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Fate and wetting potential of bio-refractory organics in membrane distillation for coke wastewater treatment

Jing Ren [a], Jianfeng Li [a, *], Zuliang Chen [b], Fangqin Cheng [a, **]

[a] *Institute of Resources and Environmental Engineering, Shanxi Collaborative Innovation Center of High Value-added Utilization of Coal-related Wastes, Shanxi University, Taiyuan, 030006, China*

[b] *Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA, 5095, Australia*

HIGHLIGHTS

- Low molecular aromatic organics pass through the membrane preferentially.
- Penetration of specific organics contributes to partial membrane wetting.
- Organics composition in the feed and fouling layer affects wetting rate and time.
- Formation of PAM-organic complexes mitigates the wetting potential of organics.

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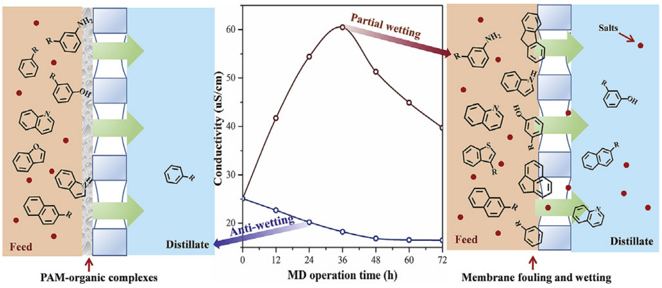
GRAPHICAL ABSTRACT



ABSTRACT

Membrane distillation (MD) has been hindered in industrial applications due to the potential wetting or fouling caused by complicated organic compositions. This study investigated the correlations between the fate and wetting potential of bio-refractory organics in the MD process, where three coke wastewater samples pre-treated with bio-degradation and coagulation served as feed solutions. Results showed that although most of the bio-refractory organics in coke wastewater were rejected by the hydrophobic membrane, some volatile aromatic organics including benzenes, phenols, quinolines and naphthalenes passed through the membrane during the MD process. Interestingly, membrane wetting occurred coincidently with the penetration of phenolic and heterocyclic organics. The wetting rate was obviously correlated with the feed composition and membrane surface properties. Ultimately, novel insights into the anti-wetting strategy of MD with bio-refractory organics was proposed, illustrating that the poly-aluminum chloride/polyacrylamide coagulation not only removed contaminants which could accelerate membrane wetting, but also retarded membrane wetting by the complexation with organics. The deposition of these complexes on the membrane surface introduced a secondary hydrophilic layer on the hydrophobic substrate, which established a composite membrane structure with superior wetting resistance. These new findings would be beneficial to wetting control in membrane distillation for wastewater treatment.

1. Introduction

Membrane distillation (MD) is a thermally driven separation process that only permits vapor molecules to transport across a

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* Corresponding author.
** Corresponding author.
E-mail addresses: lijianfeng@sxu.edu.cn (J. Li), cfangqin@sxu.edu.cn (F. Cheng).

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hydrophobic microporous membrane from the hot feed to the cold distillate (Wang and Chung, 2015). Given the advantages of high quality distillate, less fouling propensity and possible utilization of low-grade heat (Lokare et al., 2017), MD has become an appealing method for seawater desalination, food concentration and wastewater reclamation (Shaffer et al., 2013; Quist-Jensen et al., 2015). However, when MD is utilized to treat wastewaters containing hydrophobic or amphiphilic organics, membrane wetting unavoidably occurs, undermining the MD performance and constraining its industrial applications (Wang et al., 2016; Eykens et al., 2017). The underlying reason for wetting is that the strong hydrophobic-hydrophobic interactions between the contaminants and membrane promote the adhesion of organics on the membrane surface (Meyer et al., 2006), which renders the membrane pores hydrophilic and ruins the membrane separation process. One example is the application of commercial PVDF and PTFE membranes in the MD process to treat dyeing wastewater, which contains a high concentration of chemicals. Wetting problems that lead to the process failure in a relatively short time have been documented in previous studies (Lin et al., 2015b; An et al., 2016). Therefore, wetting prevention is a primary requirement for the MD application.

Since membrane wettability can be significantly affected by the physicochemical characteristics of solutes in feed (Wijekoon et al., 2014) and membrane properties (Guillen-Burrieza et al., 2015), two predominant types of approaches have been proposed to mitigate membrane wetting, which can be broadly classified as pre-treatment and membrane surface modification. Pre-treatments, such as bio-degradation, coagulation and catalytic ozonation, have been employed to remove the surface-active organics prior to the MD process for protection against membrane wetting (Wang et al., 2008; Goh et al., 2015; Zhang et al., 2016). On the other hand, modification of membranes can be subdivided into two categories: hydrophilic-hydrophobic composite membrane and superhydrophobic membrane with robust wetting resistance. Lin et al. (2015b) fabricated a hydrogel composite membrane with a hydrophilic agarose hydrogel layer on a hydrophobic PTFE membrane to suppress surfactant wetting from dyeing wastewater. Chen et al. (2017) used a negatively charged superhydrophobic membrane with superior anti-wetting properties to treat emulsified wastewaters. These studies are very helpful in providing practical anti-wetting strategies for MD application in industrial wastewaters including gas refinery wastewater, pharmaceutical wastewater, dyeing wastewater and olive mill wastewater (El-Abbassi et al., 2013; Xu et al., 2015; An et al., 2017). However, there are few studies relating the membrane wetting to the specific fate of organics during the MD process, which is critical for understanding the wetting phenomenon in membrane distillation.

