Removal characteristics of dissolved organic matter and membrane fouling in ultrafiltration and reverse osmosis membrane combined processes treating the secondary effluent of wastewater treatment plant

Jianwei Liu, Mengfei Zhao, Cui Duan, Peng Yue and Tinggang Li

ABSTRACT

The widespread implementation of municipal wastewater treatment and reuse must first ensure the safety of reused wastewater. The effluent of the municipal wastewater treatment plant contains a large amount of dissolved organic matter (DOM), which adversely affects the reuse of wastewater. In this study, the ultrafiltration (UF) + reverse osmosis (RO) process was used to treat the secondary effluent from wastewater treatment plants. The relationship between the removal performance, membrane fouling of the UF + RO process, and DOM removal characteristics of influent were studied. The results show that DOM can be removed effectively by UF + RO process. The UF mainly removes DOM with a molecular weight greater than 10 kDa, while RO has a significant removal effect on low-molecular-weight DOM, which mainly causes UF and RO membrane fouling. The UF + RO process has a significant removal rate on fulvic acid, humic acid, tyrosine, and tryptophan, and the order is humic acid > fulvic acid > tyrosine > tryptophan. Fulvic acid contributed the most to the UF membrane fouling, while fulvic acid and protein-like proteins contributed mainly to the RO membrane fouling.

Key words | combination process, DOM, membrane fouling, UF + RO, wastewater reclamation

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HIGHLIGHTS

- DOM can be removed effectively by UF + RO process.
- UF mainly removes DOM with a molecular weight greater than 10 kDa.
- Fouling of RO membrane was mainly caused by low-molecular DOM.
- Fulvic acid most contributed the most to UF membrane fouling.
- RO membrane fouling was mainly due to fulvic acid and protein-like proteins.

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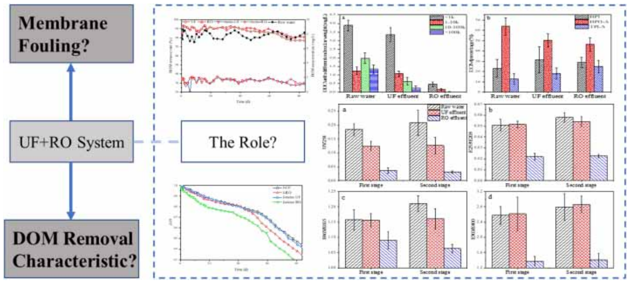
GRAPHICAL ABSTRACT



INTRODUCTION

With the rapid development of the global economy, the demand for water resources has expanded dramatically. Wastewater reclamation is an important part of the water resource cycle (Bai *et al.* 2020), and it is an effective way to improve the utilization rate of water resources and cope with the water crisis. In areas where freshwater resources are inadequate, wastewater recycling is of particular concern (Li *et al.* 2020). At the same time, wastewater reclamation strategies are increasingly important.

Wastewater reclamation methods mainly include biological treatment technology, and physical and chemical treatment technology. All of these technologies have the disadvantages of high energy consumption and secondary pollution (Horstmeyer *et al.* 2020). Membrane treatment technology is widely used in the field of wastewater treatment. Not only can membrane treatment technology efficiently remove pollutants to ensure the quality of effluent water but also concentrated water can be used for resource and energy recovery (Horstmeyer *et al.* 2020).

In recent decades, ultrafiltration (UF) membranes have been increasingly applied for wastewater reclamation because of their outstanding performance in terms of particle and microorganism removal (Liu *et al.* 2019). The pore size of the UF membrane is in the range of 1–100 nm, so it can remove pathogenic microorganisms, insoluble particulate matter, and partially soluble organic matter (Krahnstöver *et al.* 2019). It is generally recognized that the UF process can remove 80–90% of turbidity and 30–40% of dissolved organic matter (DOM) in surface water, and Bu and colleagues used coagulation–ultrafiltration to treat micro-polluted surface water, and the removal efficiency of DOM was 53.8% (Bu *et al.* 2019). Reverse osmosis (RO) filtration is a common method for the treatment of urban wastewater resources. It has a good effect in treating ions and DOM in wastewater; Lee and co-workers studied the use of RO membranes for wastewater regeneration, and the results showed that RO membranes can remove more than 98% of salt in wastewater, and the removal effect of DOM is more than 80% (Lee *et al.* 2020). During the UF/RO filtration process, a large number of inorganic and organic substances, including ionic salts and soluble organic matter, were effectively removed by the UF/RO membrane through size repulsion and solute, electrostatic and physical-chemical interactions between the solvent and the membrane (Deng 2020). Although the removal effect of UF/RO membranes on pollutants is significant, membrane fouling is one of the most critical issues in practical applications, and it will increase energy consumption and affect the stability of the entire process (Schneider *et al.* 2005; Ma *et al.* 2019).

Membrane pollution is mainly divided into inorganic pollution, organic pollution, and microbial pollution. The combined effect of different membrane fouling mechanisms is the formation of a fouling layer, which reduces membrane flux and may also adversely affect salt rejection (Schneider *et al.* 2005). Due to the complex composition of organic matter in raw water, organic pollution is more serious (Tong *et al.* 2020). DOM widely exists in wastewater, which has been a research hotspot in the field of wastewater treatment, and it is also the main cause of membrane pollution (Tang *et al.* 2010). Membrane treatment has a significant effect on removing DOM from wastewater by using the membrane's DOM retention and adsorption characteristics, its ability to generate chemical groups with DOM, etc. Tang *et al.* (2010) studied the removal performance of DOM and membrane fouling by a membrane bioreactor plus UF process and found that protein plays an important role in membrane fouling, of which hydrophilic fractions have the largest effect. Tong *et al.* (2020) studied the pollution characteristics of RO membranes in the process of wastewater reclamation and also showed that DOM has a serious impact on membrane pollution.

