



Effects of macro-porous anion exchange and coagulation treatment on organic removal and membrane fouling reduction in water treatment



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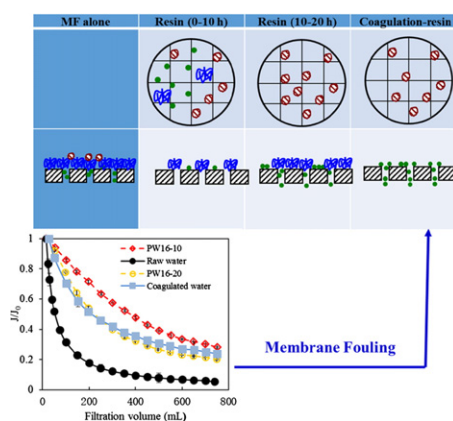
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HIGHLIGHTS

- Macroporous anion resin was used to treat NOM in low pressure membrane.
- Macroporous anion resin treatment alleviates membrane fouling to some extent.
- Integrated PAC and resin pretreatment were efficient in membrane fouling control.

GRAPHICAL ABSTRACT



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ABSTRACT

Macro-porous anion exchange, coagulation and their combination were used as pretreatment for microfiltration, and their effects on organic removal and membrane fouling reduction were evaluated. The experimental results showed that resin was effective in removing organics of medium and small molecular weight (MW), especially those of medium MW of UV absorbance, but was ineffective in removing organics with large MW. Using resin alone as a pretreatment removed organics effectively but was limited in its reduction of membrane fouling. With the combination of coagulation and resin as a pretreatment for microfiltration, not only were organics removed effectively, but membrane fouling was also reduced. Analysis of membrane surface with scanning electron microscopy (SEM), atomic force microscopy (AFM) and combined results of behaviors of MW distribution and flux indicated that biopolymer plays a key role in membrane fouling, and coagulation could remove this part of organics. Integrated coagulation and resin pretreatment by filtration columns were suggested for use in surface water prior to membrane filtration.

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1. Introduction

The formation of disinfection byproducts (DBPs), such as trihalo-methanes (THMs) and haloacetic acids (HAAs), in drinking water has been a major problem for drinking water quality and raises considerable public health concerns. The main factors affecting the formation of DBPs

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are the DBP precursor types and concentrations [1]. It has been demonstrated that natural organic matter (NOM), which is mainly composed of humic substances, is generally regarded as the main DBP precursor in surface waters [2,3]. Numerous studies have been conducted on NOM to determine its characteristics and DBP yield during water disinfection [4]. Therefore, effectively increasing the removal of NOM is very important for the reduction of DBPs during water treatment.

Conventional water treatment processes that target NOM removal include coagulation, oxidation, and adsorption. However, it has been found that coagulation can remove a portion of NOM (40–70% of total organic carbon (TOC)), particularly macromolecular weight organics, but that smaller molecules are less effectively removed [5]. Furthermore, although oxidation by chlorine, ozone, potassium permanganate, and potassium ferrate has been shown to be effective for deodorization, decolorization, and micro-pollutant removal, oxidants can still react quickly with NOM, resulting in the formation of harmful by-products [6]. While an adsorption treatment conducted by Iriarte-Velaseo et al. found that even at long contact times and low NOM concentrations, the use of powdered activated carbon for treatment still led to the potential formation of THMs [7].

Membrane filtration technology is a promising alternative to conventional water treatment processes for the removal of NOM. Two serious obstacles to wider application of membrane filtration are membrane fouling and inefficiency regarding the removal of low-molecular weight organics [8]. Appropriate pretreatment of raw water is needed for the production of drinking water from surface waters. Studies showed that 60–70% of full-scale plants use low pressure membranes with pretreatment [9–11]. However, in some cases, pretreatment has not effectively removed enough of the fractions of organic matter that are responsible for membrane blocking [12].

