Water Purification

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An Electrocatalytic Membrane Reactor with Self-Cleaning Function for Industrial Wastewater Treatment**

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Industrial wastewater has become a global issue due to its high concentration of pollutants, especially refractory organic compounds.[1] Membrane technology has attracted considerable attention in industrial wastewater purification over the past decades owing to its high flexibility regarding water quality and low investment costs. However, inherent membrane fouling caused by concentration polarization and pore blocking leads to low plant reliability and limits wide industrial application in wastewater treatment.[2] Controlling and mitigating membrane fouling has become the most critical problem in the field of membrane technology for water and wastewater treatment. To tackle this challenging issue, many strategies have been implemented, such as pretreating feed water, development of antifouling membranes, new design of membrane modules, optimizing operating conditions, and integrating membrane processes with other techniques.[3] Despite all the efforts, membrane fouling is still not completely solved. Apart from membrane technology, photocatalytic oxidation and electrocatalytic oxidation, with their low toxicity and high efficiency, have been considered competitive candidates for industrial wastewater treatment. However, low utilization of visible-light photons and difficult recycling of photocatalysts for photocatalytic oxidation,[4] as well as the huge energy consumption for electrocatalytic oxidation,[5] hinder their extensive application. Besides, their combination with membrane technology is still far from satisfactory for water treatment.

To solve the challenging problem of membrane fouling in industrial water treatment, we propose a simple strategy that could avoid membrane fouling completely. We present the design of a novel electrocatalytic membrane reactor (ECMR) with self-cleaning function (Figure 1). In the reactor, a tubular conductive membrane as anode and a stainless steel tube surrounding the membrane as cathode were connected by a dc regulated power supply (Figure S1 in the Supporting Information). During the treatment, the wastewater permeates through the membrane from the outside in by means of a suck pump operating in a dead-end manner and the "clean" water is obtained from the inside.

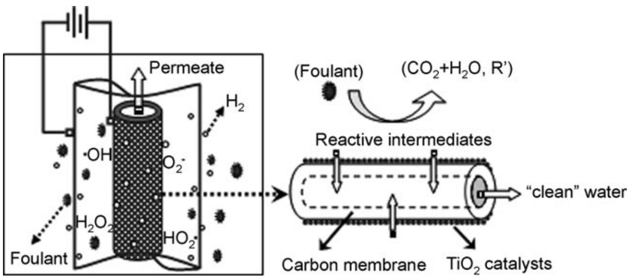

Figure 1. Scheme of electrocatalytic membrane reactor.

A tubular carbon membrane was employed as the conductive membrane substrate because of its significant mechanical strength, good chemical stability, and specific conductivity.[6] Titanium dioxide (TiO_2) is widely used as a catalytic layer of electrodes in treating various industrial wastewaters[7] as it is excellent in oxidation and reduction, chemically stable, nontoxic, and cheap. Here TiO_2 as the electrocatalyst and hydrophilic agent[8] was coated onto the membrane by a sol–gel approach to prepare a TiO_2/carbon membrane to enhance electron transfer[9] (Figure S2 in the Supporting Information) and improve membrane permeability.

The morphology of the TiO_2/carbon membrane was characterized by TEM (Figure 2). The original carbon

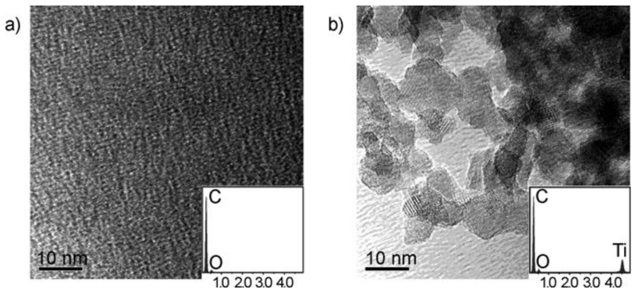

Figure 2. High-resolution TEM images. a) Original carbon membrane. b) TiO_2/carbon membrane.