Serious water pollution and shortage of water resources make urban wastewater one of the indispensable 'water sources'. However, the widespread implementation of urban wastewater treatment and reuse must first ensure the safety of reused wastewater. Among them, the removal of DOM in the secondary effluent of urban wastewater treatment plants has become one of the urgent problems to be solved in the reuse of wastewater, and it has become a key factor in determining whether wastewater can be reused. In general, to achieve wastewater reclamation, biological and membrane-based wastewater treatment processes are often used (Wu *et al.* 2013). However, the biological wastewater treatment process is limited by environmental factors, and the treatment effect is not stable (Meena *et al.* 2019). Therefore, the method of directly using membrane filtration for wastewater reclamation has received great attention. Membrane treatment technology, especially UF and RO technology, is widely used in the advanced treatment of wastewater to remove DOM because of its advantages such as good treatment effect and small footprint (Hube *et al.* 2020). And DOM is also an important factor that causes membrane pollution in the wastewater membrane treatment process. In practical applications, to ensure the quality of the effluent water and alleviate membrane pollution, two or more membrane technologies are usually integrated. However, there are few studies on the characteristics of membrane integrated technology for the treatment of DOM in municipal wastewater and the mechanism of membrane pollution.

The existence of organic matter in recycled water has become a major factor restricting the reuse of wastewater. It has caused many problems in wastewater treatment and reclaimed water treatment processes, such as treatability and membrane pollution (Hube *et al.* 2020). Therefore, it is necessary to study the removal of DOM in the process of urban wastewater reuse treatment and explore the correlation between DOM and membrane pollution. In this study, the removal performance, characteristics, and membrane blockage of DOM during wastewater reclamation were studied by using UF + RO membrane combination.

MATERIALS AND METHODS

UF + RO process operating conditions

A dynamic UF + RO experimental device was established, and the process flow is shown in Figure 1. The raw water was taken from the secondary effluent of a municipal wastewater treatment plant (the secondary sedimentation tank effluent) with the activated sludge process as the main process. The water quality parameters are shown in Table 1. After the raw water enters the inlet water tank, the flocculant ($FeCl_3$, 40 mg/L) is added at 200 r/min to remove insoluble solids in raw water, and then flocculated. After flocculation and precipitation, the pH of the inlet water is adjusted to 8.0 with 10% hydrochloric acid solution and 10% sodium hydroxide (NaOH) solution. Subsequently, the raw water is pumped into the UF process. After the UF effluent leaves the middle water tank, the UF effluent enters the RO process through the booster pump, and the RO effluent enters the clean water tank. The pre-membrane pressure of the UF process was 0.04 MPa and the recovery rate was 40%; the pre-membrane pressure of the RO process was 0.3 MPa and the recovery rate was 50%.

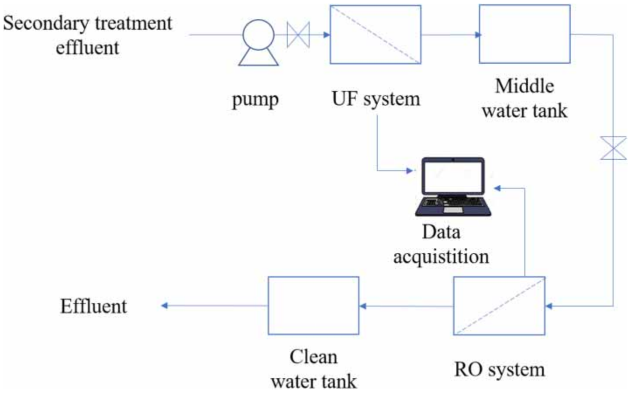


Figure 1 | Schematic diagram of UF + RO process.

Table 1 | Test water quality parameters

Index	pH	COD/(mg/L)	ORL/(μS/cm)	TN (mg/L)	TP (mg/L)	DOC (mg/L)	UV_{254} (AU/cm)
Value	6.63–7.61	41.89–54.52	648–866	9.51–14.57	2.25–2.55	6.92–8.66	0.081–0.099

COD: chemical oxygen demand; ORP: oxidation-reduction potential; TN: total nitrogen; TP: total phosphorus; DOC: dissolved organic carbon: UV_{254}: UV absorbance at 254 nm.

Determination and characterization of dissolved organic matter

Dissolved organic carbon (DOC) can be used to approximately characterize DOM in secondary effluent (Bu *et al.* 2019), and UV-visible absorbance characterization, molecular weight distribution analysis, hydrophilicity and hydrophobicity distribution analysis, and three-dimensional fluorescence spectrum characterization of DOM were performed.

A total organic carbon (TOC) instrument (Multi N/C 3100, Jena, Germany) was used to measure the DOC of the effluent, and the water sample was filtered through a 0.45 μm microporous filter membrane. A UV-visible spectrophotometer (Platinum Elmer, Lambda 650s) was used to measure the ratio of four characteristic UV-visible absorbances (UV254, E253/E203, E465/E665, and E300/E400) to determine DOM changes. The molecular weight distribution of DOM was characterized by filters with molecular weight cut-offs of 1 kDa, 10 kDa, and 100 kDa. First, the water sample to be separated was filtered through a 0.45 μm filter membrane, and the filtered water sample was labeled as 'raw water', and then the 'raw water' sample was filtered through three kinds of filter membranes, which were recorded as ' < 1 kDa', '1–10 kDa', '10–100 kDa' and '>100 kDa', the DOM distribution is represented by the DOC of the filtered sample and calculated by subtraction.

