Preparation of Cu-CNT/ceramic Hollow Fiber Membranes and Investigation of their Antibiofouling Performance under Electrochemical Assistance

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Abstract. Loading releasable biocide is a conventional method to mitigate membrane biofouling, but its application is always limited by short lifetime as a result of biocide releasing. In this study, an anti-biofouling membrane was fabricated by introducing copper nanoparticle/carbon nanotubes on ceramic substrate. Meanwhile, electrochemical assistance was applied to improve the membrane performance in filtering bacterial suspension. The flux of electrically assisted membrane was 2.6 times as high as that without electropolarization. Meanwhile, the dissolution rate of copper ions can be decreased by 55% with the assistance of applied voltage in comparison with membrane separation alone.

Introduction

Membrane separation technology has been widely used for wastewater treatment due to its simple equipment, easy operation and less added chemical reagents[1]. However, membrane fouling highly limits the application of membrane separation technology in water treatment.

Microbial contamination is the most difficult to solve, mainly because the microorganism can propagate rapidly on the surface of the membrane. The most effective way to solve membrane biofouling is to impart antibacterial properties to membrane, which can inhibit bacterial adsorption and prevent biofilm formation[2]. In practice, however, the biocidal species are easy to deplete and the surface of the bacteriostat can be covered by the microorganism and EPS, which weaken anti-biofouling ability of membrane[3].

As electrochemical technology is applied in metal recovery due to friendly environment and low cost[4,5], introducing electrochemical assistance might be an effective approach to limit biocide loss. At the same time, electrochemical assistance has been reported to prevent microbial adsorption by regulating the interaction between pollutants and membranes through electrostatic repulsion[6,7]. Therefore, the coupling of the separation membrane loaded with bactericidal materials and the electrochemical technology can not only alleviate the loss of the release bactericide, but also enhance the anti-biofouling performance of the membrane.

In order to verify the above conjecture, the Cu-CNT/ceramic hollow fiber membrane was produced on the surface of ceramic hollow fiber membrane by vacuum extraction method and in situ reduction. The anti-biofouling performance and the release account of copper ions with electrochemical assistance were investigated.

Experiment

Multiwalled carbon nanotubes (CNTs, 60-100 nm) were acidized in HNO_3/H_2SO_4 solution(1/3,v/v) at 80°C for 4 h, after which prepared CNTs were uniformly dispersed into the concentration of 0.5 g/L solution. CNTs modified by copper nanoparticles were prepared in the following steps. At the beginning, PEI solution was added to $CuSO_4$ solution and stirred for 10 min. and secondly mix $CuSO_4$ with PEI solution and CNTs solution overnight. The formation of Cu-CNTs was initiated by adding $NaBH_4$ solution, and then a vacuum-filtration process was applied to coat the Cu-CNTs onto the ceramic hollow fiber substrate. Finally, the Cu-CNTs/ceramic membrane was synthetized after being heated at 300°C for 2 h in air.

The filtration test was operated in domestic membrane module (Fig. 1). In order to evaluate the concentrate of cupric ions in the solution, the membrane was cut into one specific length of 4 cm, placing composite membrane into small a glass vial which includes 10 mL of 5 mM $NaHCO_3$ solution. After 8 h, the concentration of cupric ions in the soak solution need to be acidified with 0.1 mL of 70% nitric acid, and then be analyzed by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, model Nex ION 300D) with argon as carrier gas.

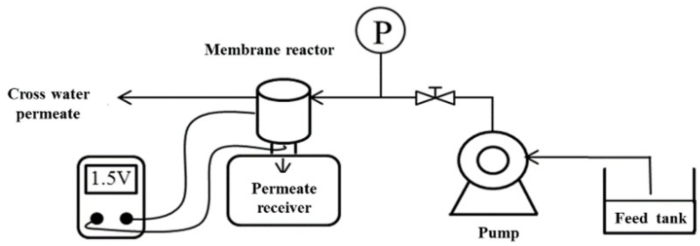

Fig. 1 Diagram of the cross-flow water filtration hollow fiber membrane

Results

The morphologies of membranes are presented in Fig. 2. In Fig. 2a, no cracks are observed on the surface of the membrane. The outer and inner diameter of ceramic support were 2 mm and 1mm, respectively (Fig. 2b). After coating CNTs onto the ceramic support, it is obvious that the CNTs strewn at random on the surface of ceramic support, which results in abundant interconnected pores (Fig. 2c). As shown in Fig. 2d, the CuNPs were uniformly deposited on the surface of the CNTs without obvious aggregation, and the size ranges from 30-60 nm.

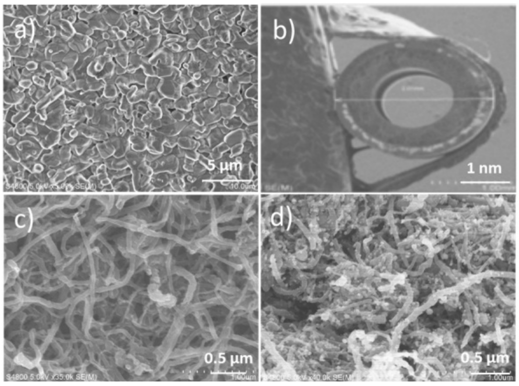

Fig. 2 SEM images of ceramic substrate (a,b) and Cu-CNTs/ceramic hollow fiber membrane (c,d)

The antibacterial property of composite membranes were evaluated against *E.coli*, and the results of inhibition ring test are shown in Fig. 3. Apparently, Cu-CNTs/ceramic membrane exhibited the zone of inhibition for *E.coli*, but neither CNTs/ceramic and ceramic membranes showed any apparent the zone of inhibition. The result above indicates the antibacterial property of Cu-CNTs/ceramic membrane and copper ions have diffused into the agar layer to prevent the growth of bacteria around the membrane.

