*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2018.22429

119 (2018) 97–106
July

# The membrane fouling and interface mechanism of reclaimed wastewater treatment by three different processes

Lihua Sun[a], Bingbing Yang[b], Xi Duan[b], Ning He[b], Cuimin Feng[a], Yajun Zhang[a,*]

[a]*Key Laboratory of Urban Stormwater System and Water Environment, Beijing University of Civil Engineering and Architecture, Beijing 100044, China, Tel. +86 10 68304273; Fax: +86 10 68304273; email: sunlihuashd@163.com (Y. Zhang)*
[b]*School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, Beijing 100044, China*

Received 7 August 2017; Accepted 29 March 2018

---

## ABSTRACT

This paper focused on the effects of powdered activated carbon (PAC) and biological powdered activated carbon (BPAC) dosages on ultrafiltration (UF) membrane flux caused by natural organic matter (NOM) fractions in secondary effluent. Moreover, the membrane fouling resistance and the membrane-foulant interaction mechanism were also investigated. The results indicated that the dosages of PAC/BPAC exhibited remarkable performance in alleviating membrane flux, the best PAC dosage for the membrane flux variation of raw water was 10 and 40 mg/L for BPAC. The BPAC-UF combination process has substantially low irreversible fouling resistance, and the best dosage in all processes caused the greatest reversible fouling resistance. The BPAC-UF process showed excellent performance with respect to NOM removal on the three-dimensional fluorescence detection of secondary effluent. The microorganisms on the surface of BPAC can strengthen the removal of organic compounds in water. The polar force plays a leading role in the whole membrane fouling process.

*Keywords:* Biological powdered activated carbon; Membrane flux; Membrane fouling resistance; Ultrafiltration.

---

## 1. Introduction

Reclaimed water, as an important unconventional water source, has attracted wide attention both at home and abroad [1,2]. However, the quality of reclaimed water in municipal wastewater treatment plant is complex, and the background value of pollutants is high. Therefore, it is very important to select the appropriate regeneration water treatment process.

Ultrafiltration (UF) is a commonly used method of reclaimed water treatment, but the plugging of membrane hole and its removal rate of organic pollutants are low, which limits the wide application of it. The combined process of powdered activated carbon (PAC) and UF can effectively adsorb organic compounds in water, thus greatly expanding the application range of UF. However, whether the activated carbon pretreatment can effectively alleviate membrane fouling has not reached the same conclusion at present. Studies have shown that PAC adsorption reduces the solubility of substances, and the formation of cake layer on the surface of the membrane can reduce the growth of transmembrane pressure difference, thereby reducing the role of membrane fouling [3–6]. However, some studies have shown that the crosslinking of organic compounds makes PAC adhere to the surface of the membrane, which can aggravate membrane fouling [7–9]. Further, PAC will be transformed into biological powdered activated carbon(BPAC) when the surface of PAC was filled with microorganisms during prolonged use, and then it has been widely adopted with membrane interception, adsorption, and biological degradation to enhance the performance of UF process and efficiently controlled the membrane fouling [10,11].

---

[*] Corresponding author.

*Presented at 2017 Qingdao International Water Congress, June 27–30, 2017, Qingdao, China.*

In the advanced treatment of wastewater, the secondary effluent organic matter is the main material causing membrane fouling, and its fouling mechanism has been a hot and difficult research topic. Related studies have shown that the extent of organic membrane fouling depends on the interaction between the organic and UF membrane, usually using extended Derjaguin–Landau–Verwey–Overbeek (x-DLVO) in the theory of Lifshitz-van der Waals force (LW), electrostatic force (EL), and acid–base force (AB) to express [12,13]. At present, there are few reports about the influence of membrane fouling and the mechanism of interfacial interaction in different membrane combination processes.

In this study, the secondary effluent of a municipal wastewater treatment plant is used as the raw water. The membrane fouling status, membrane effluent quality, and interface mechanism between organic and membrane were studied comparatively by three combinations of direct UF, PAC-UF, and BPAC-UF, analyzing the bacterial community structure characteristics of BPAC surface microorganisms and investigating the effect of microbial action on membrane fouling mechanism.

## 2. Materials and methods

### 2.1. Materials

Bovine serum albumin, hydrochloric acid, and NaOH used in these experiments were obtained from Sinopharm Group Chemical Reagent Co., Ltd., Beijing, China, analytically pure. Shell-based PAC was purchased from Heatton Environmental Protection Technology Co., Ltd. (Shanghai, China). The main properties of PAC are listed in Table 1. Polyvinylidene fluoride (PVDF) flat-sheet UF membrane purchased from AMF (USA) with molecular weight cut-off of 100 kDa was used in this study.

Water was collected from a city sewage treatment plant. The raw water was filtered through a membrane with 0.45 μm nominal pore size within 24 h of collection. Some water quality characteristics of the sample used in the study are summarized in Table 2.