The resin separation method was used to separate DOM into hydrophilic and hydrophobic fractions. XAD-8/4 resins are the most widely used resins to concentrate and fractionate DOM into operationally defined components (e.g. hydrophobic and hydrophilic fractions) based on their chemical properties and, and in this paper XAD-8 and XAD-4 resins were selected (Zhang *et al.* 2009; Tang *et al.* 2010). The water sample was filtered with a 0.45 μm filter membrane before the hydrophilic and hydrophobic separation. After filtration, the water sample was acidified to pH 2 and then 200 mL was adsorbed by XAD-8 and XAD-4 resins. The flow rate was controlled within 3 mL/min. The TOC was analyzed with a TOC instrument. The measured TOC value was the concentration of hydrophilic organic matter, denoted as HPI; 200 mL of 0.1 mol/L NaOH solution desorbed XAD-8 and XAD-4 resins respectively, and the flow rate was also controlled within 3 mL/min. The DOM contained in the effluent in XAD-8 resin was a hydrophobic organic acid, which was denoted as HPO-A, and the DOM contained in the effluent in XAD-4 resin was a transitional hydrophilic organic acid, denoted as TPI-A. From this, we can get the distribution of various hydrophilic and hydrophobic components of the DOM.

A Hitachi F-7000 three-dimensional fluorescence spectrum analyzer (Hitachi) was used to analyze the DOM in water samples. The excitation–emission spectra were collected with corresponding scanning emission spectra from 280 to 550 nm at 5 nm increments by varying the excitation wavelength from 200 to 450 nm at 5 nm sampling intervals.

Membrane specific flux characterization

Membrane fouling was characterized by membrane specific flux. In the process, when the RO effluent reached 20 L, the UF membrane flux and the RO membrane flux were measured once. The UF and RO effluent was collected with a graduated cylinder, and the volume of the collected UF effluent was 1 L and that of the RO effluent was 50 mL. Membrane flux was calculated by the following formula:

$$J = \frac{V}{S \cdot T}$$

Here J is membrane flux ($m^3/(m^2 \cdot h)$); V is water sample volume (m^3); S is membrane effective filtration area (m^2); T is time required to filter water sample (h).

The membrane flux obtained by filtering pure water was J0, and the membrane specific flux was J0/J.

RESULTS AND DISCUSSION

Performance of UF + RO

The removal of DOM is achieved through size repulsion, adsorption, formation of chemical groups with DOM, etc. (Bu *et al.* 2019). It can be seen from Figure 2 that in the stable operation stage (day 1–49), the DOM removal rates of UF and RO membranes are 29.42%–36.77% and 86.16%–93.16% respectively; in the stage of serious membrane pollution (day 50–day 84), the DOM removal rates of UF and RO membranes are 29.28%–34.04% and 80.78%–86.56%, respectively. It indicated that the performance for removal of DOM of UF or RO is not greatly affected by membrane fouling. However, the removal effect of mono-UF is poor, and mono-RO is greatly affected by membrane fouling during the removal of DOM. In the UF + RO system, the UF membrane removes larger DOM molecules through size exclusion and physicochemical action, which reduces the influence of the RO membrane on the large DOM molecules and alleviates the blockage of the RO membrane. When the small molecule DOM passes through the RO membrane, it

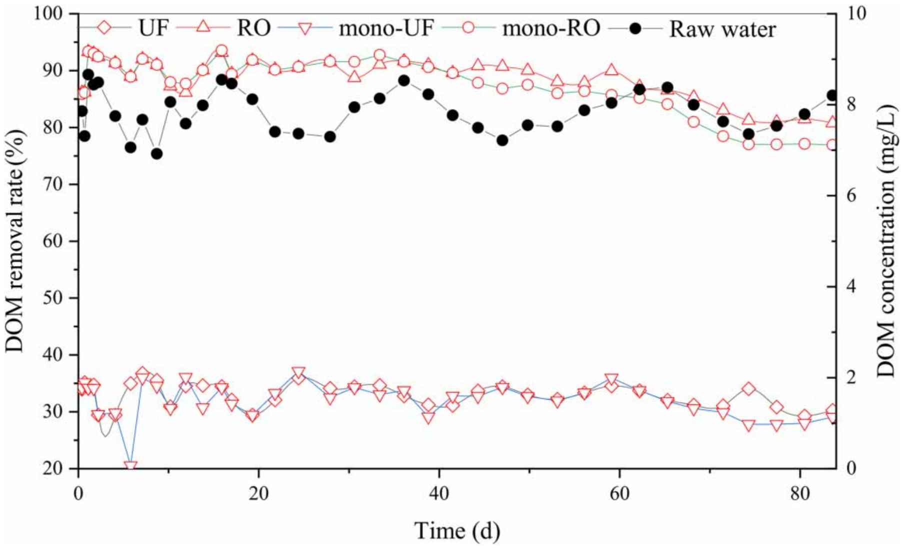


Figure 2 | DOM removal performance and membrane fouling of UF + RO.

is removed due to the electrostatic interaction and chemical bond connection between the membrane and the DOM, and size repulsion of RO membrane (Bai *et al.* 2020; Deng 2020). After the membrane fouling, a cake layer is formed on the surface of the membrane and the membrane flux is reduced, which leads to a drop in membrane treatment efficiency (Tong *et al.* 2020).

The start time of the severe membrane fouling stage is determined by the sudden decrease of the RO membrane specific flux. In this test, we determined the start time of the severe membrane fouling stage as when the RO membrane specific flux is less than 95% of the previous membrane specific flux. DOM is mainly removed in the RO process of the UF + RO. When the RO membrane is polluted (day 50), a large amount of DOC is adsorbed and agglomerated on the membrane surface, which increases the driving force of the DOC through the RO membrane into the effluent, thereby reducing the DOC removal rate of the RO (Wu *et al.* 2013).

From the overall operation effect, with the fluctuation of DOC in the raw water, the DOC concentration in the membrane effluent also fluctuates within a certain range, but the removal effect of RO to DOC is more stable than that of UF. Moreover, the composite process of UF + RO has a much better effect of removing DOM than UF/RO alone.

