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Fouling potential and cleaning characteristics of PVC ultrafiltration membrane during ultrafiltration of hydrophilic dissolved organic matter

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ABSTRACT

The hydrophilic fraction of dissolved organic matter was thought as the important foulant during drinking water treatment by membranes recently. Citric acid, polysucrose and oligopeptide were selected to represent the hydrophilic acid, neutral and base to investigate the fouling characteristics on a (modified polyvinylchloride) ultrafiltration membrane. Four kinds of cleaning methods, i.e., flushing, backwashing, flushing and backwashing and chemical cleaning with 0.5% NaOH were performed for the three hydrophilic dissolved organic matter fouled membranes to deal with the fouling mechanisms of the polyvinylchloride ultrafiltration membrane. Results showed that the citric acid may react with the membrane in pores to change the membrane properties so that the flux did not recover at all. The membrane fouling by polysucrose was mostly reversible due to the weak interaction between hydroxyl on polysucrose and carboxyl on membrane. The amino and carboxyl on the oligopeptide also reacted with the carboxyl on the membrane surface to form the stronger hydrogen bond to make the permeate flux partly recover after NaOH chemical cleaning. During ultrafiltration of the mixed hydrophilic dissolved organic matter solution composed of the three compounds, the membrane performances were always close to one of the three compounds, of which membrane flux was lowest.

Keywords: Ultrafiltration; Dissolved organic matter; Hydrophilic; Membrane fouling; Cleaning

1. Introduction

In drinking water treatment, membrane technology is increasingly gaining more and more attention, but organic substances naturally present in surface water, known as natural organic matter (NOM), have been widely reported as the primary foulant during ultrafiltration (UF) / microfiltration (MF) membranes filtration of surface water.

Many researchers have suggested that the humic substances fraction of NOM is a major foulant which controls the rate and extent of fouling [1–3]. However, recent studies have revealed that the hydrophilic fraction which is primarily composed of polysaccharide-like substances (amino sugar), polysaccharide groups and proteins, were found to play a significant role in membrane fouling. Fan

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et al. [4] identified potential foulants in order of hydrophilic neutrals > hydrophobic acids > transphilic acids. Lin et al. [5] and Amy and Cho [6] indicated that major foulant or primary foulant potential was attributed by the hydrophilic fraction within the bulk NOM. In particular, researchers strongly stated the dominant foulant as "hydrophilic NOM" [6]; "polysaccharide group such as chitin and cellulose" [7]; "macromolecular compounds and/or colloidal form in the hydrophilic NOM that is contributed by polysaccharides and/or proteins" [8]; "alcoholic compounds originated from polysaccharide-like substances" [9]; "hydrophilic NOM polysaccharides were found to be a dominant foulant" [6]; "the low aromatic hydrophilic neutral compounds were the main determinant of the rate and extent of flux decline" [4]. In fact, the composition of each hydrophilic NOM fraction varies relatively with the source water due to the heterogeneity of NOM. Besides that, the complexity of NOM content as well as the membrane characteristics has further contributed to lack of understanding of mechanisms that was primarily responsible in controlling the membrane permeability and the rejection of NOM solutes.

NOM is a mix of particulate and soluble components of both inorganic and organic origin that vary from one source to another [10]. Nevertheless among NOM foulant, dissolved organic matter (DOM) is found to have the most detrimental effect on membrane performance as it can result in irreversible fouling during surface water filtration. This inevitable phenomenon occurs through detrimental DOM interaction with the membrane, which eventually results in surface deposition of DOM either within the membrane pore matrix or into the membrane pores.

Interestingly, DOM from different origins show similar subunits after pyrolysis [11], with fulvic acid, hydrocarbons/tannins, aromatic amines, polyuronic acids, sugars, peptides/amino acids identified in hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral, and hydrophilic base fractions, respectively [12], indicating the universal presence of these functionalities in the respective DOM fractions.

In this study, citric acid, polysucrose and oligopeptide were used as model hydrophilic DOM compounds to investigate the fouling of a modified polyvinylchloride (PVC) UF membrane by the hydrophilic DOM of different molecular characteristics and cleaning efficiencies for the three hydrophilic DOM fouled UF membranes by flushing, backwashing, flushing and backwashing and NaOH cleaning methods. The fouling mechanisms on ultrafiltration of hydrophilic DOM were then revealed.

2. Materials and methods

2.1. Hydrophilic dissolved organic matter

Citric acid (Molecule weight (MW) 192 Da) (Tianjin Guangfu Fine Chemical Engineering Institute), polysucrose (MW 70,000 Da) (Tianjin Juhe Science & Trade Co. Ltd.) and oligopeptide (MW 200–700 Da) (Zhongshi Duqing (Shandong) Biotech Co., Ltd.) were used as model DOM to represent hydrophilic acid, neutral and base DOM compounds, respectively. It is noted that although the model compounds are different in MW, their MWs are all smaller than the molecular weight cutoff (MWCO) of the UF membrane studied. The fouling behavior of each model DOM compound was evaluated separately at a feed concentration of about 5 mg total organic carbon (TOC)/L in deionized water, which pH value is respectively 6, 7 and 7, shown in Table 1. A mixed hydrophilic DOM solution (about 5 mg TOC/L) composed of equal amount of citric acid, polysucrose and oligopeptide in deionized water was also prepared and evaluated for fouling potential.