### 2.2. Experimental setup

The schematic diagram of the UF experiment is shown in Fig. 1. The volume of UF filter bowl (Millipore, Amicon 8400, USA) was 400 mL. The operation pressure was controlled by a pressure gauge connected to a nitrogen-pressurized solution reservoir. The filtration experiment was performed in dead-end mode at room temperature with a constant pressure of 0.10 MPa. During the experiment, the permeate flux was recorded using an electronic scale connected to a computer, logging the data every 1 min automatically.

During the experiment, the same conditions of the test ran parallel to three filtration cycles and every period lasting 15 min. The sample was fetched in every period of filtration. At the end of every period, the UF was washed by adding 200 mL ultrapure water in the UF filter bowl which placed on a magnetic mixer with revolving speed 250 rpm for 2 min.

Table 1
Characteristics of powdered activated carbon

| Parameter | Description |
|---|---|
| Raw material | Apricot shell |
| Granularity (mesh) | 200–300 |
| Specific surface area ($m^2/g$) | 821 |
| Average pore diameter (μm) | 11.15 |
| Iodine number (mg/g) | 700–1,000 |
| Methylene blue (mg/g) | 100–150 |

### 2.3. Analytical methods

The DOC concentration was measured using a Shimadzu TOC-VCPH analyzer (Japan). Excitation emission matrix fluorescence (EEM) measurements were conducted using a spectrofluorometer (F-4600, Hitachi, Japan). Zeta potential of the solution was measured by zeta potential analyzer (Brookhaven Instrument, USA). Membrane surface zeta potential was determined using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Graz, Austria). The contact angle between the organism and the UF membrane was determined using DSA100-type optical contact angle measuring instrument (KRUSS Co., Germany). Microbial community structure was determined by Illumina HiseqV4 PE250 (Illumina, USA.) high-throughput sequencing platform.

Environment of microbial DNA samples which were tested successfully will be subjected to polymerase chain reaction amplify mix and database establish at a set of modules. Finally, the samples are distinguished using the set of tag sequences. Then on the Illumina HiseqV4 PE250 high throughput sequencing platform, the samples of qualified DNA sequences were sequenced.

Table 2
Source water quality indexes

| Parameter | Value |
|---|---|
| Turbidity (NTU) | 0.10 |
| TP (mg/L) | 1.73 |
| UV254 ($cm^{-1}$) | 0.023 |
| pH | 7.66 ± 0.1 |
| Ammonia nitrogen (mg/L) | 1.86 |
| DOC (mg/L) | 28.28 |

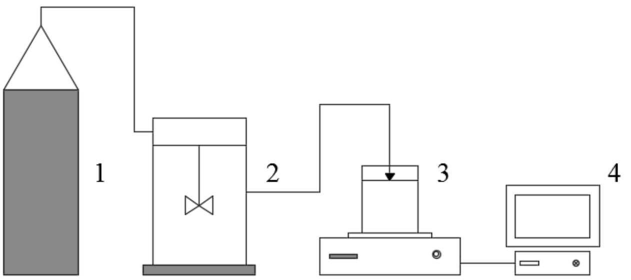


Fig. 1. The schematic diagram of UF experiment: (1) nitrogen gas, (2) UF filter bowl, (3) electronic scale, and (4) computer.

### *2.4. Analytical methods*

#### *2.4.1. The calculation of membrane flux and membrane resistance*

During the experiment, the permeate flux was described by using the normalized flux ($J/J_0$). The membrane flux could be estimated by Eq. (1).

$$J = \frac{V}{A\mathrm{t}} \tag{1}$$

where $J$ is permeate flux (L/(m$^2$·h)); $V$ is filtration volume (m$^3$); $A$ is effective filtration area (m$^2$); and $t$ is filtration time (h).

In this study, the analysis of fouling resistance distribution would favor the identification of fouling mechanisms. Total membrane resistance ($R_t$) was divided into membrane resistance ($R_m$) and the total fouling resistance ($R_f$), which was the sum of reversible fouling resistance ($R_r$) and irreversible fouling resistance ($R_i$).The reversible and irreversible fouling resistance could be determined with the normalized flux after the membrane cleaning [14].

$$R_t = R_m + R_f = R_m + R_r + R_i \tag{2}$$

Every kind of fouling resistance could be calculated as follows:

$$R_m = \frac{(J_0 - J_{s1})}{J_0} = \frac{1 - J_{s1}}{J_0} \tag{3}$$

$$R_{\mathrm{i}n} = \frac{(J_{s1} - J_{pn})}{J_0} \tag{4}$$

$$R_{\mathrm{r}n} = \frac{(J_{\mathrm{p}n} - J_{en})}{J_0} \tag{5}$$

where $R_{\mathrm{i}n}$ is the irreversible fouling of a filtration cycle $n$, $R_{\mathrm{r}n}$ is the reversible fouling of a filtration cycle $n$, $J_0$ is the flux of the new membrane (L/(m$^2$·h)), $J_{s1}$ is the initial flux in the first cycle (L/(m$^2$·h)), $J_{pn}$ is the flux at the end of the $n$ period after backwashing (L/(m$^2$·h)), $J_{en}$ is the flux at the end of the $n$ period (L/(m$^2$·h)), and $n$ is filtration cycle ($n$ = 1,2,3).

