Activated carbon fiber filler in aerated bioreactor for industrial wastewater treatment
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ABSTRACT

The aerated bioreactor is a promising technology for wastewater treatment. Activated carbon fiber (ACF) used as a biomembrane carrier in wastewater disposal has attracted much more concern recently. The high modulus polyacrylonitrile (PAN)-based ACF was successfully used as a biomembrane carrier for hard-to-biodegrade industrial organic wastewater disposal in a lab-scale aerated biomembrane reactor at room temperature. The biocompatibility test shows that the biomembrane grows quickly on the ACF filler (ACFF) surface; bacteria and microzoon can breed on the ACFF surface at high chemical oxygen demand (COD) concentration. The COD removal rate tests show that the ACFF bioreactor has high capability to remove COD.

INTRODUCTION

The bioreactor (biological membrane reactor) has been used widely for wastewater treatment (Pastorelli et al. 1997; Yamashita et al. 2006; McQuarrie & Boltz 2011; Phattaranawik & Leiknes 2011). ACFs (activated carbon fibers) have higher specific surface area and more micropores develop on the surface of the fiber than granulated active carbon. Therefore, ACFs have been widely used for the removal of pollutants in water and the adsorption of toxic molecules in gases. In wastewater treatment bioreactors, ACF fillers have good resistance to the decomposability of microorganisms and the erosion of chemical substances, and better mechanical performance, and thus were considered to be a substitute for conventional activated carbon. In addition, ACFs have higher adsorption of organic compounds and higher adsorption rates in comparison to the granular form (Brasquet et al. 1999; Chiang et al. 2007). Furthermore, ACFs used as biomembrane carriers in the wastewater treatment process for the removal of organic compounds were proved to be reliable (Qu et al. 2007; Lu & Sorial 2009), and they performed better than glass fiber and polyvinyl alcohol fiber in achieving higher pollutant removal (Gong et al. 2011). The dominant pollutant removal processes are adsorption and/or adhesion and subsequent biodegradation, and are influenced by operational conditions.

Commercial ACFs are prepared from various precursors, which generally include: viscose rayon (Brasquet et al. 2000), pitch-based (Boudou et al. 2005), resins, and polyacrylonitrile (PAN)-based (Elzbieta & Paul 2005; Kim et al. 2008; Zaini et al. 2010). There are three kinds of PAN-based ACFs: high modulus, high strength, and high strain (Hou et al. 2011). However, there are few research papers published on industrial wastewater treatment while high modulus PAN-based ACF was applied as a biomembrane carrier.

Therefore, the main objectives of this research are to determine the fundamental feasibility of the high modulus PAN-based ACF including biocompatibility and regeneration in the bioreactor, and to establish an ACF filler bioreactor (ACFFBR) system treating toxic industrial wastewater in a lab-scale aerated bioreactor.

MATERIALS AND METHODS

Industrial wastewater

The hard-to-biodegrade industrial organic wastewater used was collected from one of the Yuwang 502 series instant cohesive glue synthesis workshops in Shangdong Province.
Yuwang Industrial Co., Ltd., China. In the workshop, the main product, ethyl α-cyanoacrylate adhesive was collected after each batch of synthesis reaction, and then the synthesis reaction vessel was washed. Therefore, the extra-low concentration raw materials, product molecules, and solvents, but no metal ions and total nitrogen (TN) come into the wastewater. The pollutants in the washout wastewater mainly contain 1,2-dichloroethane, ethyl cyanoacetate, formaldehyde, phosphate detergent, and low molecular weight cyanoacrylate polymer (molecular weight is 900–1,100), most of which cannot be precisely quantified. The washout wastewater is colorless and clear but with severe biological toxicity, thus it must be treated before discharge.