Table 1
Characteristics of model hydrophilic DOM compounds

Model compound	Represented fractions	Functional groups	Feed pH
Citric acid	Hydrophilic acid	–COOH	6
Polysucrose	Hydrophilic neutral	–OH	7
Oligopeptide	Hydrophilic base	$–NH_2$	7

2.2. UF membrane and membrane module

Modified polyvinyl chloride (PVC) ultrafiltration hollow fibers with nominal MWCO of 80,000 Da and internal diameter of 0.9 mm and outer diameter of 1.4 mm were kindly provided by Litree Company (Hainan, China). Membrane modules consisting of 6 UF fibers with a length of 300 mm each were made in the laboratory. Membrane modules for the fouling/cleaning experiments were first cleaned with deionized water to remove the wetting agent, and then stored in deionized water with water replaced regularly. Membrane samples used for Fourier Transform Infrared Spectroscopy (FTIR) measurement were stored dry. All membrane modules were rinsed thoroughly with deionized water prior to use.

2.3. Bench-scale fouling and cleaning experiments

Fouling and cleaning experiments were conducted in a bench-scale dead-end filtration system with the concentrate line closed, shown schematically in Fig. 1. The filtration unit comprises a feed tank, a peristaltic pump, a UF membrane module and a permeate tank, a flushing tank, a backwashing tank. The permeate flux was determined every 5 min by collecting the permeate

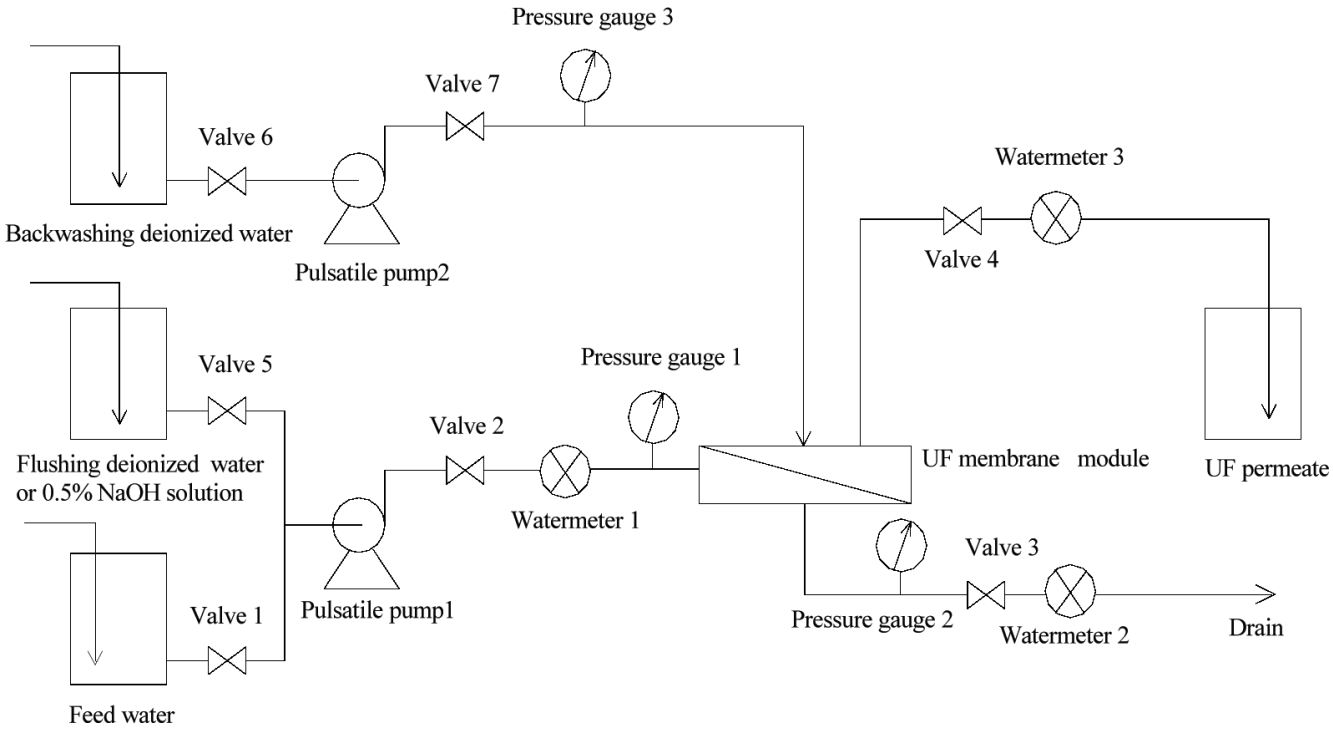

Fig. 1. Schematic of the membrane filtration system, operated in a dead-end mode with the concentrate line closed in all experiments. The fouled membrane fibers were cleaned by four cleaning methods (flushing, backwashing, flushing and backwashing, NaOH chemical cleaning).

water for 30 s and measuring the permeate volume. A new membrane module was used for each experiment.

