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Design of a New pH Switch Hollow Fiber Membrane and Analysis on Its Anti-Fouling Performance in a Membrane Bioreactor

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This paper designs a pH switch hollow fiber membrane made from polypropylene (PP) in a membrane bioreactor (MBR). The polyacrylic acid (PAA) was grafted onto the surface of the PP membrane surface by continuous ultraviolet (UV) grafting, creating the pH switch PP-g-PAA membrane. Then, the membrane was put into a bioreactor which ran continuously 90 days. Both the original PP membrane and the proposed PP-g-PAA membranes were used in the MBR, and cleaned by physical and chemical methods. The two membranes were analysed by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), field emission scanning electron microscopy (FESEM), atomic force microscope (AFM), and laser granularity distribution analyser. The results show that the new membrane achieved lower TMP and longer physical backwashing period than the original PP membrane, indicating that it has better hydrophilic and anti-fouling performance. The PP-g-PAA membrane performed a perfect switch effect in chemical backwashing, especially acid washing. Most of the pollutants clocked in membrane pores were cleaned by chemical backwashing thanks to the pH switch effect. The good performance of the PP-g-PAA membrane in the MBR system promises a low energy consumption and a long membrane life.

1. Introduction

Membrane bioreactor (MBR) is an emerging technique for wastewater treatment and water reuse. In recent years, the MBR market has been growing at a stunning annual rate of 10.9%, faster than any other advanced membrane technologies for wastewater treatment (Drews, 2010). The main bottleneck of MBR performance is membrane fouling, which pushes up the energy consumption and complicates the maintenance of the MBR (Yang et al., 2018). The term membrane fouling refers to the unwanted deposition of retained salts particles, colloids and macromolecules on membrane surface or in membranes pores (Ham et al., 2018). This phenomenon is generally divided into broad categories (e.g. inorganic fouling/scaling, organic fouling, colloidal fouling and biofouling) depending on the membrane process and chemical nature of foulants, because it is too complex to be defined precisely (Kochkodan et al., 2015).

The existing studies on MBR fouling fall into two major groups, namely fouling identification and fouling control (Capodici et al., 2015). In terms of fouling control, several ways have been developed to slow down the polluting rate of membrane in the MBR system, such as enhancing biological performance (Kim et al., 2015), changing operating conditions (Capodici et al., 2015), and improving membrane properties. It is widely agreed that hydrophilic membrane is less affected by membrane fouling than hydrophobic membrane. The latter is more likely to absorb pollutants onto its surface, forming a polluted layer. As a result, much attention has been made to reduce membrane fouling by modifying hydrophobic materials to relatively hydrophilic ones.

There are many approaches to modify hydrophobic membranes, including but not limited to atom-transfer radical-polymerization (ATRP) (Liu et al., 2015), surface hydrophilization by facile physical entanglement (Wang et al., 2015), blending with hydrophilic polymers (Eren et al., 2015) and surface modification by graft polymerization (Abednejad et al., 2014). Among them, the continuous ultraviolet (UV) grafting is a surface modification strategy that can be easily industrialized easily and effectively without any negative impact on the

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basal membrane. The pH switch is another effective way to control membrane fouling. Nevertheless, there is no report on the dynamic antifouling effect of pH switch membrane in MBR wastewater treatment.
Through the above analysis, this paper creates a pH switch polypropylene-graft-polyacrylic acid (PP-g-PAA) membrane by continuous UV grafting, and compares the performance of the PP-g-PAA membrane with the original PP membrane in a submerged aerobic MBR system. The MBR system was operated under a constant flow for 90 days. The comparison shows that the pH switch PP-g-PAA membrane outperforms the original PP membrane in antifouling and energy saving.

2. Methodology

2.1 Materials

The PP hollow fiber membrane was purchased from Tianjin Blue Cross Membrane Technology Co., Ltd. (Tianjin, China), with an average pore size of 0.46μm and a relatively high porosity of 20~50%. The chemicals were all precured from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). The PP-g-PAA membrane was prepared through continuous UV grafting (Wang et al., 2015).

2.2 Reactor setup and operating parameters

A 0.40×0.15×0.35m lab-scale submerged aerobic MBR (working volume: 21L) was used in this study. The reactor, made of acrylic, contains submerged modules (filtration area: 0.3m^2) for the PP and PP-g-PAA membranes. The MBR system was operated under a constant flow for 90 days. The membrane flux was maintained at 10L/m^2•h with intermittent suction pumps, each of which has an 8-min filtration 2-min relaxation cycle. The hydraulic retention time (HRT) was kept at 9h. High-pressure diaphragm pumps were employed for physical and chemical enhanced backwashing. A diffused aeration system was adopted to supply oxygen to microorganisms and to ensure effective membrane scouring. The aeration rates were maintained at 15L/min. The pH was monitored by using a pH meter and the temperature was set to room temperature.