Coke wastewater is one of the most challenging industrial wastewaters because of its high organic load and complex chemical composition (Zhang et al., 2012). Even after biological treatment, considerable refractory organics as well as high salinity still remain in the effluent, which demand the advanced treatments urgently (Yang et al., 2013). Nevertheless, many problems would be induced by the bio-refractory organics during the conventional advanced treatments, for instance, the formation of potentially harmful disinfection byproducts (DBPs), the large consumption of oxidants or coagulants, and serious membrane fouling in nanofiltration or reverse osmosis (Mahlangu et al., 2014; Lin et al., 2015a; Li et al., 2017). As mentioned earlier, the development of anti-wetting strategies has enabled MD to be a competitive technology to polish reluctant feed water as coke wastewater, especially with the utilization of low-grade heat from the coke plant. However, regarding the major components of coke wastewater including phenols, polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds and other active chemicals, the wetting phenomenon of these organics can't be neglected. Thus, a systematic research of these organics' wetting potential is required to expand the applications of MD.

In this study, we compared the fate and wetting potential of bio-refractory organics from three coke wastewater samples with diverse organic compositions by direct contact membrane distillation (DCMD). One sample was the bio-treated coke wastewater (BCW), while the other two were BCW pre-coagulated with polyaluminum chloride (PACl) and polyaluminum chloride/polyacrylamide (PACl/PAM), respectively. The main objectives of this study are: (1) to identify the bio-refractory organics passing through the membrane; (2) to explore the correlations between the organic permeation and membrane wetting; and (3) to propose an effective approach for wetting prevention. To achieve this goal, excitation-emission matrix (EEM) fluorescence spectroscopy and gas chromatograph/mass spectrometry (GC/MS) were conducted to track the individual organics during 72 h of MD operation. The interactions between the organics and the membrane were evaluated using a scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS). Efforts were also made to assess the role of the bio-refractory organics in membrane wetting and propose the wetting mechanism leading to the contrasting performance of the three wastewater samples.

2. Materials and methods

2.1. Wastewater samples

The wastewater samples were collected from a coke wastewater treatment plant in Shanxi, China. The effluent via steam stripping and anaerobic/anoxic/aerobic (A^2/O) bio-degradation in the coke plant was sampled as BCW1. Then the BCW1 was freshly utilized to produce other two wastewater samples: BCW2 pre-coagulated with 175 mg/L polyaluminum chloride (PACl, with a hydrogen ratio of 40%); and BCW3 pre-treated with polyaluminum chloride/polyacrylamide composite coagulant (PACl/PAM, dosage of 175 mg/L PACl and 0.5 mg/L PAM). The dosages of PACl and PAM were determined by the optimum water quality parameters of the coagulated wastewater, and a relatively low concentration of PAM was adopted to avoid serious membrane fouling (Li et al., 2016). The coagulation process was done using the jar test incorporating three steps: rapid agitation for 2 min at 200 rpm, slow agitation for 30 min at 40 rpm, and settling for 30 min.

Table 1 presents the basic quality parameters of BCW1, BCW2 and BCW3. It can be seen that all the BCW samples possessed a weakly alkaline pH and dark brown color. Although coagulation could remove a part of organic compounds, the TOC and COD value were still above the discharge limit, and the conductivity of all the samples was above 3700 μS/cm. This indicates the high salinity, high organic load and low biodegradability of these BCW samples. In addition, low concentration of ammonia also detected in these samples. These water samples were preserved at 4 °C before DCMD experiments.

Table 1
Characteristics of BCW1, BCW2 and BCW3.

Parameter	BCW1	BCW2	BCW3
pH	7.8–8.1	8.0–8.2	7.8–8.0
Conductivity (μS/cm)	3760–3866	3962–4050	3865–3890
TOC (mg/L)	68.0–69.8	51.3–52.5	43.6–45.0
COD (mg/L)	281.4–298.0	198.2–203.4	170.7–172.2
Color (°)	106–109	69–71	57–60
UV_{254} (cm^{-1})	1.15–1.19	0.68–0.70	0.59–0.62
NH_3-N (mg/L)	1.4–1.5	1.1–1.2	1.1–1.2