. When the water exceeds the level H2, the liquid might overflow to the disinfection tank, where it is disinfected by UV and then returning to the aquaculture farm to breed the fish. The contact oxidation tank is aerated by the rotary air blower and the air flow rate is measured by the rotameter (Fig. 1).

Fig. 1. Process of aquaculture wastewater treatment

Experimental procedure and analytical methods: In this study, the activated aerobic sludge, taken from a wastewater treatment plant in Beijing Qinghe (A/O process), was inoculated in the bio-contact oxidation tank. After sedimentation of 2 h in the primary sedimentation tank, the wastewater is mixed with the seeding sludge with a sludge settling ratio of 30 %. During the process of aeration, concentration of dissolved oxygen ranged from 2 to 6 mg L⁻¹ and the hydraulic residence time varied from 8 to 12 h. The removal concentration of COD, ammonia nitrogen, total phosphorus, turbidity, nitrite and nitrate-nitrogen were measured in the laboratory with samplings by the chemical experiment. The tests of dissolved oxygen took place on site using Multifunctional Water Quality Analyzer (HACH Hydro-Lab DS5), while the ammonia-nitrogen test was done by the ammonium-nessler's reagent spectrophotometry. The total phosphorus was measured by the alkali fusion-Mo-Sb spectrophotometric method, while COD was determined by the quick sealing catalytic digestion-spectrophotometry. The turbidity test is conducted by the spectrophotometer 100 (Varian Cary 50).

RESULTS AND DISCUSSION

Influence of the densities of ecological carbon fiber on the water purification: During the period from April 10 to May 25, 2011, the experiments were conducted in order to obtain the optimum performance of wastewater purification with 4 different carbon fiber densities: 0.1, 0.3, 0.5 and 1.0 kg m⁻³ with all other parameters kept constant. The wastewater flow rate was kept constant during all the experiments with a

hydraulic retention time of 8 h and the dissolved oxygen concentration was 4 mg L⁻¹. The concentrations of nitrite and nitrate-nitrogen had to be measured each day and kept lower than 0.1 mg L⁻¹ because of the strict condition acquired by the aquaculture. The evolutions are demonstrated in Fig. 2 and the average results are shown in Table-1.

Fig. 2. Evolutions of different treatment efficiencies with different carbon fiber densities

Density of fiber (kg m ⁻³)	Average COD removal (%)	Average ammonia-nitrogen removal (%)	Average total phosphorus removal (%)	Average turbidity removal (%)
0.1	30.61	28.02	20.28	51.00
0.3	48.63	36.73	40.93	66.67
0.5	50.93	37.45	41.20	68.24
1.0	51.72	38.24	43.07	69.47

With the fiber densities of 0.1, 0.3, 0.5 and 1.0 kg m⁻³, the average removal rates of COD were 31, 49, 51 and 52 %, respectively. A rapid increase of performance is clearly shown while the fiber density augments from 0.1 to 0.3 kg m⁻³ then remains relatively stable. The quantity of microorganisms attached could be increased significantly by the carrier quantity augmentation within a certain range. The organic substances are continuously consumed by the metabolism of the microorganisms leading to an increase of COD removal. However, the convective and diffusional mass transfer of organic substrate is limited with the increasing fiber density, which leads to the decrease of reaction efficiency in the tank. Consequently, the COD removal efficiency stays relatively stable with the increasing fiber density from 0.5-1.0 kg m⁻³. The same tendency is also observed about the ammonia-nitrogen concentration removal efficiency with the average removal rates of 28, 37, 37 and 38 %, respectively with different carbon fiber densities. This removal was essentially achieved by nitrification through the nitrifying bacteria, which turns ammonia nitrogen into nitrite and nitrogen and also contributed by the adsorption of ammonia nitrogen by the carbon fiber material. Both effects result in reduce of ammonia concentration. The increase of ammonia-nitrogen removal rate is most significant, when the fiber density increases from 0.1 to 0.3 kg m⁻³, then, with further fiber density increase, the removal rate remains stable because