Characterization of DOM by UV-vis

During the entire phase of the UF + RO process operation, two groups of samples of water in and out were taken for analysis: once in the stable operation period (day 1–day 49 for the first stage); once when membrane fouling began to become serious (day 50–day 84 for the second stage), which was recorded as the severe membrane pollution stage. Two groups of water samples were characterized by UV-visible absorbance to analyze the DOM removal characteristic of UF + RO separation. The water sample was filtered through a 0.45 μm filter before measurement. The changes of the four UV-visible absorbance values of DOM of the water in and out of UF + RO are shown in Figure 3.

During the process from UF inflow to RO outflow, the UV254 value decreased overall, and the degree of decline in the RO stage was greater than that in the UF stage. After passing through the UF membrane, the removal rate of UV254 is about 30%, which indicates that more than half of the DOM has not been removed by the UF membrane. After passing through the RO membrane, the UV254 decreased significantly, which indicates that the hydrophobic part and the macromolecular organic matter removal effect in the DOM are significant (Bu *et al.* 2019). The DOM removal effect of UF in the two stages was compared. The second stage has the highest reduction rate of UV254. This is because the pollutants partially accumulate on the membrane surface to form a new filter layer, and some enter the UF and RO membrane pores (Lin *et al.* 2009). Part of the DOM containing unsaturated double bonds and DOM with aromaticity was removed in this layer by physical sieving. Also, it is difficult for the trapped DOM to enter the effluent through the pore diameter of the RO membrane. This may be due to the physical and chemical reaction between the RO membrane and the DOM, which makes it difficult for the DOM to desorb from the RO membrane (Bu *et al.* 2019).

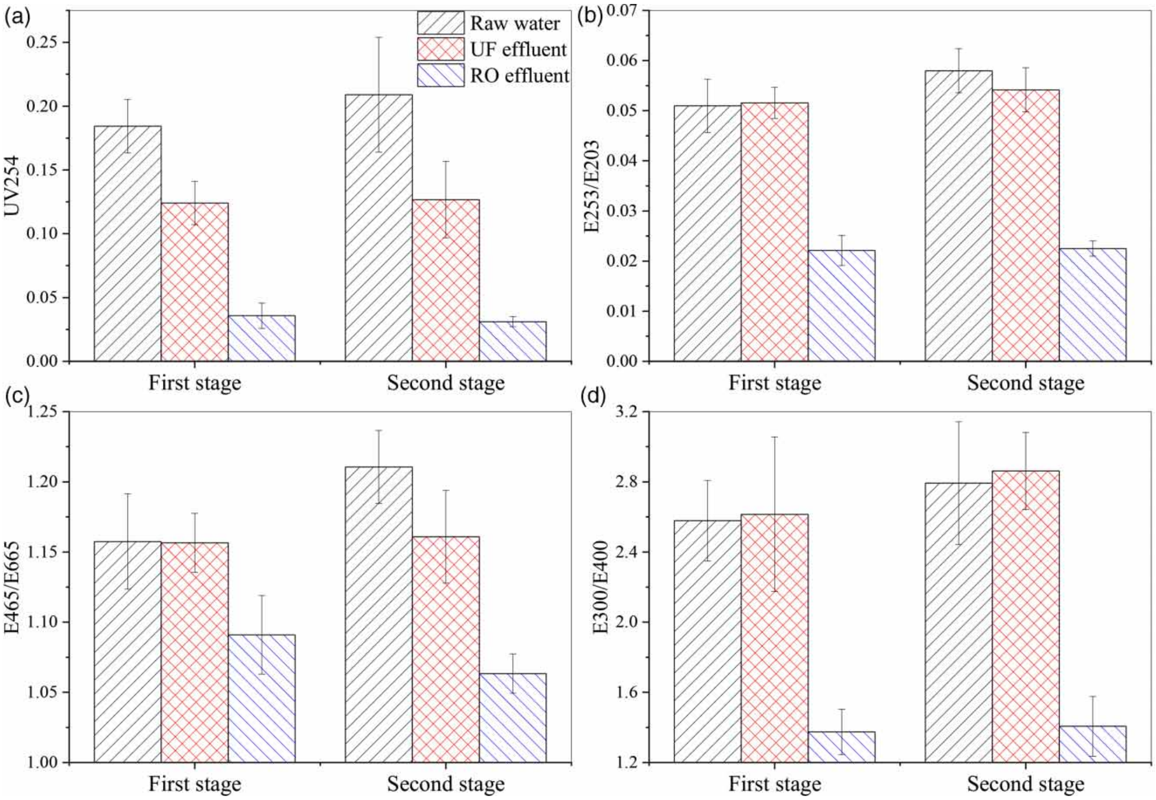


Figure 3 | UV-visible absorbance changes of the water in and out of UF + RO.

During the process from UF inflow to RO outflow, the E253/E203 values decrease overall, and the degree of decline in the RO stage is greater than in the UF stage. This indicates that the removal effect of the DOM, which easily led to the trihalomethane (THMs) generation, was mainly in the RO stage. The E253/E203 values of the UF effluent in the first and second stages showed generally no change, but they severely decreased in the RO stage. This shows that UF has almost no removal effect on THMs, while RO has a significant removal effect.

During the process from raw water to RO effluent, the overall value of E465/E665 decreased, indicating that UF + RO has a better effect on removing low-molecular-weight DOM, but most of the low-molecular organics in the process are mainly retained by the RO membrane. The E465/E665 value of UF in and out of water in the second stage also decreased, indicating that the new filter layer of UF has a certain retention effect on low-molecular DOM. In addition, the accumulation of pollutants on the surface of the RO membrane also improved the RO membrane's retention efficiency for low-molecular-weight DOM.

