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A hybrid process combining homogeneous catalytic ozonation and membrane distillation for wastewater treatment

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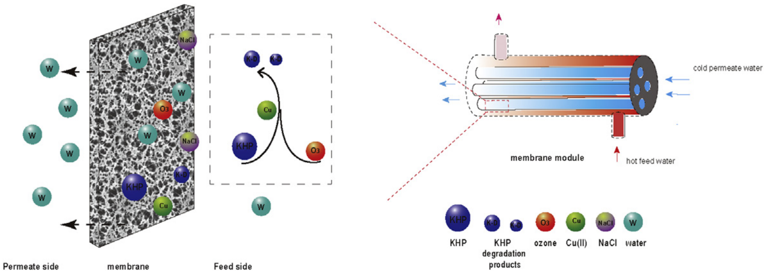
HIGHLIGHTS

- For the first time, homogeneous catalytic ozonation and membrane distillation were coupled in a membrane reactor.
- Organics and salts were efficiently removed and the homogenous catalyst was almost 100% recovered simultaneously.
- Membrane fouling was effectively mitigated compared to MD process.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel catalytic ozonation membrane reactor (COMR) coupling homogeneous catalytic ozonation and direct contact membrane distillation (DCMD) was developed for refractory saline organic pollutant treatment from wastewater. An ozonation process took place in the reactor to degrade organic pollutants, whilst the DCMD process was used to recover ionic catalysts and produce clean water. It was found that 98.6% total organic carbon (TOC) and almost 100% salt were removed and almost 100% metal ion catalyst was recovered. TOC in the permeate water was less than 16 mg/L after 5 h operation, which was considered satisfactory as the TOC in the potassium hydrogen phthalate (KHP) feed water was as high as 1000 mg/L. Meanwhile, the membrane distillation flux in the COMR process was 49.8% higher than that in DCMD process alone after 60 h operation. Further, scanning electron microscope images showed less amount and smaller size of contaminants on the membrane surface, which indicated the mitigation of membrane fouling. The tensile strength and FT-IR spectra tests did not reveal obvious changes for the polyvinylidene fluoride membrane after 60 h operation, which indicated the good durability. This novel COMR hybrid process exhibited promising application prospects for saline organic wastewater treatment.

1. Introduction

Ozone, as an important oxidant agent, had been considered for numerous applications in water and wastewater treatment (Gottschalk et al., 2000; Beltrán, 2004). It can react with compounds directly or through an indirect approach which generates

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hydroxyl radicals or metal-complexes (Pines and Reckhow, 2002; Beltran et al., 2005; Nawrocki and Kasprzyk-Hordern, 2010). In many cases, the hydroxyl radicals or metal-complexes approach had much greater reaction rate constants than direct ozonation, which were considered to be a promising method to improve the ozonation efficiency. (Pines and Reckhow, 2002; Beltran et al., 2005; Buffle et al., 2006). An important type of indirect process was catalytic ozonation which can be either homogeneous (catalyzed by transition metal ions), or heterogeneous (catalyzed by solid catalysts). The homogeneous catalysts usually showed good ozonation efficiency and low cost. However, the catalytic ions were difficult to recover which increases the process cost and introduces potential secondary pollution (Nawrocki and Kasprzyk-Hordern, 2010).

Membrane processes, such as nanofiltration (NF), reverse osmosis, and membrane distillation (MD) were reported with excellent performance for metal ion removal (El-Bourawi et al., 2006; Wachinski, 2013). MD process, in particular, only allows vapor molecules to transport across the membrane with almost 100% ion rejection. In addition, the membrane fouling was much less severe compared to those pressure-driven membrane processes (El-Bourawi et al., 2006). Further, MD process was also able to utilize low-grade waste and alternative energy sources, such as solar power (Shim et al., 2015). All the merits above made MD an attractive approach for homogenous catalyst recovery.