Every filtration experiment consists of 3 fouling–cleaning cycles. In the fouling stage of each cycle, a DOM solution was filtered at a constant trans-membrane pressure (TMP) of 0.06 MPa for 30 min. Permeate samples were taken every 5 min and their TOC concentrations were determined using a TOC analyzer (Shimadzu Corporation, Kyoto, Japan, TOC-$V_{CPN(H)}$). At the end of the fouling stage, one fouled membrane fiber was cut from the membrane module for further characterization and the two roots of the cut membrane fiber were sealed. The rest of the fouled membrane fibers were cleaned by one of four different methods: hydraulic flushing (1.5 min), backwashing (0.2 MPa, 3 min), flushing and backwashing (the flushing cleaning was performed for 15 s to make the water filled in the membrane fibers, then backwashing was done in 0.2 MPa pressure, and flushing and backwashing were simultaneously run for 2 min 45 s) [13], and chemical cleaning with 0.5% NaOH for 30 min with the cleaning solution recirculated. Every cleaning method was tested in a different experiment. After each cleaning, a cleaned membrane fiber was cut from the membrane module for further characterization and the two roots of the cut membrane fiber were sealed. The permeate flux after cutting was also determined every 5 min by collecting the permeate water for 30 s and measuring the permeate volume, but the compared flux was calculated by multiplying the determined value by the coefficient of "6/(6-cut membrane fibers)". The fouling-cleaning cycle was then resumed with the remaining to assess the membrane performance after repeated fouling and cleaning.

2.4. Measurement and characterization

FTIR (Bruke Com. Ltd., Tensor 27) was used to characterize the functional groups of the virgin UF membrane, the DOM, the DOM fouled UF membranes.

3. Results and discussion

3.1. The functional groups of hydrophilic DOM and the surface properties of PVC ultrafiltration membrane

The FTIR spectra of each hydrophilic DOM (Fig. 2), the virgin PVC membrane (Fig. 3 (1)) and the DOM fouled membranes (Fig. 3 (2)–(4)) were compared to elucidate the interactions between each DOM and the membrane.

The FTIR spectra of the three hydrophilic DOM model compounds confirm the major functional groups in each compound shown in Table 1.