2.3 Wastewater composition and sludge

The seed sludge is the dried activated sludge produced by Jizhuangzi Wastewater Treatment Plant (Tianjin, China). The initial mixed liquor suspended solids (MLSS) concentration was 10,000mg/L. There was no discharge of excess sludge throughout the treatment process. The feed water is synthetic wastewater. (Wang et al., 2016).

2.4 Analytical methods

2.4.1 Trans-membrane pressure (TMP)

The TMP was measured by an MBS 3000 pressure sensor (Danfoss, Denmark) with a paperless recorder. When the TMP increment (ΔP) reached 5kPa, the membrane filtration was terminated and the membrane was subjected to physical backwashing. Two monthly chemical backwashing operations were carried out during the MBR operation.

2.4.2 Component and morphology analysis

The membranes collected from the MBR system (Section 2.2) were oven-dried at 60°C for 24h. The organic composition of the membranes was analysed by a Vector-22 Fourier-transform infrared (FTIR) spectrometer (Bruker, Germany). Then, the wavenumber spectrum was determined over the range of 4,000~400cm^{-1}, while the surface morphology of membrane was measured by a JCM-6000 field-emission scanning electron microscope (FESEM) analyser (Japan).

2.4.3 Particle size distribution (PSD) analysis

The membrane was backwashed physically under 0.15MPa. Before the PSD analysis, the sample was centrifuged in the backwash liquor at 1,500r/min for 3min to treat the pore particulate pollutants. The PSD of these pollutants was analysed using a laser granularity distribution analyser (Malvern Instruments, UK) with a detection range of 0.3~5,000nm.

3. Results and Discussion

3.1 Membrane cleaning

(1) Physical backwashing
The system performance was evaluated against the TMP and the physical backwashing period. During the operation, the MLSS was 10,000~14,000 mg/L and the constant flux was 10 L/m^2•h. Once ΔP reached 5kPa,

the filtration operation was terminated and the membrane was subjected to physical backwashing with tap water at 100kPa. The purpose is to remove the cake layer adhered on membrane surface and pollutants whose particle size was like or smaller than that of the membrane pores. Figure 1 presents the variation in the TMP in the 90-day continuous running of the MBR.

As shown in Figure 1, although PP and PP-g-PAA membrane modules share the same filtration area ($0.3m^2$), the initial TMP of the PP membrane was 15kPa higher than that of the PP-g-PAA membrane. The TMP of the PP membrane increased rapidly and the physical backwashing period lasted 3d, while the PP-g-PAA membrane operated at a relatively low pressure and the backwashing period extended to 7d. The small TMP and ΔP of the PP-g-PAA membrane is attributable to the hydrophilic grafted layer of the PAA. Hydrophilic membrane surface can increase the water flux and suppress the absorption and deposition of foulants, thus reducing the polluting rate of membrane. The typical foulants include soluble microbial product (SMP) and extracellular polymeric substance (EPS).

(2) Chemical backwashing

Two monthly chemical backwashing operations were carried out during the MBR operation, respectively at the 30th and 61st day. The NaClO and citric acid were added in turns as chemical agents to enhance the backwashing effect. The concentration of these agents was 500ppm (pH=12) and 3,000ppm (pH=2.5), respectively. At the beginning of chemical backwashing, the membrane was quickly filled up with cleaning fluid by high-pressure diaphragm pumps. The cleaning fluid was kept in the membrane for 1h, and then backwashed with tap water at 100kPa. The chemical backwashing results of the two membrane modules in the MBR are shown in Figure 1.

The TMP recovery rate of the PP membrane was 97.33 and 95.56%, respectively for the two chemical backwashing operations, while those of the PP-g-PAA membrane was 99.67 and 99%, respectively. It is clear that the PP-g-PAA membrane had a higher TMP recovery rate than the PP membrane. The TMP of membrane relies on the membrane resistance, membrane fouling, feed water and the MLSS. In our study, the only differences between the two membranes lie in membrane resistance and membrane fouling. Compared to hydrophobic membrane, the hydrophilic membrane has a small surface resistance and a slow polluting rate. Thus, the pollutants on this membrane can be removed very efficiently through chemical backwashing.