#### *2.4.2. The x-DLVO theory calculation method*

The x-DLVO theory account for the AB interaction energy in addition to the LW and EL interaction energies according to Eq. (6) [12,15,16] is as follows:

$$U_{mlf}^{\mathrm{XDLVO}} = U_{mlf}^{\mathrm{LW}} + U_{mlf}^{\mathrm{AB}} + U_{mlf}^{\mathrm{EL}} \tag{6}$$

where $U_{mlf}^{\mathrm{XDLVO}}$ is the total interaction energy between the membrane and natural organic matter, $U^{\mathrm{LW}}$, $\mathrm{U}^{\mathrm{AB}}$, and $\mathrm{U}^{\mathrm{EL}}$ are the LW, AB, and EL interaction terms, respectively. The subscripts $m$, $l$, and $f$ correspond to the membrane, bulk feed solution, and foulants, respectively.

The interfacial interaction energy between organic and UF membrane is as follows:

$$U_{ml\mathrm{f}}^{\mathrm{LW}}(d) = 2\pi\Delta G_{d_o}^{\mathrm{LW}} \frac{d_o^2 a_f}{d} \tag{7}$$

$$U_{mlf}^{\mathrm{AB}}(d) = 2\pi a_f^{\lambda} \Delta G_{d_o}^{\mathrm{AB}} \exp[\frac{d_o - d}{\lambda}] \tag{8}$$

$$U_{mlf}^{\mathrm{EL}}(d) = \pi\varepsilon_r\varepsilon_0 a_f [2\zeta_f\zeta_m \ln(\frac{1+e^{-\kappa d}}{1-e^{-\kappa d}}) + (\zeta_f^2 + \zeta_m^2)\ln(1 - e^{-2\kappa d})] \tag{9}$$

The interfacial interaction energy between organic matter and cake layer is as follows:

$$U_{flf}^{\mathrm{LW}}(d) = 2\pi\Delta G_{d_0}^{\mathrm{LW}} d_0^2 \frac{a_1 a_2}{d(a_1 + a_2)} \tag{10}$$

$$U_{flf}^{\mathrm{AB}}(d) = \frac{2\pi a_1 a_2}{a_1 + a_2} \lambda \Delta G_f^{\mathrm{AB}} \exp(\frac{d_0 - d}{\lambda}) \tag{11}$$

$$U_{flf}^{\mathrm{EL}}(d) = \pi\varepsilon_0\varepsilon_r \frac{a_1 a_2}{a_1 + a_2} \varsigma_f^2 \ln(1 + e^{-\kappa d}) \tag{12}$$

where $a_1$ and $a_2$ is the apparent hydrodynamic radius of two spherical organic compounds, respectively, which is particle size; $d$ is the distance between two planes; $\varepsilon_r$ is the relative dielectric constant of solution, 81.5; $\varepsilon_0$ is vacuum dielectric constant of 8.85 × 10$^{-12}$ F/m; $\kappa$ is the reciprocal of Debye shielding length, 10193776.59 m$^{-1}$; $\zeta_m$ is the Zeta potentials of membrane (V); and $\zeta_f$ is Zeta potential of pollutants (V).

## 3. Results and discussion

### *3.1. Membrane flux and fouling resistance analysis*

In order to investigate the membrane fouling mechanism of treating reclaimed water by three different processes of direct UF, PAC-UF, and BPAC-UF, during the experiment, PAC and BPAC with different concentrations (10, 40, and 60 mg/L) were added to the raw water, UF was performed after adsorption and degradation of 24 h. Then the change of normalized membrane flux ($J/J_0$) in the three filtration cycles are shown in Fig. 2(a), the distributions of intrinsic membrane resistance ($R_m$), irreversible fouling resistance ($R_i$) and reversible fouling resistance ($R_r$) at the optimum dosage were calculated and are illustrated in Fig. 2(b).

As shown in Fig. 2(a), there was a big difference in membrane flux change while treating reclaimed water with three different treatment processes. During the filtration periods, it is clearly indicated that membrane flux decline continuously with the final $J/J_0$ were 0.51, 0.46, and 0.44 at the end of the three filtration periods. By direct UF process, with different amounts of PAC were added, the membrane flux decreasing with the increase of the dosage. However, there is a most appropriate dosage (40 mg/L) for BPAC and adding less or more BPAC than it will result in a sharp decrease in membrane flux.