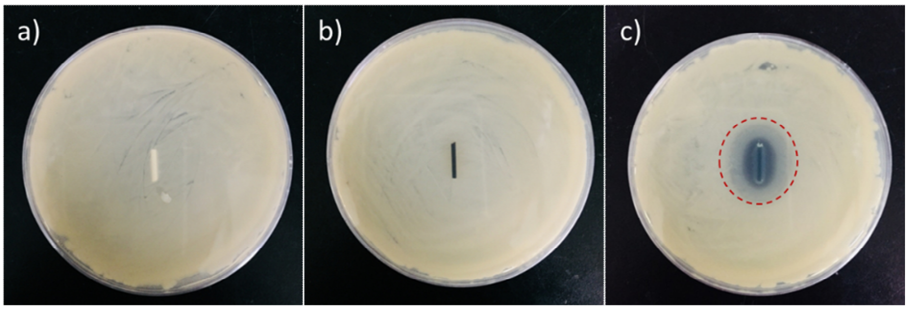

Fig. 3 Inhibition zones for ceramic membrane (a), CNTs membrane (b) and Cu-CNTs/ceramic membrane (c)

As presented in Fig. 4, the flux of membranes are decreasing with filtration time going, which means *E.coli* cause a dramatic flux loss. After running 60 min, the flux of Cu-CNT/ceramic, CNT/ ceramic at -1.5 V and Cu-CNT/ceramic at -1.5 V decrease to 102 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$, 186 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$ and 265 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$, respectively. It is considered that, although Cu-CNT/ceramic membrane has a strong ability of antibacterial, the *E.coli* in the water will still enter the membrane hole and adhere on the surface due to extra potential in the practical condition[8]. The flux of the CNT/ ceramic hollow fiber membrane with the external electric field decreased slowly. As discussed previously, the electrostatic repulsion and electrophoretic action between the membrane and bacteria prevented the adhesion of bacteria, thus slowing down the speed of membrane flux decline. It is interesting to find that the flux of Cu-CNT/ceramic at -1.5 V decrease at a lowest speed. This is because the applied electric field inhibits the adhesion of bacteria to a large extent, and the bacteriostat (CuNPs) on the membrane inactivate the bacteria adsorbed on the surface of the membrane, which reduces the interaction between the bacteria and the membrane, and further weaken the effect of the bacteria on the membrane permeation flux.

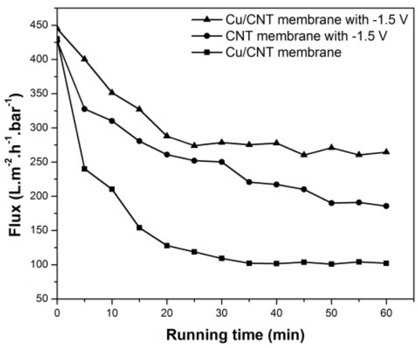

Fig. 4 Flux of Cu-CNT/ceramic, CNT/ceramic at -1.5 V and Cu-CNT/ceramic hollow fiber membrane at -1.5 V

The antibacterial property of modified membrane mainly focuses on the release of copper ions from the CuNPs. The rapid depletion of CuNPs, however, limits its widely application in the continuous membrane system[9]. For controlling CuNPs depletion, the electrochemical method was used to reduce cupric ions. As shown in Fig.5, with the increase of applied voltage from 0 V to -1.5 V, the release of cupric ions from the composite membrane decreased from 1.72 mg L^{-1} cm^{-2} to 0.78 mg L^{-1} cm^{-2}. Lower concentration of cupric ions under electropolarization suggests cupric ions were reduced on the Cu-CNTs/ceramic membrane, prolonging the lifetime of the CuNPs[10]. Thus, electrochemical assistant technology can solve the problem of loss of antibacterial agents.

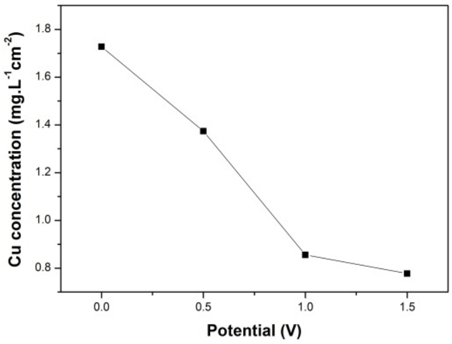

Fig. 5 Concentration of Cu^{2+} at open circuit, -1.0 V and -1.5 V

Conclusions

In this study, we developed an anti-biofouling membrane by in situ fabrication of CuNPs onto the CNT ceramic hollow fiber membrane. It exhibited excellent antibacterial property to mitigate biofilm formation by antimicrobial modification. Under a voltage of -1.5 V applied on the membrane, the Cu^{2+} concentration released from the membrane is 55% lower than that of the membrane without any treatment. Such low copper nanoparticles dissolution rate and excellent anti-biofouling ability would ensure the prepared membrane with long-term application in water treatment.

Acknowledgements

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