Contribution of different effluent organic matter fractions to membrane fouling in ultrafiltration of treated domestic wastewater
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ABSTRACT

In the present work, effluent organic matter (EfOM) in treated domestic wastewater was separated into hydrophobic neutrals, colloids, hydrophobic acids, transphilic acids and neutrals and hydrophilic compounds. Their contribution to dissolved organic carbon (DOC) was identified. Further characterization was conducted with respect to molecular size and hydrophobicity. Each isolated fraction was dosed into salt solution to identify its fouling potential in ultrafiltration (UF) using a hydrophilized polyethersulfone membrane. The results show that each kind of EfOM leads to irreversible fouling. At similar delivered DOC load to the membrane, colloids present the highest fouling effect in terms of both reversible and irreversible fouling. The hydrophobic organics show much lower reversibility than the biopolymers present. However, as they are of much smaller size than the membrane pore opening, they cannot lead to such severe fouling as biopolymers do. In all of the isolated fractions, hydrophilics show the lowest fouling potential. For either colloids or hydrophobic substances, increasing their content in feedwater leads to worse fouling. The co-effect between biopolymers and other EfOM fractions has also been identified as one of the mechanisms contributing to UF fouling in filtering EfOM-containing waters.

INTRODUCTION

In wastewater reclamation, ultrafiltration (UF) membranes have been widely used to meet the increasingly strict requirements for improving quality of water for reuse. Membrane fouling is an important limitation to the economic operation of UF. With respect to treated wastewater, membrane fouling refers to the hydraulically irreversible deposition of effluent organic matter (EfOM) on the membrane surface or in membrane pores. To control fouling development, understanding of the properties of EfOM and its contribution to fouling is necessary.

Previous studies showed that biopolymers – the hydrophilic macromolecular proteins and polysaccharides (Huber et al. 2011) in EfOM – are major organic foulants in UF (Haberkamp et al. 2008; Zheng et al. 2010). In contrast, Kim & Dempsey (2008) demonstrated that hydrophobic and hydrophilic acids in EfOM contribute much more to fouling than do colloids. By comparing fouling effect and biopolymer content of different waters, Gray et al. (2008) and Henderson et al. (2011) found that it was not the content of biopolymers but certain organics (especially protein-like substances) that play a crucial role in fouling phenomena. Xiao et al. (2009) verified that organics with stronger hydrophobic character (e.g. proteins, humic substances) adsorb onto the membrane surfaces more readily than hydrophilic substances (polysaccharides) do and form conditioning fouling. The interplay between hydrophobic and hydrophilic organic substances is further considered as an important mechanism determining the severity of irreversible fouling (Jermann et al. 2007). These conflicting results indicate that it is questionable if biopolymers themselves can lead
to irreversible fouling, or if it is only a result of co-effect with other fractions. To answer this question, the present study focuses on isolating and characterizing EfOM fractions and identifying their fouling effect in UF.

It should be mentioned that in fouling phenomena, the character of the membranes (such as hydrophobicity, pore size, roughness, etc.; Gray et al. 2007) and solution chemistry (such as pH, calcium concentration, etc.; Gray et al. 2008) influence the fouling effect as well. To stress the influence of the character of EfOM material, the present work focuses on using one kind of commonly used polyethersulfone (PES) membrane and well-defined water solution.

MATERIALS AND METHODS

EfOM isolation and characterization

EfOM isolation and extraction was conducted according to the methods described by Leenheer (2009) with minor modifications. In brief (Figure 1), secondary effluent (SE) from the wastewater treatment plant, Jeddah (Kingdom of Saudi Arabia), after 1.2 μm pre-filtration was pumped through XAD8 resin to separate hydrophobic neutrals (HPO neutrals). The effluent was acidized and evaporated under vacuum to obtain concentrated EfOM solution (100-fold concentration). Using a dialysis bag (12 kDa, Spectra/Por®, Spectrum Labs) soaked in acid (HCl, pH 2) colloids and other fractions were separated from each other. The dialysis effluent was further transferred into XAD8 and XAD4 resins used in series to isolate hydrophobic acids (HPO acids) and transphilic acid and neutrals (TPI). Hereafter, hydrophilic compounds (HPI) were collected as the fifth isolated fraction. EfOMs adsorbed on XAD8 and XAD4 were eluted using acetonitrile mixed with pure water (acetonitrile/water: 75%/25% (volume)) and further concentrated and freeze-dried. Colloids were also freeze-dried after removing salts and silica for further utilization. The isolated fractions were characterized using Fourier transform infrared spectroscopy, solid state 13C-nuclear magnetic resonance and elemental analysis. The size distribution of these organics was determined after re-solubilization using liquid chromatography with online organic carbon detector (LC-OCD) (Huber et al. 2011).