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membrane consisted of a uniform graphite-like carbon structure (Figure 2a). TiO_2 particles, which were anatase crystallites with an average crystal size of around 7.8 nm (Figure S3 in the Supporting Information), were well distributed on the membrane surface (Figure 2b).

To prevent membrane fouling, the TiO_2/carbon membrane, acts both as a filter and an anode during electrolysis. In ECMR operation, once the membrane anode is electrified, excitation of TiO_2 leads to holes in the valence band and electrons in the conduction band at the TiO_2 surface [Eq. (1)]. The obtained electrons and holes not only electrochemically decompose H_2O into O_2 and H_2 [Eqs. (2) and (3)],[10] which induce gas and liquid microflows (Figure S4 in the Supporting Information) to reduce concentration polarization and avoid membrane fouling,[11] but can also react with the adsorbed H_2O[12] and O_2 at the TiO_2 surface to generate reactive intermediates such as $^{\bullet}OH$, O_2^-, $HO_2^{\bullet}$, and H_2O_2 [Eqs. (4)–(8)]. This can indirectly decompose the organic foulants on the membrane surface or in the pores into CO_2 and H_2O or biodegradable products, and thus a self-cleaning function of the electrocatalytic membrane is achieved. Simultaneously, CO_2 bubbles also induce microflows to strengthen the antifouling effect.

$$TiO_2 \rightarrow TiO_2(h^+ + e^-) \tag{1}$$

$$H_2O + 2\,h^+ \rightarrow {}^1\!/_2\,O_2 + 2\,H^+ \tag{2}$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \tag{3}$$

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \tag{4}$$

$$O_2 + e^- \rightarrow O_2^- \tag{5}$$

$$O_2^- + H^+ \rightarrow HO_2^{\bullet} \tag{6}$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{7}$$

$$O_2^- + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{8}$$

Figure 3 verifies the excellent antifouling performance of the electrocatalytic membrane in an ECMR in which $200\,mg\,L^{-1}$ of oily water was treated under 2.0 V supply voltage and 10.0 mA current. Na_2SO_4 ($15\,g\,L^{-1}$) was added to the oily water as aqueous electrolyte. Filtration of oily water was also conducted with the original carbon and TiO_2/carbon membranes for comparison.

As shown in Figure 3A, the permeate fluxes of both the original carbon membrane and the TiO_2/carbon membrane declined rapidly with increasing operation time, especially in the case of the former, due to heavy membrane fouling caused by concentration polarization and pore blocking during the pressure-driven membrane process. The permeate flux decreased to 19.4% of the pure-water flux ($122.6\,L\,m^{-2}\,h^{-1}\,bar^{-1}$) for the original carbon membrane and 48.8% of the pure-water flux ($401.3\,L\,m^{-2}\,h^{-1}\,bar^{-1}$) for the TiO_2/carbon membrane after 200 min of operation. At the same time, the removal rates of oil and chemical oxygen demand (COD) were 68.0 and 58.6% for the original carbon membrane and 78.6 and 83.7% for the TiO_2/carbon membrane, respectively (Figure 3B). Although the permeability and rejection of the TiO_2/carbon membrane was higher than that of the original carbon membrane, it still suffered from serious membrane fouling.

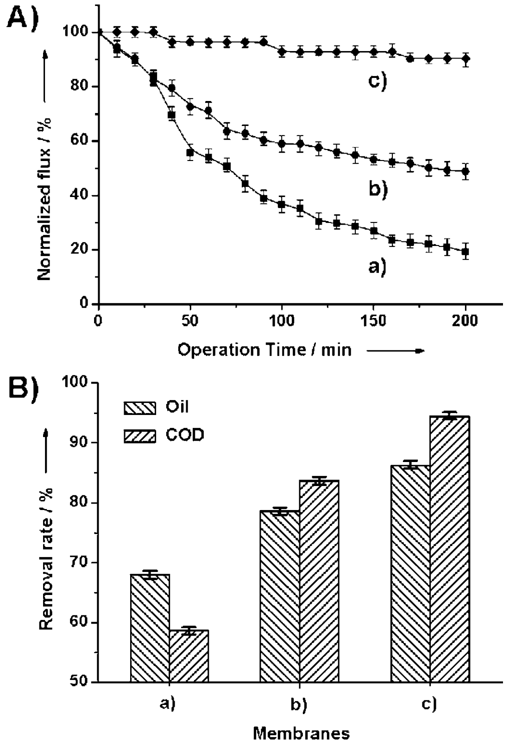

Figure 3. A) Changes in the permeate flux of membranes and B) removal rates of oil and COD. a) Original carbon membrane. b) TiO_2/carbon membrane. c) Electrocatalytic membrane in ECMR.