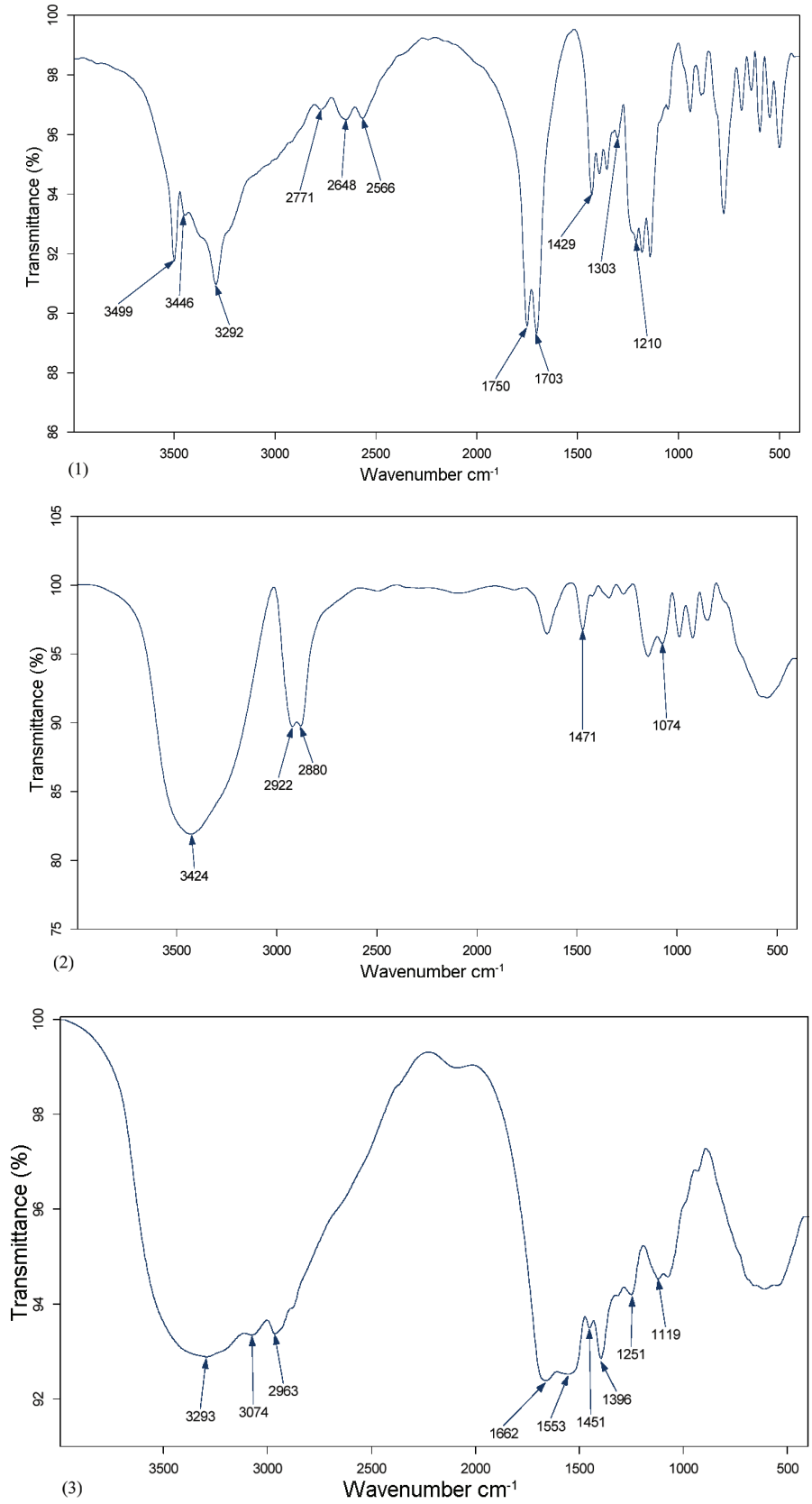

Fig. 2. The FTIR spectra of three hydrophilic DOM characterized by FTIR spectrometer (Bruke Com. Ltd., Tensor 27) in the transmission mode. (1) citric acid. (2) polysucrose. (3) oligopeptide.

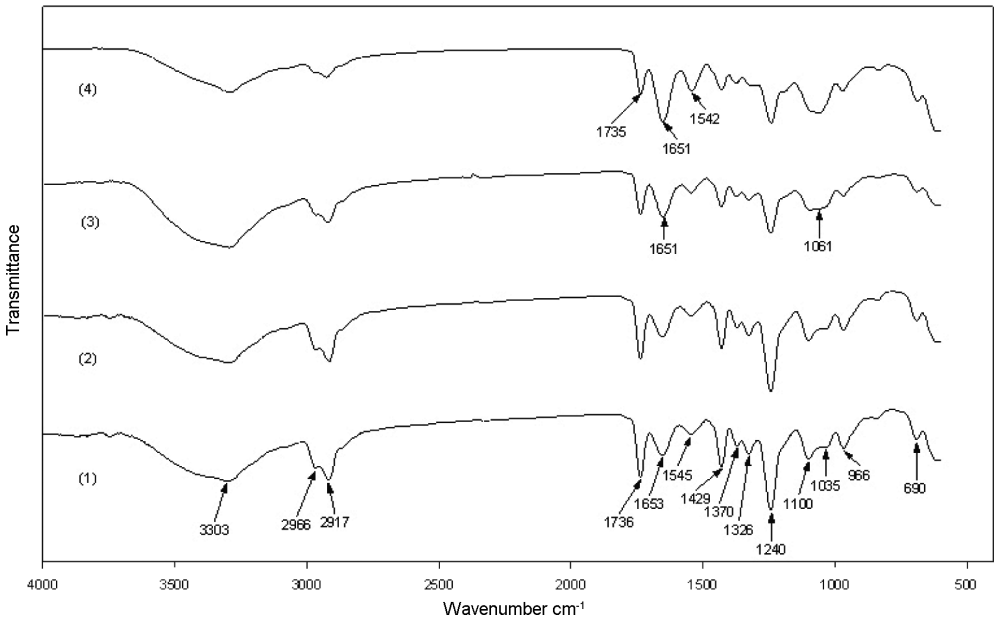

Fig. 3. The FTIR spectra of PVC UF membranes characterized by FTIR spectrometer (Bruke Com. Ltd., Tensor 27) in the transmission mode: (1) virgin membrane; (2) citric acid fouled membrane; (3) polysucrose fouled membrane; (4) oligopeptide fouled membrane.

In addition to the peaks corresponding to PVC, the presence of –COOH in the virgin PVC membrane was evident as shown by the peaks at 1736 cm^{-1} (C=O stretch), 1240 cm^{-1} (C–OH vibration), 1370 cm^{-1} (COO– symmetric vibration), 1326 cm^{-1} and 966 cm^{-1} (in-plane and out of plane bending of C–OH), and 3303 cm^{-1} (–OH from carboxylic acid [14,15]). The peak at 1653 cm^{-1} indicates the presence of the intermolecular OH.