UF membrane, module and filtration system

Capillary UF membranes (hydrophilized PES, molecular weight cut-off 150 kDa) are used to filter different waters. Mini-membrane modules were manufactured in the laboratory. The manufacturing process is similar to that described by Nguyen et al. (2011). In the present work, each module contains six capillaries with an effective filtration area of around 0.006 m². The module is in dead-end operation with filtration and backwash flux around 100 L/(m² h). Filtration direction is inside-out. The membrane system was constructed with automatic backwash using UF permeate and control to continuously monitor and record the trans-membrane pressure. For each experiment a new membrane module was used.

Water source and feedwater to UF

Freeze-dried EfOM organics were weighed and dosed back into salt solution which has similar Ca²⁺ (100 mg/L) and Na⁺ (800 mg/L) concentration and conductivity (4.5 mS/cm) as analysed in the Jeddah SE. The dissolved organic carbon (DOC) concentration of each synthetic water sample was controlled at around 1 mg/L and pH was controlled at 7.8 ± 0.2 using NaOH.

To test the co-effect of colloids with other fractions, 0.2 mg/L isolated biopolymers (in terms of DOC) was dosed into: (i) UF permeate of SE and (ii) reconstituted UF permeate according to their DOC content in treated wastewater (Shimadzu TOC-VCSH). The fouling development
RESULTS AND DISCUSSION

Primary characterization of EfOMs

According to DOC measurement during EfOM isolation processes, the contribution of different fractions to the total DOC of Jeddah SE is shown in Figure 2. The most abundant organics in the treated wastewater are HPO acids isolated using XAD8 resin. More than one third of DOC is from this fraction. Other main contributors are hydrophilic substances (HPI) and transphilic neutrals and acids (TPI), which contribute 28 and 21% of DOC, respectively. The HPO neutrals and hydrophilic colloids are minor contributors to the total DOC. With respect to the relative elemental content in colloids, HPO acids and TPI (Table 1), it is evident that around 50% of the elements in these organics are organic carbon. They present similar hydrogen content but show a significant difference in organic nitrogen amount.

The size distribution of SE and EfOM fractions is shown in Figure 3. Biopolymers in SE are mostly in the colloidal size range (elution time 25–35 min). Other fractions elute later than colloids, indicating their comparatively smaller sizes. Using LC-OCD data, the comparative hydrophobicity of organics can also be reflected by calculating the ratio between chromatogram DOC (C-DOC) and by-pass DOC (B-DOC) because the difference between them is regarded as a result of hydrophobic retention within the size exclusion column (Huber et al. 2011). Table 1 shows that HPI and colloids are of the lowest hydrophobicity and HPO organics the highest, which is in agreement with the general description of their hydrophobic character (Leenheer 2009). As a mixture of these organics, SE shows medium hydrophobicity within the range presented (Table 1). From the results it is also evident that using the currently applied size exclusion column (HW50S) some hydrophobic materials in water cannot elute through the column and appear in its corresponding LC-OCD chromatogram. For instance, only 13% of the injected HPO neutrals can be recovered in its chromatogram measurement. This phenomenon indicates that LC-OCD technology needs further improvement with respect to this problem.

Fouling effect of different EfOM fractions

The fouling effect of isolated EfOM fractions in UF using this PES membrane is shown in Figure 4. It is evident that each...
fraction leads to irreversible flux reduction. Compared to the other organics, colloids lead to the most significant flux decline during each filtration cycle (Figure 4(b)). Although the reduced flux can be partly recovered by backwash, after eight filtration cycles the permeability of the fouled membrane is only around 50% of its original value (after backwashing). This is much lower than that caused by filtering other organic solutions after 10 cycles. The result indicates clearly that under similar DOC load colloids themselves lead to much higher irreversible fouling than other fractions do.

Although filtering XAD8 and XAD4 separated EfOM leads to much less flux decline compared to colloids, permeability loss could not be recovered during backwash demonstrating mainly irreversible fouling properties (Figure 4(a), (c), (d)). Considering that these organics are of higher hydrophobicity than colloids (Table 1) but with a smaller size (Figure 3), the humic material exerts high adsorption affinity with the membrane polymer (on surface and into the pores).