The characteristics of the wastewater are: the COD (chemical oxygen demand) is 1,900 ± 50 mg/L, the BOD₅ (biochemical oxygen demand) is 450 ± 20 mg/L, the TP (total phosphorus) is 1.0 ± 0.3 mg/L, and the TSS (total suspended solids) is null. In this study, the washout wastewater was held in a precipitation tank; NH₄⁺-N, PO₄³⁻-P, and metal elements (K, Na, Ca, Mg, et al.) were added before the test, they were then mixed thoroughly with an agitator. The mass ratio of COD:NH₄⁺-N:TP was adjusted to 100:5:1 to meet the needs of the microorganisms in the bioreactor. The pH value of the influent was adjusted to 7.0–8.0 by adding NaOH solution.

**Experimental system**

Experiments were conducted in a laboratory-scale aerated biomembrane wastewater treatment process, as shown in Figure 1(a). The process includes: a precipitation tank with a cover; an ACFFBR equipped with pH and DO (dissolved oxygen) detector, peristaltic pumps with silicone tube, air pump, air and wastewater distributors; and a sedimentation tank.

**ACF filler**

The ACF used in the bioreactor was manufactured by the National Carbon Fiber Engineering Research Center, China. The ACFs are highly mineralized materials whose micropores directly connect to the external surface and can simultaneously adsorb and/or adhere to the low-molecular-weight pollutants and bacteria in aqueous solution. The characteristics of the PAN-based ACFs are: specific surface area 1,200 m²/g, Young’s modulus 390 GPa, tensile strength 4.5 GPa, linear density 66 (1k) g/km, filaments in a bundle 3,000, volume density 1.81 g/cm³, diameter 6.5 μm, carbon content >93%. Prior to use, the ACFs were dried in an oven at 105°C for 2 days to remove any moisture present, and then were stored in a desiccator until use.

The ACF filler was made as shown in Figure 1(b). The ACFs (200 mm length) were held tightly by two pieces of thin hard PVC plastic strip. Four pieces of filler (10 g each piece) were used in the ACFFBR.

**Experimental conditions design**

The seed activated sludge was obtained from another pilot-scale aerated apparatus for septic sewage treatment in which the MLSS (mixed liquor suspended solids) was above 4.0 g/L. After seeding, the ACFF bioreactor was kept under a semi-steady condition: the influent flow was 1.5 L/h, the HRT (hydraulic residence time) was 20 h, and the DO was 4.0 mg/L. After the COD removal rate rose up to 50%, all the fiber fillers were covered by a steady layer of microorganism membrane, and the MLSS of the liquid was higher than 2.5 g/L, the ACFFBR was kept under continuous flow and ran for 40 days, then all the COD removal rate tests under different DO and HRT were carried out.

The operational conditions were designed as follows. The influent flow increased gradually from 1.5, 2.0, 3.0 to

![Figure 1](https://iwaponline.com/wst/article-pdf/65/10/1753/441944/1753.pdf)
6.0 L/h (HRT were 20, 15, 10, 5 h accordingly), DO increased from 3.0, 4.0, 5.0 to 6.0 mg/L, room temperature was kept between 27 and 33 °C, pH was kept between 7.0 and 8.0, SRT (sludge retention time) was 20 days. The removal rate of COD under different DO and HRT were investigated for 7 days continuously at each group of operational parameters. When the operational condition changed, all the tests stopped for 13 days when the aerated biomembrane wastewater treatment system could adapt itself to the new environment. The discharged activated sludge was partially kept and cultured in a cylinder in case it needed to be used to adjust the MLSS of the ACFFBR variation between 2.5 and 2.6 g/L when the operational parameters alternate.