3.2. The fouling and cleaning characteristics on ultrafiltration of hydrophilic DOM

Fouling experiments were conducted using each hydrophilic model DOM compound. The fouling potential of each compound was evaluated based on the membrane permeate flux decline rate and the DOM rejection showed in Fig. 4. For the fouled membrane by each hydrophilic DOM, four different cleaning methods were used to investigate the interaction of the hydrophilic DOM and the membrane based on the recovered permeate flux and DOM rejection after cleaning shown in Fig. 5, and the FTIR spectra of the each hydrophilic DOM fouled membrane surfaces shown in Fig. 3 also presented the interaction of the DOM and membrane.

Fig. 4 (1) shows that oligopeptide and citric acid only caused slight decline in membrane flux, approximately 12–15% of the initial flux. In contrast, severe membrane fouling was observed in filtration of polysucrose, with flux decreasing by 45% of the initial flux. These results indicated that hydrophilic neutral DOM was the primary foulant responsible for membrane flux decline in surface water filtration. In addition, the polysucrose rejection rate was observed a little higher than the other two DOM. Although polysucrose has the highest MW, close to the MWCO of the PVC membrane, it is a linear macromolecule. The low rejection of polysucrose observed indicates that polysucrose molecules can penetrate the membrane by orienting the chain structure of the molecule along the membrane pores.

The FTIR spectrum of the polysucrose fouled membrane surface shown in Fig. 3 (3) was changed from the original membrane presented in Fig. 3 (1), the peak strength at 1 651 cm^{-1} was apparently enhanced, due to the hydrogen bond formed by the –OH on polysucrose and –COOH on membrane. Fig. 3 (2) shows that the FTIR spectrum of the citric acid fouled membrane surface was same to the virgin membrane, indicating that the membrane surface was not fouled. However, the citric acid rejection on membrane was over zero, possibly the rejected citric acid remained in the membrane pore. Four cleaning methods did not make the fouled membrane permeate flux recover, possibly the interaction of citric acid and the membrane pore was very strong. Thus the rejected citric acid was accumulated in the membrane pore, the citric acid rejection should be increased, but actually it was stable, possibly other filtration mechanism existed during ultrafiltration of citric acid, except for the membrane pore sieving and adsorption mechanism. Though the MW of oligopeptide and citric acid were close, the FTIR spectrum of the oligopeptide fouled membrane

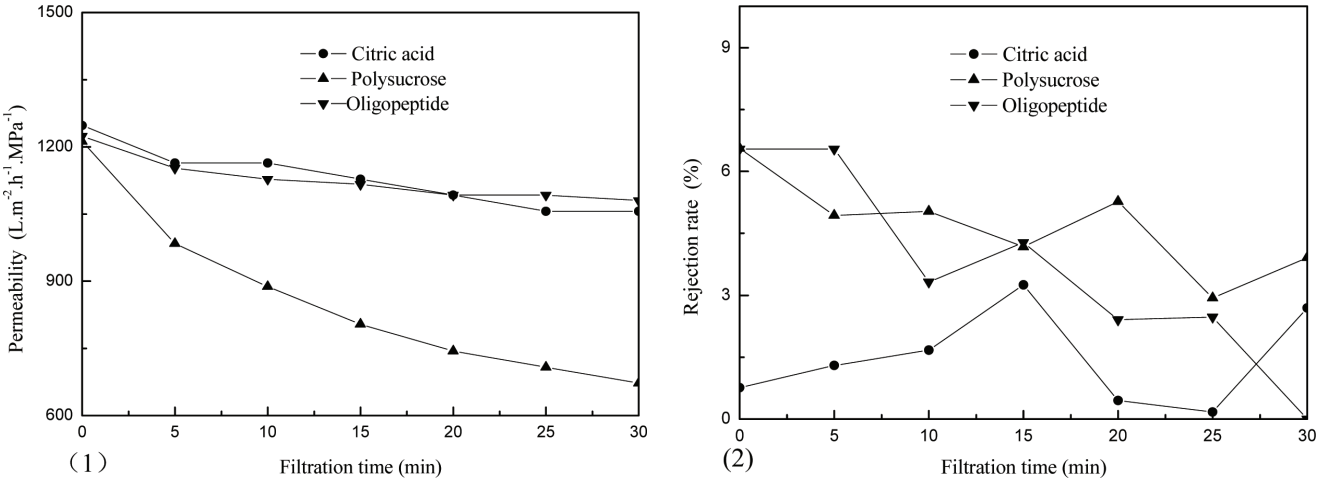

Fig. 4. Membrane permeate flux (1) and hydrophilic DOM rejection (2) during ultrafiltration at a constant trans-membrane pressure (TMP) of 0.06 MPa for 30 min.

surface shown in Fig. 3 (4) was different from the virgin membrane, the peak strength at 1 651 cm^{-1} was apparently enhanced, indicating that the $–NH_2$ and –COOH on oligopeptide formed hydrogen bond with the –COOH on the membrane. It revealed that the compound structure was also important for ultrafiltration process, except for the molecular size.