With NaClO as the chemical agent, the backwashing removed most biological pollutants (e.g. EPS and SMP) from the surface and pores of both membranes. However, the PP-g-PAA membrane achieved a higher TMP recovery rate, owing to the pH switch by PAA which was grafted onto the surface/ into the pores of the membrane. Since the feed water and NaClO solution were less acidic than the PAA (pKa: 4.28) (Kajiwara K et al., 1992), the PAA chain elongated and became hydrophilic. As a result, the pore size of membrane surface was reduced to a certain extent. By contrast, the citric acid (pH: 2.5), with a strong H+ ionic strength, was more acidic than the PAA, such that the PAA chain protonated and contracted and then the pore size of PP-g-PAA membrane increased. Thus, the pollutants larger than the original pore size were washed away by acid cleaning.

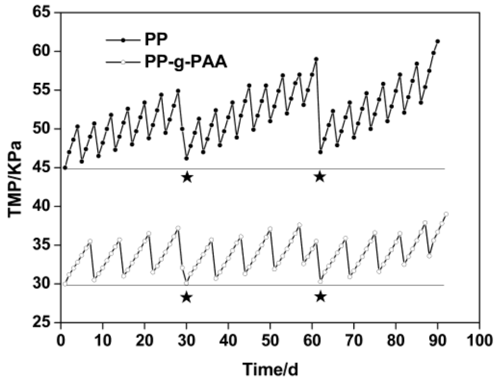

Figure 1: TMP profiles of PP and PP-g-PAA membranes bioreactor systems
★: Chemical backwashing

3.2 Contaminant analysis

The attenuated total reflection (ATR) was used in conjunction with the FTIR to characterize the chemical composition of membrane surface (Figure 2). Through the comparison between Figures 2(a) and 2(b), it can be seen that a new peak appeared at $1,648cm^{-1}$ due to the C=O carboxyl from grafted PAA.

In Figures 2(c) and 2(d), the peaks near 3,320 and 1,050cm^{-1} signify the presence of polysaccharides or polysaccharide-like substances on the polluted membrane surface during the 90-day operation of the MBR. The polluted PP membrane had a higher peak intensity than the polluted PP-g-PAA membrane, indicating that the former contained more polysaccharides or polysaccharide-like substances.

In addition, the peaks near 1,669 and 1,648cm^{-1} were the characteristic peaks of protein. Similarly, the polluted PP membrane had a higher peak intensity than the polluted PP-g-PAA membrane, an evidence for the higher content of protein in the former membrane. The PP-g-PAA membrane enjoyed better anti-fouling capability because its membrane surface was transformed from hydrophobic to hydrophilic thanks to the PAA grafted layer.

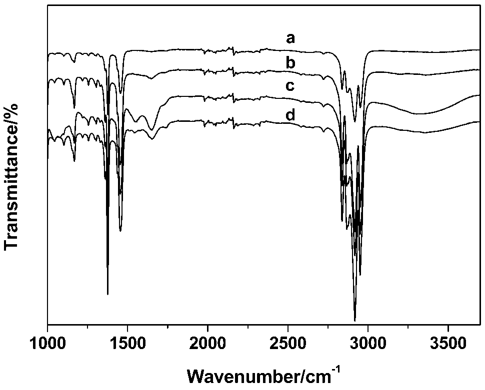

Figure 2: ATR-FTIR spectra of membrane surfaces

(a) PP membrane, (b) PP-g-AA membrane, (c) PP membrane in MBR, (d) PP-g-AA membrane in MBR

3.3 Membrane morphology

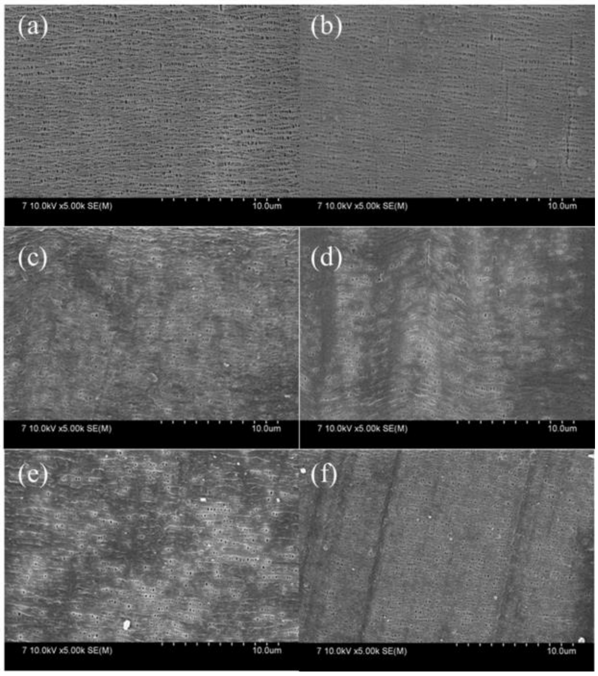

Figure 3: FESEM micrographs of membrane surface

(a) unpolluted PP membrane; (b) unpolluted PP-g-AA membrane; (c) polluted PP membrane after physical backwashing; (d) polluted PP-g-AA membrane after physical backwashing; (e) polluted PP membrane after chemical backwashing; (f) polluted PP-g-AA membrane after chemical backwashing