While comparing the membrane flux of reclaimed water treated by three different processes was: BPAC + UF (40 mg/L) > PAC + UF (10 mg/L) > UF, this can be explained that the excess PAC which leads to rate of the filter cake layer formation acceleration, the packing was dense, blocking the membrane pores, and thus lead to a more rapid decline of membrane flux [17]; in addition, the BPAC particles compared with PAC, the structural properties have changed by attaching to the viscous microbial metabolites on the surface which result in the particle size increases and a certain thickness of the frame structure could be formed on the surface of the membrane with the appropriate dosage, which result in the reduce of the filtration resistance and decline the transmembrane pressure difference [18]. What's more, the reason for this phenomenon is that BPAC carries extracellular polymers and microorganisms, and BPAC would acted as both an adsorbent and flocculant, which contributed to improving membrane flux by reducing the adsorption and filling of contaminants in the membrane surface or membrane pores [19].

According to Fig. 2(b), both intrinsic membrane resistance of direct UF process and PAC/BPAC process that under the optimum dosage were around 0.10, which reduces the influence of intrinsic membrane resistance on the reversible and irreversible pollution, furthermore the irreversible fouling resistance was increased continuously with the filtration goes on, this can be explained that membrane pores were constantly blocked by organic pollutants and lead to membrane fouling becoming serious correspondingly. In the end of the first period, the irreversible fouling resistance with a most appropriate dosage was 0.45, 0.40, and 0.42, respectively, and then irreversible membrane fouling of UF and 10PAC + UF increased dramatically.

It can be seen from Fig. 2(b) that the increase of 40BPAC + UF is relatively slow, and irreversible resistance value was smaller than direct filtration and PAC + UF process. While the conclusion was consistent with the effect of different dosage on membrane flux, and it is obvious to observe that the viscosity of the surface of BAPC filter cake layer could reduce the irreversible fouling resistance, which result in the recovery of membrane flux after backwashing was better.

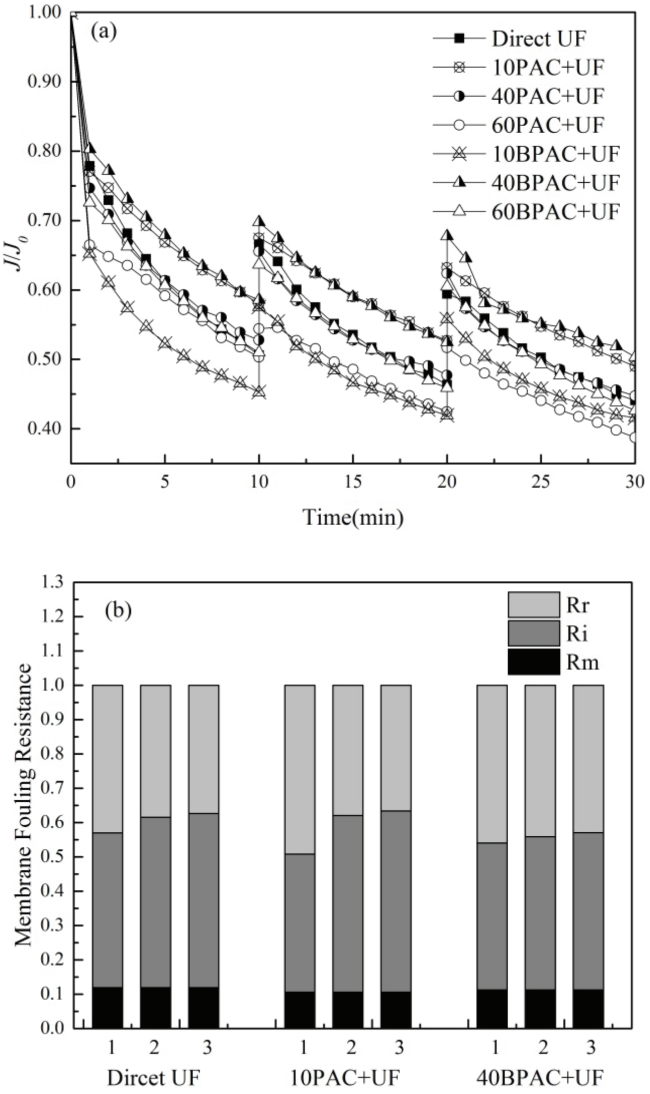


Fig. 2. (a) Normalized membrane flux and (b) membrane contamination resistance distribution situation by three different treatment process.

### 3.2. The water quality of membrane effluent by different processes

#### 3.2.1. The removal effect of DOC

In order to study the effect of three different processes on the membrane filtration performance in the process of reclaimed water, the raw water was adsorbed and degraded by PAC and BPAC (10 mg/LPAC, 40 mg/LBPAC), and then compared with the direct UF water sample. The DOC content in membrane influent and membrane effluent was detected, and the result is shown in Fig. 3.