3.3. Influences of acid/neutral/base properties of hydrophilic DOM on UF filtration characteristics

As the hydrophilic acid, the citric acid possibly interacted with the membrane in pores so strongly that hydraulic cleaning and NaOH chemical cleaning did not make the citric acid fouled membrane performance recover at all. The further research on citric acid filtration through PVC membrane should be done.

For the hydrophilic neutral, the –OH on the polysucrose and the –COOH on the PVC membrane formed the hydrogen bond, which was not so strong that the physical cleaning methods, i.e., the flushing, backwashing, flushing and backwashing, made the polysucrose fouled membrane recover the fluxes in first cleaning cycle by 87%, 97% and 99% of initial flux, respectively.

As shown in Fig.3 (4), the $–NH_2$ and –COOH on the oligopeptide formed the hydrogen bond with the –COOH on the PVC membrane, and the hydrogen bond interaction was so strong that the flushing, backwashing, flushing&backwashing hydraulic cleanings did not recover the permeate flux of the oligopeptide fouled membrane, presented in Fig. 5. However, NaOH chemical cleaning made its permeate flux recover to 94% of initial flux, which indicated the –COOH on the oligopeptide reacted with NaOH to destroy the hydrogen bond, but the flux did not resume to initial flux due to the existence of $–NH_2$.

3.4. Hydrophilic DOM fouling mechanism explained from different cleaning methods and cleaning efficiencies

Each hydrophilic DOM fouled membrane was cleaned by the four cleaning methods, i.e., flushing, backwashing, flushing and backwashing and chemical cleaning with 0.5% NaOH, respectively, and their cleaning efficiencies were used to deduce their fouling mechanism. Such as the polysucrose, just as the above stated, the recovered fluxes were 87%, 97% and 99% by the three hydraulic cleaning methods, which meant that the fouling of membrane surface and membrane pore existed, because the polysucrose rejected on the membrane surface can be cleaned by the flushing, the matter rejected in the membrane pore and some rejected in the intersection of membrane surface and pore can be cleaned by the backwashing, and the compound rejected on the membrane surface and in the membrane pore can be effectively cleaned by the flushing and backwashing. The highest flux recovery was obtained by flushing and backwashing cleaning, because the flushing can make the water filled in the hollow fibers, the membrane inflexibility became stronger, thus the efficiency of backwashing improved more than the only backwashing, at the same time, flushing cleaning can efficiently rinse the backwashed matter from the membrane pore [13]. In addition, most of membrane fouling resulted from polysucrose on the membrane surface and in the membrane pore was reversible, which can be removed by the hydraulic cleaning. However, the membrane fouling by oligopeptide was irreversible, and the flux was only recovered to 94% of the initial flux after chemical NaOH cleaning. For the citric acid, the three physical cleaning methods did not work, which indicated that there was no reversible fouling, and the NaOH chemical cleaning cannot make the membrane permeate flux recover, indi-