A large number of research investigated employing membrane process, including MD process, for catalyst recovery (Mozia and Morawski, 2006; Mozia et al., 2006; Choo et al., 2008; Benotti et al., 2009; Mozia, 2010; Mozia et al., 2010, 2014; Leong et al., 2014; Qu et al., 2014). Among these, photocatalytic membrane reactors (PMRs) were widely studied. In a PMR, TiO_2 particles (one type of photocatalyst) were commonly used to suspend in reactors, whilst the membrane processes, such as microfiltration, UF, NF and MD, were used to separate catalysts. The use of PMRs shortened the process route for catalyst recovery, reduced the size of installation, and also enabled the continuous production with low energy consumption (Mozia, 2010). In this regard, PMRs were considered to be a promising technology in natural organic matter (Choo et al., 2008), pharmaceuticals and endocrine disrupting compounds removal (Benotti et al., 2009), municipal wastewater (Mozia et al., 2014), and dye wastewater treatment (Mozia et al., 2006, 2009, 2010). Mozia et al (Mozia et al., 2014). compared two types of PMRs (utilizing UF or direct contact membrane distillation (DCMD)) for treating primary and secondary effluents of municipal wastewater plant. Photocatalysis-DCMD system offered better performance, with much lower flux decline and less membrane fouling. The total organic carbon (TOC) removal efficiency was significantly higher and the organic carbon in permeate water was less than 0.5 mg/L. Another work of Mozia et al (Mozia et al., 2006). compared the above two systems for dye wastewater treatment. The photocatalysis-DCMD system also exhibited better permeate water quality and less membrane fouling, with 80% TOC removed in permeate stream.

The aforementioned examples confirmed that the photocatalysis-DCMD process using heterogeneous catalysts can effectively remove organic contaminants from aqueous solutions. It was postulated that the use of homogenous catalysts might bring in excellent performance as heterogeneous ones. In this regard, we proposed to combine homogeneous catalytic ozonation and DCMD for a hybrid catalytic ozonation membrane reactor (COMR) process. In this process, DCMD is used as catalyst separator and clean water producer, just similar to that of photocatalysis-DCMD process. Catalysts employed here are metal ions instead of the solid ones. The ionic catalysts were difficult to remove in conventional processes, however when combined with a MD process, an easy removal can be envisioned. Although the concept appeared to be promising, the COMR had been barely investigated in previous studies.

In this work, the feasibility of utilizing COMR for water treatment was evaluated in terms of the permeate water quality, catalyst recovery efficiency, MD flux and membrane fouling behavior. The membrane properties before and after operation were also evaluated to assess the material stability.

2. Experimental

2.1. Wastewater

The model saline wastewater used in this work contained NaCl and KHP with concentrations ranging from 200 to 1000 mg/L. KHP was a non-volatile and stable refractory pollutant, it represented a class of endocrine disrupting compounds which is a major concern in environment (Heng et al., 2007; Kit Chan et al., 2012). Further, the addition of NaCl was to evaluate the rejection performance of COMR on monovalent ions. To avoid the sedimentation of catalysts, feed water was adjusted to pH value of 2 by adding certain amount of sulfuric acid.

2.2. Membrane and membrane module

Polyvinylidene fluoride (PVDF) hollow fiber membranes were prepared in-house via the dry-jet wet spinning technique. The detailed hollow fiber fabrication protocol can be found in literature (Hou et al., 2012). The dope solution comprised 15 wt% PVDF (Solef® PVDF1010, Solvay, Belgium) and 85 wt% dimethylacetamide. The resultant PVDF hollow fiber had an outer diameter of 1.36 mm and an inner diameter of 1.10 mm. The average pore size was 168 nm and the pore size distribution and membrane section morphology can be seen in Fig. S1. The contact angle between membrane and water was 95.8°, and the porosity was 66%. Each membrane module contained 20 PVDF hollow fibers with an effective area of 0.00854 m^2.

2.3. COMR hybrid process

A laboratory-scale COMR set-up was presented in Fig. 1, which consisted of a PVDF hollow fiber membrane module, an ozone generation and injection system, a feed water circulation system

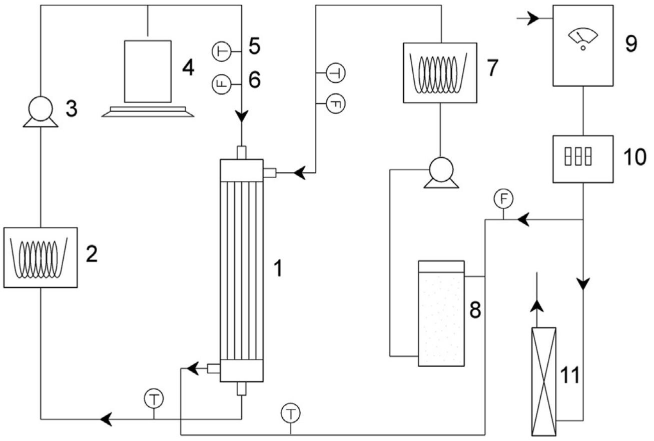

Fig. 1. Schematic diagram of the COMR system. (1) PVDF membrane module; (2) cryostat; (3) peristaltic pump; (4) water tank and balance; (5) thermometer; (6) flow meter; (7) thermostat bath; (8) glass reactor; (9) ozone generator; (10) ozone concentration analyzer; (11) KI wash bottle.