During the process from raw water to RO effluent, the E300/E400 value rises first and then decreases, indicating that UF + RO has a certain separation effect on the humus DOM in the UF stage, and the humus retention effect in the RO stage will be further analyzed by the three-dimensional excitation–emission matrix (3D-EEM) spectra. In the two stages, the effluent value of E300/E400 of the UF membrane was higher than the influent value, and the growth rate was not much different, indicating that the degree of humification of the UF process effluent was lower than that of the influent, but the new filtration generated in the second stage has little effect on the reduction of effluent humification.

The comprehensive analysis found that the rejection rate of most DOMs by UF membranes in the second stage is high. The rejection rate of DOM by RO membranes generally increases with the increase of membrane processing time, and the pollutants in membrane surface accumulation will improve the retention efficiency of RO membranes for most DOM.

Characteristics of DOM molecular weight and hydrophilicity

Due to the unstable retention efficiency of UF + RO in the influent DOM in the stable operation period, part of the

DOM retained in the late stage of the membrane pollution stage diffused into the effluent, which is not conducive to accurately analyzing the separation mechanism of UF + RO to DOM. The characteristics of UF + RO separation of DOM with different molecular weights were analyzed in the early stage of severe pollution. The resin separation method was used to separate the DOM in and out of the UF + RO process according to the hydrophobicity, and the content was characterized by DOC. The DOC concentration and DOC composition in each molecular weight distribution interval of UF and RO in and out of the water are shown in Figure 4.

Removal characteristics of DOM with different molecular weights using UF and RO membranes were investigated (Figure 4(a)). Total DOC decreased from 8.49 mg/L in raw water to 5.31 mg/L after UF filtration and 0.63 mg/L after RO filtration, which indicated that the removal rate of total DOM by UF was 37.46% and by RO was 88.14%.

Generally, all parts are reduced to varying degrees after passing through UF and RO. Among them, >100 kDa components had the highest UF and RO removal rates, 81.46% and 98.68%, respectively, Due to the smaller film holes and the presence of the cake layer, the UF and RO membrane has also efficient removal effect on the DOM components >100 kDa (Bu *et al.* 2019). The UF has a poor removal effect for DOM <10 kDa, which is determined by the mechanism by which UF separates DOM; these molecules can partially pass through the pores of the UF membrane (Hube *et al.* 2020). The separation of DOM by UF mainly depends on the sieving effect of DOM on the membrane surface (Tang *et al.* 2016). DOM with low molecular weight can often pass through the pore diameter of the UF membrane, making it difficult to be trapped by the UF membrane. The molecular weight of DOM in raw water is mainly <1 kDa. This is because the raw water is the secondary effluent after the biochemical treatment of the wastewater plant. The DOM with large molecular weight is often separated during the previous processing or by flocculation and sedimentation, or it is adsorbed by microorganisms or reduced to low-molecular substances by microbial metabolism so that the low-molecular-weight DOM in the secondary effluent accounts for a large proportion (Tong *et al.* 2020). Therefore, the removal effect of the UF membrane on DOM in secondary effluent of the wastewater treatment plant is not ideal. With the aggravation of membrane fouling, smaller membrane pores are more likely to be blocked by DOM, and the removal efficiency of low-molecular DOM and total DOM will become worse (Bu *et al.* 2019). In UF + RO system, the effect of the UF membrane is more inclined to remove macromolecular DOM, which is conducive to slowing down the fouling of the RO membrane.

RO has a large removal efficiency of DOM in each molecular weight range, which is related to the smaller membrane pores of the RO membrane (Lee *et al.* 2020). Only a small amount of DOM with a molecular weight of less than 10 kDa remains in the RO effluent; this is similar to previous research results (Deng 2020). Almost all DOM with a molecular weight greater than 10 kDa is retained by the RO membrane, which is because the RO membrane has selective permeability in addition to sieving (Schneider *et al.* 2005). When the DOM comes into contact with the

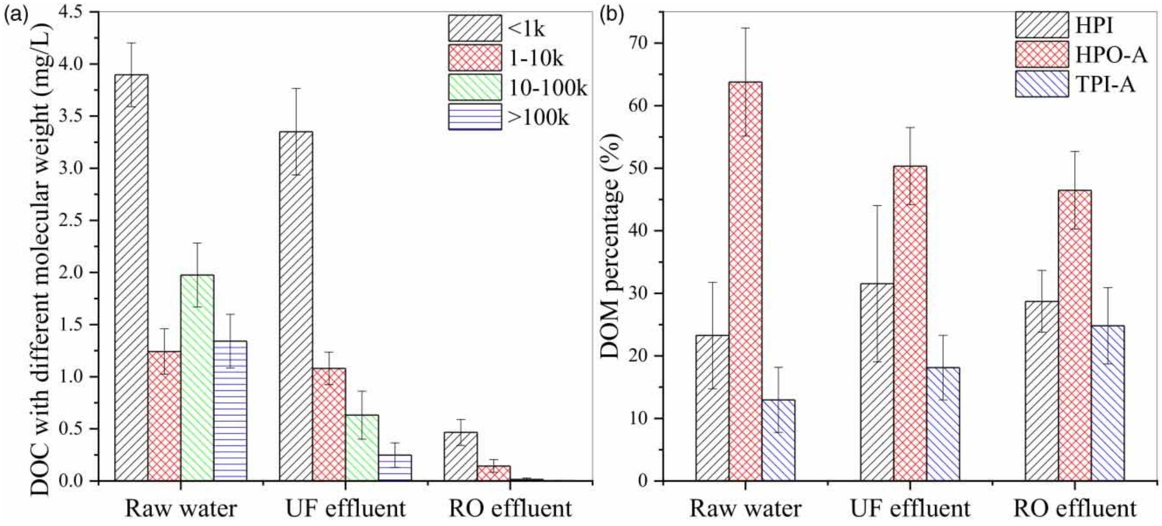


Figure 4 | Molecular weight distribution and hydrophobicity distribution of DOM in and out of UF + RO.