The results showed that before UF test, the membrane influent DOC was the initial DOC content in the raw water, and the DOC content in the solution after 10 PAC adsorption was the lowest. This is because the PAC powder

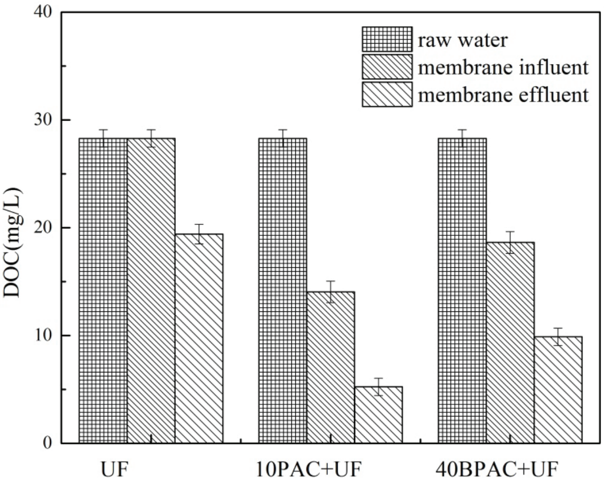


Fig. 3. The removal of DOC by three different processes.

activated carbon is fresh, can give full play to its adsorption performance, and the biological activated carbon adsorption capacity is mature, the adsorption capacity is greatly reduced by microbial filling, so the removal of DOC mainly rely on biodegradation. After UF experiments, the DOC in the three processes decreased in different degrees, and the removal rates were 31.4%, 62.7%, and 47.1%, respectively, this is because the PAC on the solution of small and medium molecular weight organic matter has a significant removal, while BPAC can be a good degradation of macromolecular organic matter, after a certain hydraulic retention time, membrane influent in the small and medium molecular organic content increased, because the membrane pore size of UF membrane of small molecular retention effect is limited, so UF and BPAC-UF process effluent DOC value is higher than the value of PAC-UF [20].

### *3.2.2. The EEM analysis of organic compounds before and after membrane UF*

During the test, the three-dimensional fluorescence analysis of raw water and the solution in best dosage of PAC/BPAC was carried out to further reveal the classification and content of organic matter in the solution after three kinds of processes, so as to explore the membrane fouling performance of different processes, the results are shown in Fig. 4.

It is clear from Fig. 4 that the direct UF, 10PAC-UF and 40BPAC-UF processes have reduced the fluorescence intensity of the solution before treatment. There were only two obvious peaks in the water samples treated by direct UF and 10PAC-UF process, namely, protein-like organic matter and homo-lysine. And 40BPAC-UF water samples had three peaks, more of a soluble microbial metabolites peak, which is considered to be related to the protein-like substances produced by microbial degradation [21], indicating that microbes play an important role in the removal of protein-like organic matter [22].

As shown in Table 3, for protein-like organic matter, the removal rate of PAC and BPAC by UF before of organic compounds in solution is 42.2% and 70.1%, respectively. The fluorescence intensity values of UF, PAC-UF, and BPAC-UF were lower than those before UF, and the peak reduction rates were 68.2%, 53.1%, and 19.8%, indicating that UF had a certain effect on the interception of organic matter. Moreover, the results showed that the concentration before UF of amino acids in the solution was 22.3% and 75.2%, which indicated that the adsorption of PAC and the degradation of microorganisms were the best, furthermore, for the three different processes of UF, PAC-UF, and BPAC-UF, the removal rate of UF were 63.7%, 66.3%, and 8.8%, indicating the UF membrane can retain large organic molecules is very good, the removal rate can reach more than 60%, but for small molecular biological degradation after the interception ability is limited, the removal rate is only 8.8%.

In the course of the experiment, the microorganism in the BPAC-UF combined process solution was characterized by high-throughput sequencing, and the microbial population structure was further studied, discussing the mechanism of membrane fouling in the process of reclaimed water. The community structure of BPAC samples of the order level and the ratio of major bacterial colonies are shown in Fig. 5.

As shown in Fig. 5(a), the microbes in the sample before and after adsorption on BPAC include the following colonies: *Burkholderiales*, *Nitrosomonadales*, *Rhizobiales*, *Rhodospirillales*, *Caulobacterales*, *Sphingobacteriales*, *Myxococcales*, *Cytophagales*, *Planctomycetales*, *Nitrospirales*, and other 20 kinds of main microbial colonies.

Fig. 5(b) shows the five main microbial colonies in the sample, the proportion of *Burkholderiales*, *Cytophagales*, *Sphingobacteriales*, and *Planctomycetales* is higher than that before the adsorption, while the proportion of *Rhizobiales* is reduced, this is because the above microbial can in aerobic condition with ammonium, nitrate and most amino acids as a nitrogen source, can also through the organic autotrophic and heterotrophic uptake in the solution to meet the needs of metabolism, some strains can reduce nitrate to nitrite as well. *Rhizobiales* can flourish only when the atmospheric pressure is less than 0.01 atm. In addition, the *Cytophagales* can form an extracellular polymeric substance that causes the attachment to become rather sticky, whereas older strains of cells in the *Planctomycetales* can develop into mucus handles [23]. This can explain the phenomenon of new peak in EEM detection of BPAC-UF membrane effluent.