Because most of the NOM in water has ionic characteristics, ion-exchange processes have gained popularity. It has been demonstrated that ion exchange, alone or in combination with other processes, holds promise for removing a broad spectrum of DBP precursors [13]. Bolto et al. found that anion exchangers of open structure and high water content were the best resin types for efficient removal of any charged, aquatic NOM [14]. Other studies on the adsorption of various NOM fractions on styrene resins indicated that more highly charged smaller ions were preferred, with size effects being predominant [15]. Recently, ion-exchange processes based on the use of a new magnetic ion exchange resin (MIEX resin) has received considerable attention [16–20]. MIEX resin is an anionic resin consisting of magnetic iron oxide particles coated by polymers with positively charged quaternary amine functional groups. Huang et al. investigated the effects of MIEX pretreatment on low pressure membrane filtration of natural surface waters and found that MIEX pretreatment was effective for DOC removals but less effective in controlling short-term membrane fouling or removing viruses [21]. Mergen et al. reported that the removal of NOM using magnetic resins was water specific; increasing water hydrophobicity resulted in reduced dissolved organic carbon (DOC) removal [22]. It was also demonstrated that MIEX pretreatment can decrease the hydraulically irreversible fouling of a microfiltration (MF) membrane, resulting in less frequent chemical cleaning, which may be beneficial to long-term operation [23]. Despite these important findings, MIEX still has some shortcomings, such as low resin mechanical strength, high price, difficult recovery and the need for further investigation regarding membrane fouling, which limit any further large-scale applications [24].

Considering that the use of ion-exchange processes may be an effective way of increasing the separation and transport properties of membrane filtration, there is a strong need for further research on the use of ion exchange resins in water treatment, particularly with lower cost resins. As is commonly known, an effective way to reduce resin cost in the application is through resin recycling and regeneration. Compared with MIEX and using the fully mixing method for the purpose of aggregation and separated regeneration, resins used in filtration columns

were more conducive for online regeneration; moreover, the resins used during the experiment will not be easily lost. However, there is little information in the literature on the impact of membrane fouling during filtration using resins in filtration columns. Therefore, the objectives of this work were to evaluate the effects of resin pretreatment on organic removals and MF membrane fouling using filtration columns. Macroporous anion exchange resins were selected in this research because resins with macroporous structure were reported to remove more NOM than gel-type resins [14], and there has been little research conducted on membrane fouling using macroporous ion exchange resin treatment; coagulation followed by macroporous anion resin treatment was also conducted to compare MF fouling behaviors.

2. Materials and methods

2.1. Characteristics of the granular macro-porous anion exchange resins

The resins used in this study were obtained from Dow Company, US. The two types of resin, AMBERLITE™ PW16 and AMBERLITE™ PWA9 (PW16 and PWA9), were selected because both are styrene macroporous resins, and the functional groups are quaternary ammonium. The characteristics of the resins are shown in Table 1. As detailed in Table 1, PWA9 are white, opaque beads with sizes and water contents that are lower than PW16; however, the total exchange capacity and shipping weight are comparatively larger.

Because the pretreatment and activation process were conducted by the resin manufacturer, no extra pretreatment was needed before the experiment other than washing with Milli-Q water.

2.2. Experimental setup

Resin dynamic adsorption experiments were conducted on filtration columns. A schematic diagram of the experimental setup is shown in Fig. 1. The setup consisted of three parts, i.e., the influent section, the effluent section and the adsorption column section. The filtration column was fixed on a formwork unit. The inner diameter of the column was 2.3 cm, and the outer diameter was 2.5 cm. The material of the column was plexiglass, and the upper part of the column was fat belly shaped to buffer the flow differences between the two peristaltic pumps at the influent and effluent sections. Before fixing, the filtration column was filled, and a certain amount of glass beads was used as a supporting layer before filling the resin layer. After the filling was finished, a certain amount of Milli-Q water was used to rinse the columns so that the impurities can be removed. Additionally, the filter column bubbles were

Table 1
Characteristics of the resins used.

Resin	PW16	PWA9
Type	Macroporous	
Skeleton structure	Styrene-divinylbenzene cross linked copolymer	
Functional groups	Quaternary ammonium groups	
Ionic form	Cl ⁻ , OH ⁻	
Physical form	White opaque beads	
Wetting pore size	100–500 nm	
Total exchange capacity (eq/L)	≥0.7	≥0.8
Water content (%)	70–82	66–72
Particle size (mm)		
Screen grading	0.42–1.2 (below 0.42 < 5%;	0.3–1.18
Fines content	above 1.2 < 3%)	(below 0.355 < 1%)
Shipping weight (kg/m ³)	689	700
Maximum operation temperature (°C)	60 (OH ⁻), 100 (Cl ⁻)	40
Swelling index	17%	25%
Void volume	25%	29%
Maximum adsorbing capacity (mg/mL)	DOC 1.0328	0.9363
(cm ⁻¹ /mL)	UV 0.0124	0.0112

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