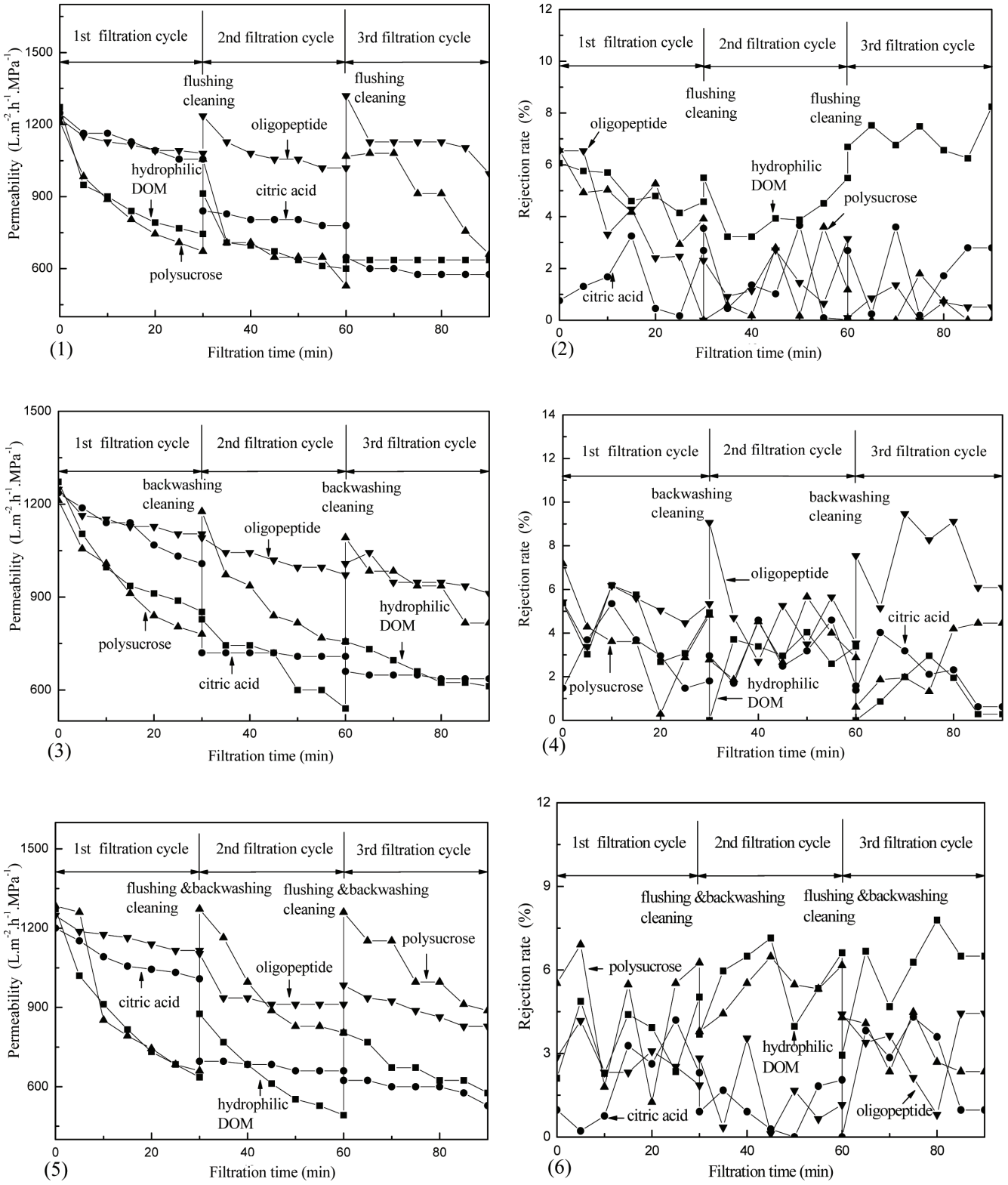

Fig. 5. Membrane permeate flux and hydrophilic DOM rejection during 3 cycles of ultrafiltration of hydrophilic DOM at a constant TMP of 0.06 MPa for 30 min and cleaning the hydrophilic DOM fouled membrane by flushing((1)(2)) for 1.5 min, backwashing ((3)(4)) at 0.2 MPa for 3 min, flushing and backwashing((5)(6)) (the flushing cleaning was performed for 15 s, then backwashing was done in 0.2 MPa pressure, and flushing and backwashing were simultaneously run for 2 min 45 s) and 0.5% NaOH ((7)(8)) for 30 min with the cleaning solution recirculated.

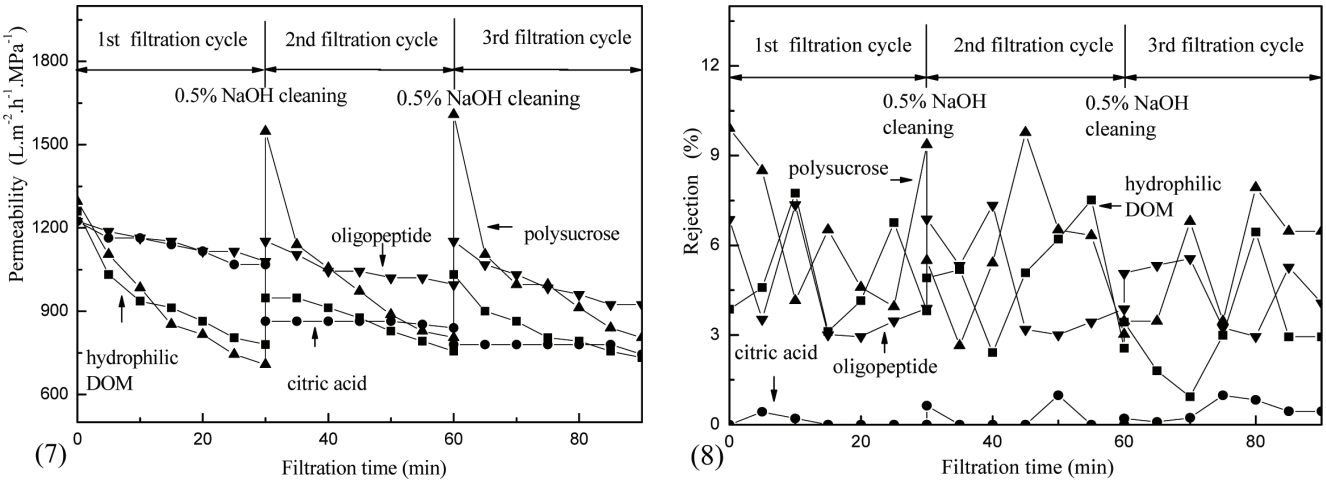

Fig. 5. (Continued from previous page).

cating that the NaOH was not the appropriate cleaning agent, and the filtration mechanism of citric acid should be further studied.