**Influence of concentration on fouling development**

The influence of biopolymer concentration on fouling development was investigated. It can be seen that an increase of colloid concentration from 0.2 to 0.5 mg/L (in terms of DOC) leads to a permeability reduction from 25 to 40% after 10 filtration cycles and backwashing. Combined with the permeability decline presented in Figure 4(b), it is evident that increasing biopolymer concentration in feed water results in more irreversible fouling although these organics are partly removed during backwash. Increasing the concentration of humic-like substances (HPO acids) leads also to more irreversible flux decline. The LC-OCD chromatograms of the HPO acids, its UF permeate and backwash water (backwash performed with permeate water) are very similar (data not shown), indicating that UF cannot remove these organics much and that accumulated material on the membrane surface or in membrane pores is also difficult to remove by backwashing (similar phenomena occur in filtering other EfOM fractions; data not shown).

**Co-effect of EfOM fractions**

The co-effect between colloids and other EfOM fractions in fouling is further demonstrated by dosing colloids back into UF permeate, reconstituted UF permeate (to form reconstituted SE) and salt solution. It is evident that performing UF of the UF permeate leads to some flux decline (data not shown). This result confirms that small molecular weight EfOM molecules adsorb in the pores leading to internal pore restriction. Dosing colloids into UF permeate or using the reconstituted SE can achieve a similar normalized flux decline, which is higher than that using colloids dissolved in salt solution. As the three samples have the same colloid content (0.2 mg/L in terms of DOC), the main difference lies in the presence of other EfOM fractions. This indicates that the co-effect between colloids and other EfOM fractions enhances the overall fouling effect which has been identified in previous studies (e.g. Gray et al. 2008, 2011). In addition, the similar fouling effect dosing colloids into UF permeate or reconstituted one implies that both samples are of similar character.

Comparison of flux decline using reconstituted and real SE (after 1.2 μm pre-filtration, biopolymer concentration 0.18 mg C/L) shows that both samples present similar normalized flux decline after backwashing when the experiments were finished (data not shown). It seems that the foulants in both samples are of similar fouling potential forming irreversible fouling. However, the comparison
shows also that during each filtration cycle the performance of the UF is different. Filtering SE leads to a much more significant flux decline than treating the reconstituted water, but the lost permeability is more reversible. Comparing flux decline in UF of SE and reconstituted SE with isolated biopolymers mixed with UF permeate leads to the same impression. These results imply that certain substances might be lost during the isolation of colloids from water samples. Noting that during the separation process, silica is removed using hydrofluoric acid, Song et al. (2010) reported that silica plays an important role in connecting biopolymers in UF or microfiltration of treated wastewater. Thus, re-evaluation of the separation process and testing the effect of silica in biopolymer fouling is necessary and is being undertaken in our group.

CONCLUSIONS

The present work investigates separation and characterization of EfOM fractions and explores the fouling effect of those fractions using a hydrophilized PES UF membrane.
According to laboratory scale results, the following conclusions can be made.

1. EfOM can be separated into hydrophobic neutrals, colloids, hydrophobic acids, transphilic acids and neutrals and hydrophilic compounds. In treated domestic wastewater the major DOC contributors are the latter three fractions which contribute to almost 90% of the DOC in Jeddah SE. Colloids constitute several percentage of the DOC but are of the largest molecular size compared to the other isolated fractions.

2. All of the separated organics can lead to irreversible attachment with this kind of membrane. The fouling potential of different fractions is different. At a similar DOC load, colloids lead to much more significant fouling than any other fraction does. Although colloidal fouling is partly reversible, backwash can only remove a portion of the adhered biopolymers. Due to their smaller size, XAD8 and XAD4 isolated fractions can easily pass through membrane pores and cause slight flux decline. However, the fouling produced is highly irreversible, which is consistent with their high hydrophobicity measured using LC-OCD. In all of the isolated fractions, the hydrophilic acids and neutrals show the lowest fouling potential.

3. Both concentration and interaction with other EfOM fractions influence the fouling effect of colloids. Increasing biopolymer concentration in feedwater leads to more severe fouling. The presence of other EfOM fractions also enhances biopolymer fouling to some extent. Significant reduction of membrane fouling can be achieved by removing biopolymers from SE, indicating the core role of these organics in UF membrane fouling.

4. During UF of real and reconstituted SE (with similar DOC content and distribution), similar irreversible fouling is formed under similar operating conditions. This demonstrates that reconstitution of separated EfOM fractions into water can reflect the fouling potential of the corresponding raw water in terms of interaction with the membrane. Nevertheless, the flux decline during each filtration cycle is different. This indicates the loss of certain constituents (e.g. silica) during the isolation of colloids. The re-evaluation of the isolation procedure and investigation of the effect of silica in biopolymer fouling is in progress.

REFERENCES


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