of limited quantity of nitrifying bacteria and mass transfer. Considering the total phosphorus, the removal efficiency is significantly restrained (20 %) by the low carbon fiber density (0.1 kg m^{-3}), then increases rapidly to around 41 %. Under the aerobic condition, O_2 is used as electron acceptor by the phosphorus accumulating organisms (PAOs), the PHB stored in cells takes in excessively the phosphorus in the environment forming high-energy phosphate bond in the organisms in order to reduce the concentration of total phosphorus in the wastewater. Therefore, the uptake of phosphate by the phosphorus accumulating organisms could attain a degree of saturation which becomes the limited factor for removing the phosphorus causing stable removal efficiency. The influence of carbon fiber density on the turbidity removal efficiency is quite obvious. Because of the internal carbon fiber material, the large specific surface area gives the material an extremely strong adsorption capacity, especially with the increase of carbon fiber density from 0.1 to 0.3 kg m^{-3} . A high turbidity removal rate is attained for only a short period of time. However, the effective contact area between wastewater and attached material as well as the availability of carbon fiber decline with the increasing carbon fiber density from 0.3 to 1.0 kg m^{-3} , which explains the slight increase of turbidity removal.

However, the treatment efficiency obtained above is not quite satisfactory, which is certainly due to the short HRT and low dissolved oxygen concentration set in the beginning of all the experiments, which limit the aerobic microorganism activities and carbon fiber absorption capacity. Consequently, the influences of these parameters are subsequently studied in order to optimize the treatment performance.

Influence of the concentration of dissolved oxygen on the water purification: During April 25 to May 11, 2011, tank #2 with the same dimension was used for determining the influence of dissolved oxygen concentration on the water purification test. Dissolved oxygen concentration affects directly the growth of aquaculture microorganisms and aerobic sludge. The wastewater flow rate was kept constant during all the experiments with a HRT of 8 h and the carbon fiber concentration was 0.3 kg m^{-3} . Three different air rates were used in order to obtain 3 different dissolved oxygen concentrations in the wastewater of 2, 4 and 6 mg L^{-1} . The COD, total phosphorus, ammonia-nitrogen and turbidity concentrations were measured to evaluate the treatment efficiency. The concentrations of nitrite and nitrate-nitrogen had to be measured each day and kept lower than 0.1 mg L^{-1} . The evolutions are demonstrated in Fig. 3 and the average results are shown in Table-2.

The results shown in Fig.3 indicate that the dissolved oxygen concentration plays an important role in the COD concentration removal by the ecological carbon fiber. The COD removal rate attains around 72 % with a dissolved oxygen concentration of 6 mg L^{-1} because of the aerobic microorganisms capacities enhanced by the increasing dissolved oxygen concentration, which could be clearly testified by the decline of COD removal rates (27 and 48 %) with lower dissolved oxygen concentrations (2 and 4 mg L^{-1}). The removal of ammonia-nitrogen was also significantly influenced by the concentration of dissolved oxygen, leading to an increase of ammonia-nitrogen removal rate from 22-52 % with an augmentation of the dissolved oxygen concentration from 2 to 6 mg L^{-1} . Because

Fig. 3. Evolutions of different treatment efficiencies with different concentrations of dissolved oxygen

TABLE-2
INFLUENCES OF THE CONCENTRATION OF DISSOLVED OXYGEN ON THE TREATMENT EFFICIENCY

Concentration of dissolved oxygen (mg L^{-1})	Average COD removal (%)	Average ammonia-nitrogen removal (%)	Average total phosphorus removal (%)	Average turbidity removal (%)
2	27.27	22.36	17.39	40.26
4	47.78	35.83	37.72	70.32
6	72.00	52.24	42.59	86.66

nitrifying bacteria is extremely sensitive to environmental conditions such as pH, temperature, dissolved oxygen concentration *etc.*, the variance of ammonia-nitrogen removal efficiency is observed even with the same concentration of dissolved oxygen. Meanwhile, the capacity of nitrifying bacteria is greatly enhanced by the dissolved oxygen concentration, resulting in a maximum ammonia-nitrogen removal rate of 52 % with a dissolved oxygen concentration of 6 mg L^{-1} . The rate of total phosphorus removal also increases from 17 to 43 % with the augmentation of dissolved oxygen ranging from 2-6 mg L^{-1} , which is because the metabolic activity of PAOs is enhanced by the increasing concentration of dissolved oxygen, leading to a significant uptake of phosphorus in the environment as well as the capacity of aerobic microorganisms of the sludge attached on the carbon fiber material is, likewise, stimulated by the increasing oxygen content in the wastewater. In a similar way, the turbidity removal mainly depends on microbial metabolism and adsorption of materials, both affected directly by the dissolved oxygen concentration. With the increase of dissolved oxygen concentration, the turbidity removal rate could achieve a quite significant value of 87 %. With a lower concentration of dissolved oxygen of 2 mg L^{-1} , the metabolism of the aerobic microorganism and the absorption capacity of material are extremely restrained, leading to a low turbidity removal rate of 40 %.