**Analytical methods**

Samples for off-line analysis were collected regularly from the supernatant of the sedimentation tank at the same time interval for three times in one day (at 7:00–8:00, 15:00–16:00, 23:00–24:00, respectively) as a group. All the samples were centrifuged (KOKUSAN H-9R, Japan) at 14,000 rad/min for 5 min at 5 °C. Then the tests were carried out and the final value was calculated by average. The analytical methods and equipment used were as followed: the standard method of potassium dichromate was used for the COD test, the JF-870 air pressure rapid BOD measurement system was used for the \( \text{BOD}_5 \) test, Nesster’s reagent colorimetric method was used for the \( \text{NH}_4^+ \)-N test, PMA-Malachite green Spectrophotometry was used for the TP test, a HANA HI 8424 portable pH/ORP meter was used for the pH test, a HANA HI 9146 DO meter was used for the DO/Temperature test. In this study, the extra \( \text{NH}_4^+ \)-N and TP were added as nutrients for the microorganisms to grow, so that both of were tested in order to adjust the concentration balance in the precipitation tank. The TN and \( \text{NO}_x^- \)-N weren’t raw pollutants in the wastewater, so they were not tested. All the experiments were carried out by referring to the standard methods in the Monitoring and Analyzing Methods of Water and Wastewater (4th edition), Environmental Protection Agency of P.R. China.

**RESULTS AND DISCUSSION**

**Biocompatibility test**

The investigation of biocompatibility of the ACFF was observed by OLYMPUS CX-51 biological microscope fixed with a CANON 550D camera (amplify 400 times). On the 4th day after the seed activated sludge was added into the aerated bioreactor, the microorganisms tended to grow around the ACFF (Figure 2(a)). The test showed that there were protozoa (mainly *infusorian*) and mini-metazoa (*rotifer* and *daphnia*) communities around the biomembrane. On the 15th day, the surface of the ACFF was covered by a layer of biomembrane, as shown in Figure 2(b). After the ACFFBR
was run at a relatively steady-state condition for 30 days, the ACFF samples were collected and dried at room temperature for microscopic observation, which showed the biomembrane had reached the maximum thicknesses as shown in Figure 2(c, d). Meanwhile, the concentrations of COD, NH₄⁺-N and TP in the bioreactor decreased to a very low level.

The result of this test show that bacteria and other microorganisms may breed on the ACFF in the bioreactor, which indicate that the PAN-based ACFF had good biocompatibility and thus it could be used as a biomembrane carrier for the industrial wastewater treatment.

**COD removal test**

The novel PAN-based ACF was used as a biomembrane carrier in the aerated bioreactor to remove organic pollutants in chemical industrial wastewater. When the ACFFBR is operated at room temperature, the biomembrane develops on the outer surface and the inner micropores of the ACF filler. An air diffuser was placed under the ACFF so that the up-flow bubbling air and mixed liquor could remove the fouling layer formed on the filler. The organic compounds in the wastewater were intercepted, then were adhered and/or adsorbed by the biomembrane, and finally were degraded to CO₂ and H₂O. After the ACFFBR was started-up the removal efficiency of COD was tested. The effects of HRT and DO on COD removal efficiency are shown in Figure 3 and Figure 4, respectively.

The ACFFBR performed well for removal of organic compounds. From Figure 3, we can see clearly that COD removal efficiency is proportional to DO concentration. When DO is 6.0 mg/L at different HRT, the COD removal efficiencies reach a maximum value. In Figure 3(a), when HRT is 20 h the maximum COD removal rate is 82.5% and the mean value is 67.0%; the COD removal rate is not the highest because the organic pollutants are not enough to provide a carbon resource and energy resource for large amounts of biomass to grow. In Figure 3(b), when the HRT is 15 h the COD removal rate reached the maximum value of 88.5% and the mean value was 73.4%, which are the biggest values during all the tests. In Figure 3(c), when HRT is 10 h the maximum COD removal rate is 75.3% and the average value is 60.6%, which are smaller than those of the former test for the reason that the excess organic pollutants are pumped into the reactor in a limited time. In Figure 3(d), when HRT is 5 h the maximum COD removal rate is 55.2% and the mean value is 38.8%, which are the smallest values because HRT is not enough for the organic molecules to be digested by the microorganisms.