## *3.3. The interfacial interaction energy analysis*

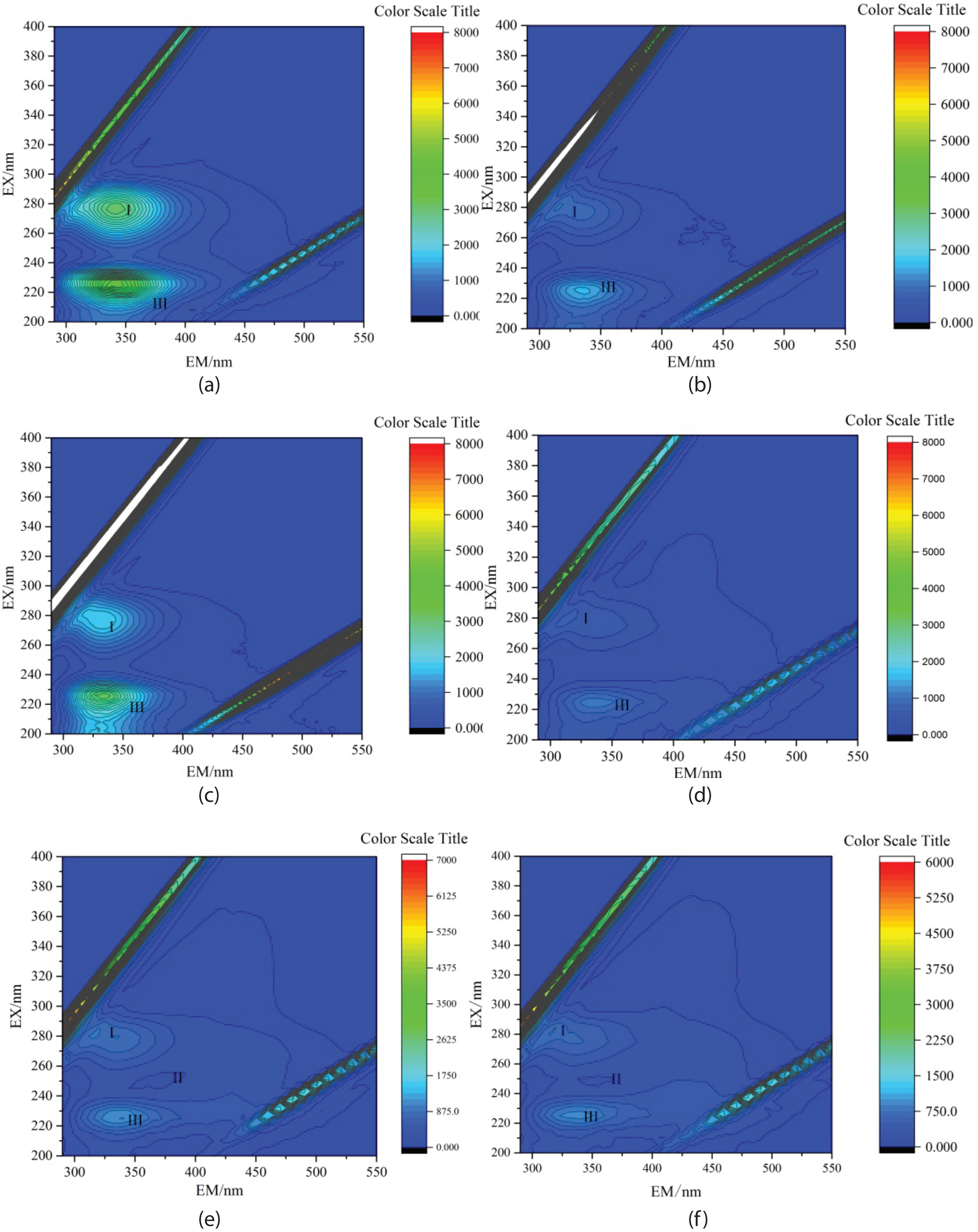
In the experiment, the contact angle between the organic matter (organic matter in raw water, raw water by PAC after the adsorption of organic matter, and water adsorption by BPAC degradation of organic matter) and the surface of the UF membrane was measured by the method of sessile drop method, and the interaction energy of the interface was calculated according to the x-DLVO theory.

The contact angle and Zeta potential data of UF membrane and organic matter are shown in Table 4. Under pure water conditions, the contact angle is less than 90 degrees, which is hydrophilic. Therefore, the hydrophilicity of PVDF membrane and BPAC organics is larger, but the hydrophilicity of raw water and PAC organics is smaller. Studies have shown that [24,25] the membrane fouling of organic hydrophilic stronger caused by more serious, so the membrane pollution of raw water by organic BPAC adsorption after degradation caused by more serious, and the original organic matter in water and the organic film after adsorption is light pollution PAC.