The electrocatalytic membrane in the ECMR showed only a slight drop of 9.6% in permeate flux (Figure 3A). The removal rates of oil and COD were up to 86.2% and 94.4%, respectively (Figure 3B). The permeate flux of the electrocatalytic membrane was 15.2 and 1.85 times higher than those of the original carbon membrane and TiO_2/carbon membrane, respectively, after 200 min of operation. The electricity consumption for this membrane reactor was 0.166 kW·h per ton of water, which indicates that the electrocatalytic membrane has a very strong antifouling ability. It also implies that there is a synergistic effect between membrane separation and electrocatalytic oxidation in the ECMR.

Firstly, the gas and liquid microflows arising in the ECMR would hinder foulant adsorption and deposition on the membrane surface and reduce the concentration polarization. Secondly, if the foulants are adsorbed and deposited on the membrane surface or in the pores to cause concentration polarization and block the pores, the higher electrocatalytic activity of the electrocatalytic membrane would decompose the foulants into CO_2 and H_2O or small biodegradable products (Figure S5 and Table S1 in the Supporting Information) and thus result in a strong self-cleaning function. Certainly, the microflows would also restrain water permeation through the membrane, and salts and a small amount of organics might be absorbed in pores of the membrane and interfere with the penetration of water molecules. Perhaps this is the reason for the observed slight drop in flux of the electrocatalytic membrane.

Besides oily water, the ECMR also exhibited good performance and antifouling ability for treatment of other industrial wastewaters, such as phenol wastewater and dye wastewater (Figure S6 and S7 in the Supporting Information), which is of broad interest.

In conclusion, an antifouling electrocatalytic membrane reactor with self-cleaning function was successfully designed and manufactured for industrial wastewater treatment. It exhibited excellent performance in the treatment of oily water compared with conventional membrane filtration. Such an ECMR would have wide potential applications in industrial wastewater purification.

Experimental Section

Preparation of TiO_2/carbon membrane: TiO_2 sol–gel was prepared by using tetrabutyl titanate as precursor. A tubular carbon membrane, with electrical resistivity of approximately $1.0\times10^{-3}\,\Omega\,m$, an average pore size of 0.44 μm, and a filtration area of 15.0 cm^2, was used as the substrate. The membrane was first pretreated in 65 wt% HNO_3 solution for 1 h, cleaned in an ultrasonic bath, and dried. Then the membrane was dipped into TiO_2 sol for 10 min. After removing from the sol and drying at room temperature, the TiO_2-coated membrane was finally placed in a muffle furnace to sinter at 400 °C for 2 h.

Characterization: The morphologies and structures of membranes were observed by HRTEM (FEI Tecnai G2 F20). XRD patterns were obtained on Bruker AXS D8 Advance diffractometer ($Cu_{K\alpha}$ radiation, $\lambda = 1.5406$ Å).

Evaluation of ECMR performance: The permeate flux of membranes was calculated by Equation (9) where J is the flux ($L\,m^{-2}\,h$), V the volume of permeate (L), A the area of membrane (m^2), and t the filtration time (h).

$$J = \frac{V}{At} \qquad (9)$$

The normalized flux is the ratio of the membrane flux obtained at a running time to the initial membrane flux.

The oil concentration was measured by detecting the absorption at 195 nm on a UV/Vis spectrophotometer (Shimadzu UV-2401PC), and COD was measured by a Hach 2800 spectrophotometer. GC-MS (HP5890-5971) was used to analyze the compositions of the feed and permeates.

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