Figure 3 presents the FESEM micrographs of membrane surface. Compared with unpolluted PP membrane (Figure 3a), the unpolluted PP-g-AA membrane surface (Figure 3b) had a much smaller pore size. This is because the membrane surface and pores were covered by the PAA grafted chain.

As shown in Figure 3(c), the pores of the PP membrane were plugged or covered （X. S. Yi et al., 2013） by pollutants, owing to the reduced pore size and porosity of the membrane. This phenomenon reveals that the physical backwashing only removed part of the pollutants, while the rest of the pollutants were still stuck in the membrane pores.

In Figure 3(d), however, fewer pollutants were stuck in or adhered to membrane pores or surface than Figure 3(c). A possible reason lies in the longer physical backwashing period and lower TMP and ΔP of the PP-g-AA membrane. Besides, this phenomenon indicates that the efficiency of the PP membrane was enhanced by the grafting of PAA, a result of the hydrophilicity and biocompatibility of PAA.

The chemical backwashed membrane exhibited relatively large pore size and high porosity (Figures 3(e) and 3(f)), an evidence to the efficiency of chemical backwashing on pollutants removal. Furthermore, the chemical backwashing, especially acid cleaning, achieved desirable recovery of PP-g-AA membrane (Figure 3f) surface and pore size. This reveals that the grafted PAA chain performed a perfect pH switch role in membrane cleaning and foul control.

3.4 PSD analysis

Figure 4 displays the PSD of pollutants in physical and chemical backwash liquors. Before physical backwashing, the membrane surface was cleaned by a banister brush. Then, the physical backwashed membrane was further backwashed chemically. It is observed that the physical backwash liquor of the PP membrane had a broad range of PSD between 250nm and 530nm (Figure 4a), while that of the PP-g-PAA membrane had a narrow PSD range between 280nm and 520nm (Figure 4b). The small range is attributed to the replacement of pollutants with PAA in the pores of the PP-g-PAA membrane.

Compared to that of physical backwash liquor, the PSD of chemical backwash liquor of both the PP and the PP-g-PAA membranes was high in terms of size and range, because the pollutants in pores were removed by chemical backwashing. The particle size of PP-g-PAA chemical backwash liquor increased faster and greater than that of PP chemical backwash liquor. Besides the same effect of chemical agent, the pores size of PP-g-PAA membrane increased when the pH is less than the pKa of PAA, which performed as a pH switch. The pH switch enhanced the effect of chemical backwashing and removed more pollutants from membrane pores.

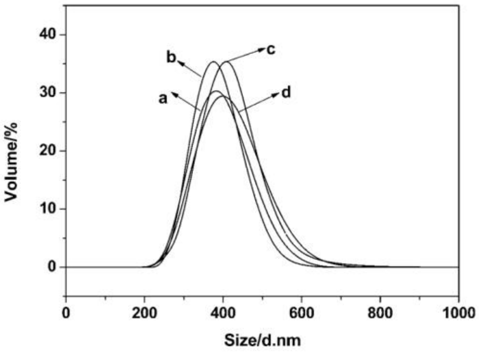

Figure 4: Pollutants particle size distribution of backwashed solution: a- physical backwashed of PP membrane; b- physical backwashed of PP-g-PAA membrane; c- acid backwashed of PP membrane; d- acid backwashed of PP-g-PAA membrane.

4. Conclusions

This paper prepares a pH switch PP-g-PAA membrane through continuous UV grafting in the MBR system. The new membrane achieved lower TMP and longer physical backwashing period than the original PP membrane, indicating that it has better hydrophilic and anti-fouling performance. The PP-g-PAA membrane performed a perfect switch effect in chemical backwashing, especially acid washing. Most of the pollutants clocked in membrane pores were cleaned by chemical backwashing thanks to the pH switch effect. The good performance of the PP-g-PAA membrane in the MBR system promises a low energy consumption and a long membrane life.

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