### *3.3.1. Interfacial energy at the early stage of UF*

In the early stage of UF, the adhesion stage occurs when the minimum equilibrium distance between organic substance and UF membrane is reached. In Fig. 6, the interfacial effects of the change of the distance between the organics and the UF membrane in the three process solutions are demonstrated, and the adhesion freedom energy of each part is shown in Table 5.

It can be seen from Fig. 6 that AB action is dominate and is consistent with the general trend of interaction. Related studies show that both LW and EL are long distance forces, so the change is weaker in 10 nm range, while the AB action is short-range force, and it decreases sharply with the increase of distance [26,27]. Therefore, in the adhesion stage, AB acts as a dominant pollutant in the short distance interface between organic compounds and UF membranes.

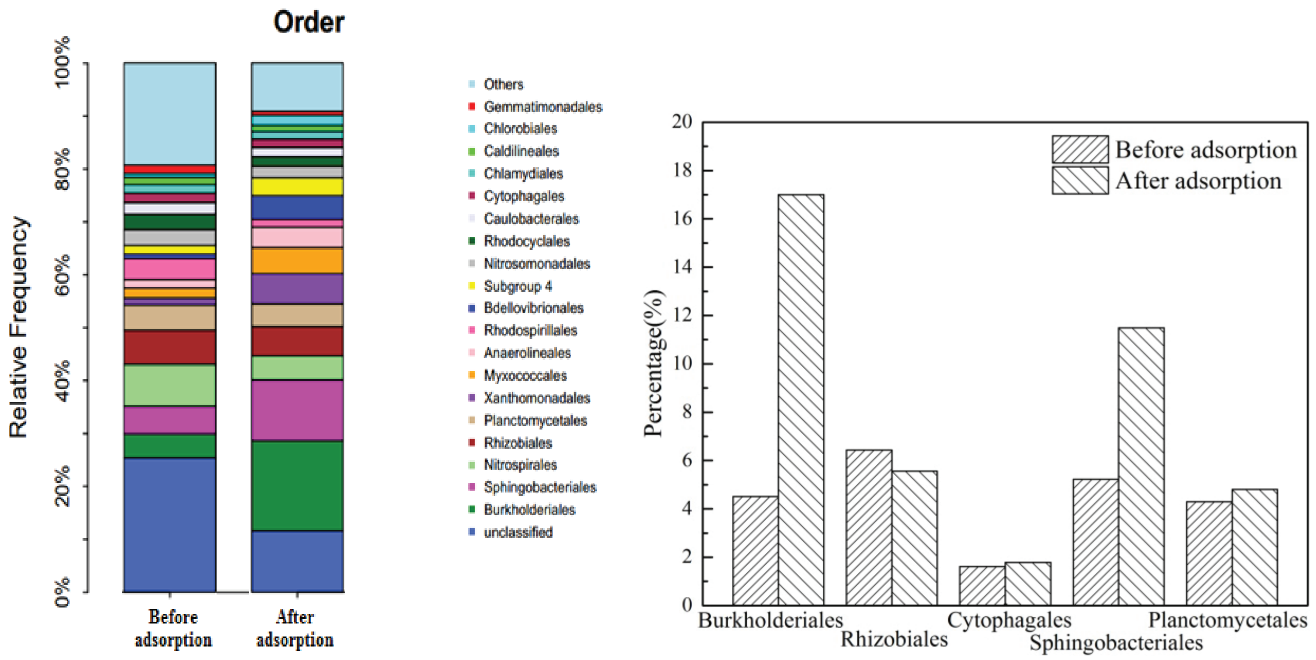


(a) (b) (c) (d) (e) (f)

Fig. 4. EEM of water samples before and after UF by different combination process: (a) raw water, (b) direct UF, (c) PAC, (d) PAC+UF, (e) 40BPAC, (f) 40BPAC+UF.

Table 3
The peak position and intensity of fluorescent substances in each treatment unit

| Water sample | Protein organic matters | | Dissolved microbial metabolites | | Class of lysine | |
|---|---|---|---|---|---|---|
| | λex/λem (I) | Peak intensity | λex/λem (II) | Peak intensity | λex/λem (III) | Peak intensity |
| Raw water | 276/342 | 3,138 | – | – | 228/342 | 4,205 |
| Direct UF | 276/318 | 998 | – | – | 226/333 | 1,532 |
| 10PAC | 278/338 | 1,814 | – | – | 226/334 | 3,266 |
| 10PAC + UF | 280/315 | 850 | – | – | 225/335 | 1,100 |
| 40BPAC | 285/315 | 939.6 | 250/370 | 271.8 | 225/335 | 1,044 |
| 40BPAC + UF | 285/320 | 753.5 | 250/355 | 230.6 | 225/340 | 952.5 |



