Modeling organic fouling of reverse osmosis membrane: From adsorption to fouling layer formation

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HIGHLIGHTS

- Adsorption/fouling-layer model analyzes the flux decline during RO filtration.
- The model provided a qualitative appreciation of the flux decline.
- The factors of filtration time and membrane flux are considered in the fouling model.
- The main interfacial interaction in each fouling step was discussed.

GRAPHICAL ABSTRACT
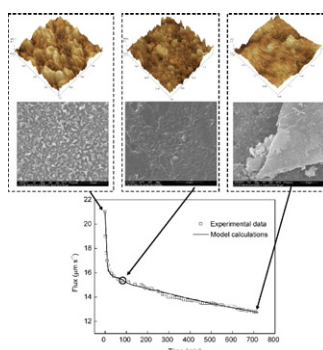
The development of membrane fouling.

ARTICLE INFO

ABSTRACT

A combined model is developed for flux decline of reverse osmosis (RO) membranes, which accounts for initial fouling due to adsorption and subsequent fouling due to the growth of a fouling layer. The predicted data are in excellent agreement with the experimental ones obtained over crossflow filtration of organic wastewaters using aromatic polyamide RO membranes over the entire course of the filtration. The model also provides a smooth transition from the adsorption regime to the fouling layer filtration regime. Based on the flux profiles and the analysis of the membrane surface, a two-step fouling mechanism is proposed to describe the evolution of fouling during continuous crossflow operation of RO membranes.

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1. Introduction

Reverse osmosis (RO) has been widely used for industrial wastewater treatment. One of the recalcitrant obstacles is membrane fouling, particularly irreversible fouling caused by the organics. Previous studies have generally related organic fouling to adsorption [1–4]. Adsorption of the organics on the membrane surface obeys Langmuir model [5–7], indicating the formation of an adsorption monolayer on the membrane surface. Adsorption can be determined and quantified by quartz crystal microbalance [8], thermogravimetric method [9] and Fourier transform infrared (FTIR) spectrometry [10,11].

In addition to adsorption, membrane fouling is also determined by concentration polarization and the formation of a fouling layer. The solute concentration at the membrane surface will be eventually greater than that in the feed solution because of solute accumulation that makes further movement of solute from the feed to membrane surface unlikely, which is known as concentration polarization. When solute

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concentration at the membrane surface reaches a limiting value, a gel layer begins to form. The gel layer develops until the flux reaches critical flux. The fouling layer deposited on the membrane surface has been reported in previous work [12,13]. Sioutopoulos et al. [14] studied the rheological property of typical membrane fouling layers, and the result offers valuable insights into the development of the fouling layer on RO membranes.

It is customary to consider a single fouling mechanism prevailing throughout the filtration [15–17]. The combined fouling model, previously uncharted, has become an emerging field recently [18–20]. However, most the combined fouling models are proposed for macroporous membranes such as microfiltration (MF) membranes and ultrafiltration (UF) membranes. It is proposed that the flux decline arises from the pore blocking followed by the cake formation. Few combined fouling models are reported for RO membranes or nano-filtration (NF) membranes which are considered as loose RO membranes. Tu et al. [21] develops the combined model incorporating the concentration polarization and fouling-layer formation for predicting NF membrane flux. However, adsorption generally related to organic fouling is not discussed. Some works considering the flux decline due to adsorption of the organics just describe the initial fouling but not the subsequent fouling [2,3]. A fouling mechanism model proposed by Srebnik [22] indicated the transition in fouling mechanism from adsorption to fouling layer formation. But the model was not developed to predict the flux decline. These works paved the way for developing a combined adsorption and fouling layer model to analyze the flux decline during the continuous crossflow RO filtration of the organic foulants.

Therefore, the purpose of this work was to develop a new fouling model capable of explaining water flux data over the entire filtration process, accounting for both adsorption and fouling layer formation. In this model, the fouling rate is not only affected by filtration time but also the initial membrane flux. The model was verified with experimental data obtained during constant pressure filtration of synthetic wastewater. The mechanism involved in the evolution of fouling was evaluated according to the model established.