3.5. Influences of mixed hydrophilic DOM on UF filtration characteristics

Fouling experiments were conducted using the mixed hydrophilic DOM compounds. The four different cleaning methods, i.e., flushing, backwashing, flushing and backwashing, and 0.5% NaOH were also used to clean the mixed hydrophilic DOM fouled ultrafiltration membranes. These results are shown in Fig. 5.

During ultrafiltration of the mixed hydrophilic DOM solution in the first cycle, the flux decline was similar with polysucrose, one reason was that the polysucrose with lots of -OH was prone to adsorb on the membrane and held more adsorption sites to influence the permeate flux, another one was that the MW was a more important factor than other characteristics, such as acid/neutral/base properties, at the beginning of filtration. The filtration characteristics in the first cycle were dominated by the compound, of which the flux declined most rapidly. The filtration characteristics in the next cycles were close to the compound that was not easy to clean.

The membrane permeability and the mixed hydrophilic DOM rejections during ultrafiltration and flushing and backwashing cleaning were alike to the ones during the ultrafiltration and flushing cleaning, which indicated that mixed hydrophilic DOM fouling occurred more on the membrane surface than in the membrane pore. Compared with the three hydraulic cleaning methods, the initial permeate flux in next cycle was the highest after NaOH chemical cleaning, but the filtration characteristics were also dominated by citric acid.

In all, the hydrophilic neutral and acid DOM were more responsible for influencing the ultrafiltration characteristics in surface water than hydrophilic base.

4. Conclusions

The hydrophilic DOM with different acid/neutral/base properties revealed respective fouling and cleaning characteristics by flushing, backwashing, flushing and backwashing and 0.5% NaOH cleaning. The citric acid fouled membrane fluxes were not recovered by the four cleaning methods, possibly because the interaction of citric acid with PVC membrane was strong. The future study can select other cleaning agent to clean the citric acid fouled membrane. Most of membrane fouling by polysucrose was reversible, because it was easily removed by hydraulic cleaning methods. The membrane fouling by oligopeptide was irreversible, which can be recovered partly after NaOH chemical cleaning. During ultrafiltration of the mixed hydrophilic DOM solution composed of citric acid, polysucrose and oligopeptide, the membrane performances were always close to the compound, of which membrane flux was lowest among the three compounds.

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References

[1] C. Combe, E. Molis, P. Lucas, R. Riley and M.M. Clark, The effect of CA membrane properties on adsorptive fouling by humic acid. J. Membr. Sci., 154 (1999) 73–87.

[2] W. Yuan and A.L. Zydney, Humic acid fouling during microfiltration. J. Membr. Sci., 157 (1999) 1–12.

[3] K.L. Jones and C.R. O'Melia, Protein and humic acid adsorption onto hydrophilic membrane surface: effects of pH and ionic strength. J. Membr. Sci., 165 (2000) 31–46.

[4] L. Fan, J.L. Harris, F.A. Roddick and N.A. Booker, Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. Wat. Res., 35 (2001) 4455–4463.

[5] C. Lin, T. Lin and O.J. Hao, Effects of humic substance characteristics on UF performance. Wat. Res., 34 (1999) 1097–1106.

[6] G. Amy and J. Cho, Interactions between natural organic matter (NOM) and membranes: rejection and fouling. Wat. Sci. Technol., 40 (1999) 131–139.

[7] F.H. Frimmel, F. Saravia and A. Gorenflo, NOM removal from different raw waters by membrane filtration. Wat. Sci. Technol.: Wat. Supply, 4 (2004) 165–174.

[8] N. Lee, G. Amy, J.P. Croué and H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). Wat. Res., 38 (2004) 4511–4523.

[9] H.-C. Kim, J.-H. Hong and S. Lee, Fouling of microfiltration membranes by natural organic mater after coagulation treatment: a comparison of different initial mixing conditions. J. Membr. Sci., 283 (2006) 266–272.

[10] S. Hong and M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. J. Membr. Sci., 132 (1997) 159–181.

[11] S.W. Krasner, J.P. Croué, J. Buffle and E.M. Perdue, Three approaches for characterizing NOM. J. AWWA, 88 (1996) 66–79.

[12] J.A. Leenheer and J.P. Croué, Characterizing aquatic dissolved organic matter. Environ. Sci. Technol., A 37 (2003) 18A–26A.

[13] X. Guo, The cleaning method of membrane processes, CN, Patent 1,994,537, 2007.

[14] S.F. Weng, Fourier Transform Infrared Spectrometer, Chemical Industry Press, Beijing, 2005.

[15] L. Chen and M. Chen, Polyvinyl chloride hollow fiber membrane and preparation methods, CN, Patent 1,579,600, 2005.