The results of COD removal efficiency tests under different DO are shown in Figure 4 from which we can clearly draw the following conclusions. Firstly, the 30 L ACFFBR

![Figure 3](https://iwaponline.com/wst/article-pdf/65/10/1753/441944/1753.pdf)

Figure 3 | The effect of HRT on COD removal efficiency.
can endure organic load change at a large range and perform well. When the initial COD concentration varied between 1.85 and 1.95 g/L, as the influent flow increased from 1.5, 2.0, 3.0 to 6.0 L/h (HRT are 20, 15, 10, 5 h accordingly), the utmost COD loads were 2.34, 3.12, 4.68, 9.36 kg/(d·m³) and were removed largely along with the DO rise. Secondly, the ACFFBR can bear high speed airflow and HRT variation between ranges. Each of the point in Figure 4 on behalf of a group of operational parameters and predicts a COD removal rate value. When the parameters are controlled within the zone of 5.0 < DO < 6.0 mg/L and 13 < HRT < 19 h, the COD removal rate will be above 75%. When the DO is 6.0 mg/L, the COD removal rate is above 55%, no matter how the HRT varies. Thirdly, the optimum operational conditions of the ACFFBR are observed as follows: ACFF is 40 g, HRT is 15 h, DO is 6.0 mg/L, SRT is 20 days, MLSS varies between 2.5 and 2.6 g/L, room temperature varies between 27 and 33 °C, and pH varies between 7.0 and 8.0.

However, it is difficult to control DO to be higher than 6.0 mg/L in water because much more air is needed and thus more energy costs. In addition, the high speed airflow may wash away the activated sludge and biomembrane, which may decrease the total biomass in the bioreactor. In this study, as the airflow increased gradually, the erosion effect of airflow to the biomembrane on the ACFF surface and biomass in the sludge become more obvious, thus the extra activated sludge must be added in to keep the MLSS of the liquid higher than 2.5 g/L and lower than 2.6 g/L.

The continuous usage of the PAN-based ACFF also indicates that airflow and up-flow mixed liquids can efficiently regenerate the biomembrane in situ in the bioreactor, which is considered easy to handle without the costly ex situ regeneration of the industrial treatment process.

**Suspended biofacies observation**

In the novel ACFFBR, the biofacies are very rich, both on the ACFF surface and in the liquid, as shown in Figure 2 and Figure 5. The ACFFBR shares the characteristics of the conventional suspended carrier biofilm process and activated sludge process, which has much richer microbial communities that can biodegrade the severe biological toxic industrial
wastewater obviously. Figures 5(a,b) (×400) are taken at the ACFFBR start-up. Figures 5(c, d) (×100) are taken while the ACFFBR got its maximum COD removal rate, which showed a large amount of microzoon, such as ciliated protozoa, Tubifex, rotifers, Aeolosoma hemprichicci, et al. The microzoon in the ACFFBR can digest sludge into energy, H₂O, and CO₂ through predatoriness, thus reducing the sludge yield. That might be the main reason to explain why there is little sludge discharged during the COD removal tests.

CONCLUSIONS

The PAN-based high modulus ACFs were successfully used as biomembrane carrier for biological toxic industrial organic wastewater disposal in a lab-scale aerated bioreactor in this study. The ACFF displayed good biocompatibility in the bioreactor, and the biomembrane carried by it loaded rich biofacies and could regenerate in situ. The bioreactor could endure organic load change and HRT variation, and bear high speed airflow. The ACFFBR shares the characteristics of the conventional suspended carrier bio-film process and activated sludge process with a much richer microbial community structure in the industrial wastewater. The ACFFBR performed well in achieving high COD removal rate which was proportional to DO. When the parameters were controlled within the zone of 5.0 < DO < 6.0 mg/L and 13 < HRT < 19 h, the COD removal rates were above 75%. Thus, the ACFFBR is a promising technique for industrial wastewater disposal.

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