2. Materials and methods

2.1. Wastewater, membrane and filtration experiment

The wastewater used here is the synthetic wastewater. The pH was adjusted to 7.0 by 1.0 M NaOH and 1.0 M HCl. The model organic foulants added into the distilled (DI) water include phenol, benzoic acid, 2-chlorophenol and 2-nitrophenol. All agents (AR) are purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The selected membrane for the study is the aromatic polyamide thin-film composite membrane CPA2 RO membrane provided by Nitto Denko Co., Ltd. (Osaka, Japan). Its permeability is $7.5 \, L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$.

All the experiments were conducted on a laboratory-scale crossflow test unit which consists of a membrane cell, high-pressure pump, electromagnetic mixer, feed reservoir and temperature control system. The membrane cell has a rectangular channel with dimensions of 11.6 cm length, 4.0 cm width and 0.3 cm height. The system was operated in a closed-loop mode and both permeate and retentate were recirculated into the feed reservoir. A new membrane specimen was used for each crossflow experiment. For the permeation procedure, the membrane was first compacted with DI water (foulant-free) at 10 bar for at least 12 h until the permeate flux stabilized. Then, the feed reservoir was filled with the feed solution instead of DI water. The temperature and pH of the feed solution were adjusted and maintained at the desired values. After the initial permeate flux and crossflow velocity were fixed at $21.0 \, \mu m \cdot s^{-1}$ and $9.8 \, cm \cdot s^{-1}$, respectively, fouling experiments were initiated. The permeate flux, the model foulant concentration in permeate and bulk was continuously monitored for the next 12 h. The amount of the foulants adsorbed on the membrane was calculated. The adsorption characteristics were described by Langmuir isotherms.

Nine sets of experiments were conducted and the experimental conditions were summarized in Table 1. The model monoaromatic compounds which are relatively high toxicity at low levels abound in the effluent released by the textile, pesticide, paper and petrochemical industries.

2.2. Characterization of the effluent and the membrane

The concentration of a single organic compound was analyzed with a high performance liquid chromatography (LC-10AVP Plus, SHIMADZU, Japan) equipped with an UV detector. Regression factor (R^2) obtained for calibrations within the experimental concentration range was above 0.999.

The attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy analyses were performed on a FT-IR Spectrophotometer (AVATAR 360, Nicolet, USA). The spectra measurements were conducted at 10 different locations, with each spectrum averaged from 64 scans. The membranes were vacuum dried at ambient temperature before the IR test.

Surface morphological features of the membranes were analyzed with a scanning electron microscopy (SEM) (FEI Quanta 200, Holland). The membrane samples were vacuum dried at ambient temperature before each analysis. All specimens were coated with a conductive sputtered gold layer.

Surface roughness was determined by atomic force microscopy (AFM) analysis (SPM-9500 J3, SHIMADZU, Japan), quantified by root mean square (RMS) roughness. RMS is the deviation of the peaks and valleys from the mean plane [23].

Contact angle measurements were performed with an automated contact angle goniometer (DSA100; KRÜSS GmbH, Germany). At least 12 contact angle measurements were performed and the highest and lowest values were discarded before taking the average.

3. Model for predicting permeate flux of RO membrane

Several studies [2,14] have demonstrated that membrane fouling during filtration of a solution containing organic compounds occurs primarily by adsorption of the organics on the membrane surface. Initially, the organics deposit onto the membrane surface, reducing the available area for membrane filtration. The initial deposit leads to the increase in the hydrophobicity of the membrane surface. The fouling monolayer is quickly formed on the membrane surface. Subsequent accumulation of the organics on the membrane surface due to convective deposition leads to a fouling layer which makes the hydrophobicity of the membrane surface further increasing. In addition, an increase in the hydraulic resistance is also caused by the fouling layer. This is exactly the phenomenon depicted in the classical cake filtration model. Bacchin et al. [24] described the characteristics of foulants at different phases: 1) glass phase where particles are so stable in the feed solution that particles being adsorbed onto the membrane surface (monolayer); 2) solid phase when particles are so concentrated that particles aggregating on the membrane surface (multilayer). Based on phase transition

Table 1
The information of each fouling experiment with the model compounds under the condition of 5 mg·L^{-1} and 25 °C.

Experiment set (EX)	Model	pH
1	Benzoic acid	3.0
2	Phenol	7.0
3	Benzoic acid	7.0
4	2-Chlorophenol	7.0
5	2-Nitrophenol	7.0
6	Benzoic acid	9.0
7	Phenol	9.0
8	2-Chlorophenol	9.0
9	2-Nitrophenol	9.0