RO membrane, it may have electrostatic adsorption with the membrane surface or be connected by chemical bonds, so that the low-molecular-weight DOM can also be largely retained by the RO membrane (Hube *et al.* 2020). There may also be chemical groups on the surface of the RO membrane that have a repulsive effect on the DOM so that the DOM is taken away by the concentrated liquid without contacting the RO membrane (Lee *et al.* 2020). There is still a very small amount of DOM passing through the RO membrane into the RO effluent. It may be because these DOMs have not been chemically reacted with the RO membrane and were trapped by the RO membrane. There are also some chemical groups that have a repulsive effect on the RO membrane and are taken away by the concentrated solution. And the separation makes them enter the effluent through the slow diffusion in the RO membrane (Tong *et al.* 2020). A small amount of DOM in the effluent does not affect the removal performance of RO membranes on DOM.

Figure 4(b) shows the chemical fractions of DOM in UF and RO effluent separated by XAD-8 resin. The DOC content of HPI, HPO-A, and TPI-A components as a percentage of the total DOM content changed from 23.28%, 63.76%, and 12.96% in raw water to 31.56%, 50.33%, and 18.11% in UF effluent. The proportion of hydrophilic organic substances and transitional hydrophilic organic acids in the effluent increased and the proportion of hydrophobic organic acids decreased, indicating that the retention capacity of UF membranes for hydrophobic organic acids is greater than that for hydrophilic organic substances and transition hydrophilic organic acids. However, the hydrophobic organic acids in UF effluent still account for the largest proportion. This shows that UF has almost no removal effect on hydrophobic organic acids, which is similar to the results of previous studies (Bu *et al.* 2019). The retention of DOM by UF mainly depends on physical screening (Hube *et al.* 2020). When the molecular weight is smaller than the membrane pore size, it is difficult for the UF membrane to retain it. The content of hydrophobic organic acids in UF influent water is the most, which may be related to the quality of the raw water.

The DOC content of HPI, HPO-A, and TPI-A components in RO effluent was 28.69%, 46.48%, and 24.83%. The proportion of hydrophilic organic substances and hydrophobic organic acids in the effluent decreases, and the proportion of transition hydrophilic organic acids increased slightly. It can be seen that the RO process has a high removal efficiency of the DOM of each hydrophilic and hydrophobic component, and the removal rate of each component is not much different, indicating that the selective permeability of the RO membrane can affect both hydrophilic and hydrophobic components. RO membranes show strong retention ability for hydrophilic organic compounds and transitional hydrophilic organic acids, indicating that most of the hydrophilic components can be retained through electrostatic interaction with the membrane or chemical bond with the membrane (Tang *et al.* 2016). The relatively large proportion of the hydrophobic component in the RO effluent is due to the large difference in the total DOC content in the inlet and outlet water, and the RO membrane also has a higher rejection rate of the hydrophobic component (Deng 2020).

3D-EEM characterization of DOM

The inlet and outlet water of UF + RO in the early stage of membrane fouling was characterized by 3D-EEM to analyze the characteristics of the UF + RO separating different types of DOM. The water sample was filtered through a 0.45 μm filter before measurement. The three-dimensional fluorescence spectrum is shown in Figure 5.

The UF + RO process DOM in and out of the water are mainly divided into four categories: tyrosine (peak T1, excitation/emission (Ex/Em) = (200–250)nm/(280–330) nm), tryptophan (peak T2, Ex/Em = (200–250)nm/(330–380)nm), humic acid (peak C, Ex/Em = (250–400)nm/(380–550)nm) and fulvic acid (peak A, Ex/Em = (200–250) nm/(380–550)nm). Both raw water and UF effluent contain peak T1, T2, C, and A, and the peak T1, T2, and C type of the raw water and effluent appear at the same position, which indicates that the three types of DOM content distribution in raw water and UF effluent water are close. The contents of various types of DOM in raw water and UF effluent are fulvic acids (peak A) > humic acid (peak C) > tyrosine (peak T1) > tryptophan (peak T2). After UF treatment, the intensity of various fluorescence peaks decreased to a certain extent, indicating that the content of various types of DOM has decreased to a certain extent, among which the rate of fulvic acid reduction was the largest, followed by proteins (peak T1 and T2), then humus The reduction rate of acid content is the lowest. This shows that although UF has a certain retention rate for all kinds of DOM, the retention efficiency is not high. The retention rate of UF to fulvic acids is relatively high, while the retention rate to humic acids is relatively low. Peak T1 and T2 belong to protein-like substances; such macromolecular hydrophobic substances are easily trapped by the membrane and are the main substances causing UF membrane pollution (Neemann *et al.* 2013).