From an economic point of view, the carbon fiber concentration of 0.3 kg m^{-3} and a dissolved oxygen concentration of 6 mg L^{-1} are obtained by the experiments for achieving the optimum treatment performance of aquaculture wastewater, which are used as fixed parameter in the following experiment to investigate the influence of HRT.

Influence of the hydraulic retention time on the water purification: Hydraulic retention time reflects the contact time between biofilm on the surface of carbon fiber material and the organic substrate in the wastewater, which determines the efficiency of biological and chemical reaction. During the period between May 27 to June 17, tank #3 was used to study the influence of 3 different HRT (8, 10, 12 h), controlled by the peristaltic pump. The carbon fiber concentration and the dissolved oxygen concentration were 0.3 kg m^{-3} and 6 mg L^{-1} , respectively. The same parameters, COD, total phosphorus, ammonia-nitrogen and turbidity concentrations, were measured to evaluate the treatment efficiency. The concentrations of nitrite and nitrate-nitrogen had to be measured each day and kept lower than 0.1 mg L^{-1} . The evolutions are demonstrated in Fig. 4 and the average results are shown in Table-3.

Fig. 4. Evolutions of different treatment efficiencies with different HRT

TABLE-3
INFLUENCES OF HRT ON THE TREATMENT EFFICIENCY

HRT (h)	Average COD removal (%)	Average ammonia-nitrogen removal (%)	Average total phosphorus removal (%)	Average turbidity removal (%)
6	69.02	44.08	28.37	60.42
8	76.35	52.83	45.98	87.58
10	80.50	62.53	53.75	92.58

With the increase of hydraulic retention time from 6 to 10 h, the COD removal rate rises slightly from 69 to 81 %. The augmentation of HRT decreases the liquid velocity across the material and reduces the shear force exerted on the biofilm and carbon fibers, leading to a better mixture and contact between the attached material and the organic substrate, which eliminates the COD more efficiently. Gradually increased over time, the COD removal rate remains relatively stable until a maximum value of 81 % with a HTR of 10 h, which indicates that the performance of device could remain efficient under different hydraulic loading rates in a certain range. Considering the ammonia-nitrogen concentration, with a HRT of 6 h, the low growth rate of nitrifying bacteria and small quantity of biomass make it more vulnerable to the environmental conditions and thus the average ammonia removal efficiency remains only 44 %. Besides, the lower liquid velocity and shear rate make the growth of biofilm more stable, achieving a maximum ammonia-nitrogen removal rate of 63 %. The total phosphorus

and turbidity removal efficiencies increase both with the augmentation of HRT until an optimum value of 54 and 93 %. Especially, with a higher HRT, the ecological carbon fiber has a remarkable effect on the turbidity removal by absorbing a great deal of suspended solid in the wastewater and the sedimentation of suspended solid is also enhanced which leads to a longer absorption time, makes the water at outlet clear and fresh, which could be directly recirculated back to the aquaculture farm.

Finally, the optimum experimental conditions were obtained and the results showed that performance of eco-materials as ecological carbon fiber attached by aerobic biofilm was satisfactory compared with other technologies. In treating the aquaculture wastewater with a relatively low organic loading rate, the COD removal still achieves 80 %. Besides, this ecological carbon fiber used in this study has a extremely significant effect on purifying the aquaculture wastewater with a turbidity removal of 93 %.

Conclusion

In this study, the optimal experimental conditions, carbon fiber density, dissolved oxygen concentration and HRT, in ecological carbon fiber material application were obtained in purifying and treating the aquaculture wastewater. The increasing ecological carbon fiber density could improve the performance of treatment. However, the optimum material density is around 0.3 kg m^{-3} with a satisfactory purification performance and relatively low cost. Optimum dissolved oxygen concentration and HRT were obtained around 6 mg L^{-1} and 10 h, respectively. The optimum COD, ammonia-nitrogen, total phosphorus and turbidity removal rates were achieved around 81, 63, 54 and 93 %, respectively.

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