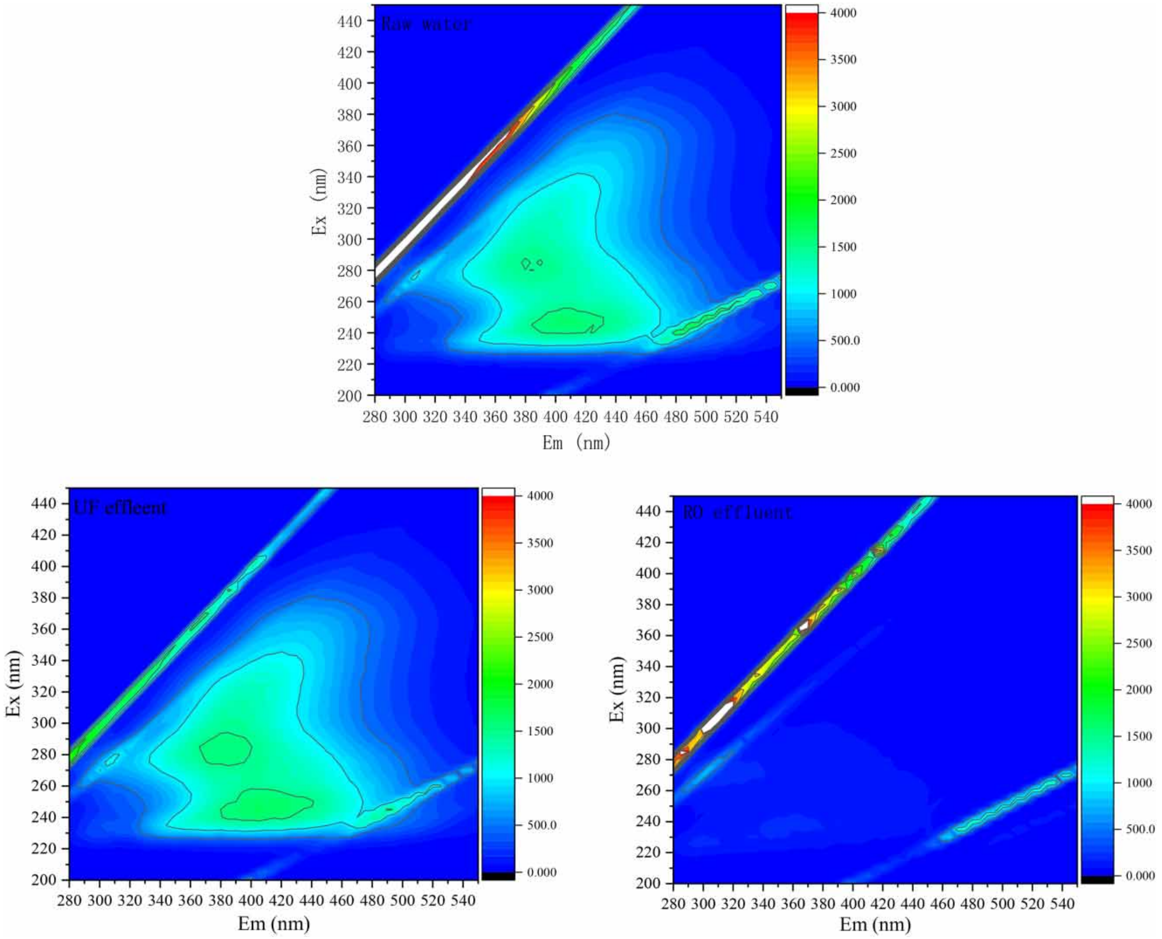


Figure 5 | Three-dimensional fluorescence spectrum of UF + RO in and out water.

The fluorescence peaks of various DOMs in RO effluent have been reduced to a great extent, which indicates that RO membranes have better retention efficiency for various DOMs. Compared with the UF effluent, the reduction rate of peak C and A fluorescence peaks in the RO effluent is higher, which indicates that the RO membrane has a higher removal rate of DOM of humic acid and fulvic acid. The reduction rate of protein (peak T1 and T2) fluorescence peaks in the RO effluent is relatively low, indicating that the DOM retention rate of protein by the RO membrane is relatively low. The content of DOM in the RO effluent changed to tryptophan (peak T2) > tyrosine (peak T1) > fulvic acid (peak A) > humic acid (peak C). In addition, the content of humic acid DOM in the RO effluent is very low, and the content of fulvic acid DOM is also low, mainly protein (peak T1 and T2) DOM. The removal effect of the UF + RO process on fulvic acid and humic acid is stronger than on protein-like DOM. This may be due to the size of the fulvic acid and humic acid, which were intercepted by the membrane or electrostatically combined to form larger molecules, which were adsorbed or intercepted by the cake layer, and then removed by the UF + RO (Yue *et al.* 2015). It may also be because the hydrophobic aromatic groups of fulvic acid and humic acid are combined with the membrane, while the hydrophilic part forms a hydrated layer, thereby intercepting more fulvic acid and humic acid (Zhao *et al.* 2019).

Fouling of UF + RO

Membrane fouling refers to the clogging caused by the deposition or adsorption of colloidal particles, inorganic solutes, or dissolved organic matter in the raw wastewater on the membrane surface or in the membrane pores, resulting in increased transmembrane pressure or reduced permeate flux (Meng *et al.* 2009). Generally speaking, for the UF and RO membrane, with the operation of the device, the normalized flux (J/J0) decreases significantly, especially when membrane fouling is severe (Figure 6). The decrease in permeate flux can be divided into three stages. In the initial stage, due to the concentration polarization phenomenon, the permeate flux of the UF and RO membranes decreased, and then due to the adsorption and deposition of DOM molecules on the membrane, the permeate flux decreased. Finally, due to the formation of the cake layer, the permeate flux dropped rapidly (Zhang *et al.* 2009; Yue *et al.* 2015; Zhou & Meng 2016).

In the process of removing DOM caused by the UF + RO process, the flux of the membrane decreases; the characteristics of DOM have a significant effect on the decline of membrane flux (Bai *et al.* 2020). Therefore, combined with the previous research on the characteristics of DOM (sections 'Characterization of DOM by UV-vis', 'Characteristics of DOM molecular weight and hydrophilicity' and '3D-EEM characterization of DOM'), the relationship between DOM characteristics and membrane fouling in the UF + RO process water in and out was analyzed.

We analyzed the removal performance of DOM with different molecular weights with the combined UF + RO process. For the UF, due to its pore size, the UF intercepts mainly macromolecular DOM with molecular weight >10 kDa, and the UF membrane fouling is also mainly caused by macromolecular DOM (Bai *et al.* 2020). The low-molecular DOM will also contribute to the UF membrane pollution. This is because when the large-molecular-weight DOM gradually blocks the pores of the UF membrane or produces a bridging effect on the membrane surface, the molecular weight of the DOM retained by the UF membrane will gradually decrease, and make low-molecular DOM gradually deposit on the surface and pores of the UF membrane (Bu *et al.* 2019). For the RO membranes, due to the removal mechanism of the RO membranes, low-molecular DOM condenses on the surface of the RO or diffuses into the interior of the RO structure, so the main cause of the RO membrane pollution is low-molecular DOM (Tang *et al.* 2016).

The contribution of UF + RO membrane pollution caused by different hydrophilic and hydrophobic DOM is different. In general, the hydrophobic organic acid HPO-A contributes the most to UF + RO membrane fouling, which may be for three reasons. On the one hand, both UF and RO membranes are hydrophobic membranes, and the adsorption capacity for hydrophobic DOM is stronger than for other types of DOM (Hube *et al.* 2020). On the other hand, hydrophobic DOM is less likely to be washed away by water and return to the water phase than other DOM (Neemann *et al.* 2013). Finally, since the components of the hydrophobic DOM in the influent account for the largest proportion of the total DOM, the hydrophobic DOM has the largest load on the UF and RO membranes, and is also the most likely to cause membrane contamination.

The severity of UF + RO membrane pollution caused by different types of DOM varies. It can be seen from section '3D-EEM characterization of DOM' that the DOM content of raw water and UF effluent are fulvic acids (peak A) > humic acid (peak C) > tyrosine (peak T1) > tryptophan

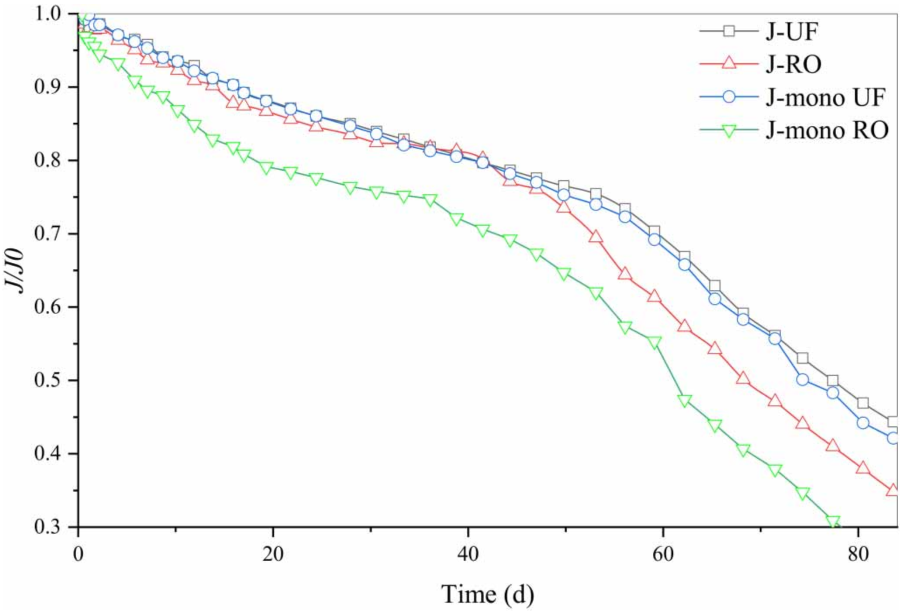


Figure 6 | Membrane specific flux change.

(peak T2). The UF membrane has a high removal rate of fulvic acids (peak A) and proteins (peak T1 and T2). Both of these DOMs are important membrane fouling factors, which play a key role in the UF membrane fouling in the UF + RO process (Tang *et al.* 2010).

The removal effect of the RO membrane on the four DOMs is high, and the total DOM content is very low (0.63 mg/L, and reduced by 88.14% for UF effluent). The DOM content in RO effluent is tryptophan (peak T2) > tyrosine (peak T1) > fulvic acid (peak A) > humic acid (peak C). Since the removal effect of RO on these four types of DOM is significant, these four types of DOM may all contribute to RO membrane contamination. Previous studies have shown that protein-like DOM (peak T1 and T2) significantly contributes to RO membrane fouling (Teixeira & Sousa 2013). In this study, the RO membrane has a better effect of removing fulvic acid (peak A) and protein-like DOM (peak T1 and T2), and these DOMs have a greater contribution to RO membrane fouling, while humic acid (peak C) contribution is low, which is similar to other studies (Chen *et al.* 2017).

CONCLUSION

The removal rate of DOM in the UF + RO process is high and stable, regardless of whether membrane fouling occurs. UF mainly removes DOM with a molecular weight >10 kDa, and RO has a significant effect on the removal of DOM of various molecular weights, especially low-molecular DOM. Similarly, UF membrane fouling is mainly caused by DOM with molecular weight >10 kDa, while RO membrane fouling is mainly caused by low-molecular DOM. The UF + RO process has a high removal effect on hydrophilicity and hydrophobicity component; UF mainly removes the hydrophobic components, while the RO has a higher removal effect on hydrophilic components. UF membrane is mainly fouled by the hydrophobic DOM, and both hydrophilic and hydrophobic DOM contribute to the fouling of RO membrane. 3D-EEM research results show that the UF + RO process has a higher removal effect on fulvic acid, humic acid, tyrosine, and tryptophan, which is mainly the role of the RO membrane, while the removal effect of UF membrane differs. In addition, the order of removal rate of DOM is humic acid > fulvic acid > tyrosine > tryptophan. Fulvic acid contributed the most to UF membrane fouling, while fulvic acid and protein-like proteins contributed more to RO membrane fouling.

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DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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