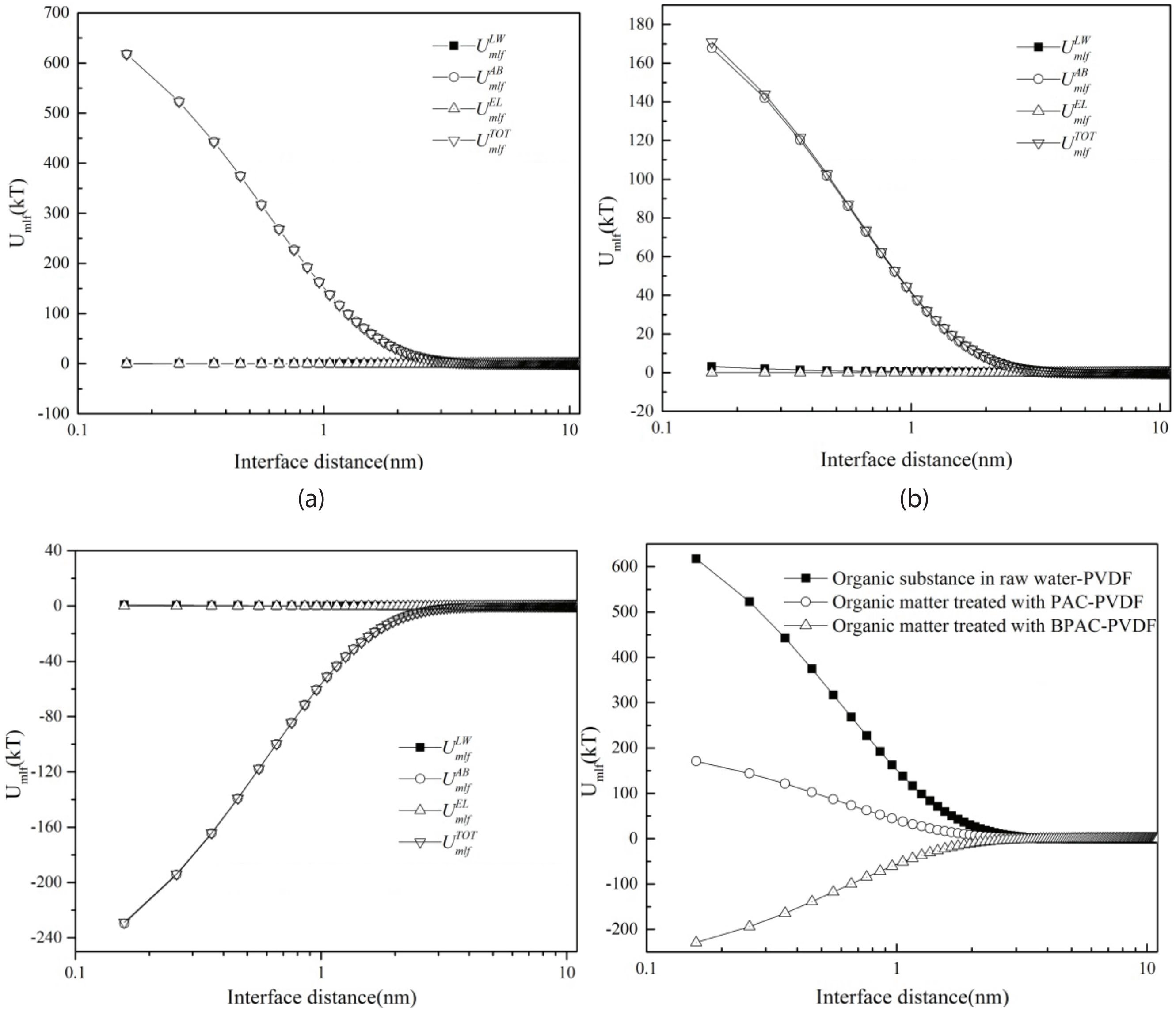
(a) (b)

Fig. 5. BPAC samples in the order level of colony chart: (a) the colony structure distribution of BPAC samples and (b) percentage of major colonies before and after BPAC sample adsorption.

Table 4
Contact angles and zeta potentials of PVDF membrane and organic matters

| Substance | Contact angle (°) | | | Zeta potential data (mv) | Particle size (nm) |
|---|---|---|---|---|---|
| | Pure water | Formamide | Diiodomethane | | |
| PVDF | 69.52 (±1.6) | 64.06 (±1.2) | 77.59 (±1.9) | –15.92 (±0.2) | – |
| Organic matter in raw water | 32.99 (±3.2) | 52.28 (±2.6) | 72.05 (±2.7) | –35.63 (±0.9) | 8.7 (±0.2) |
| organic matter treatment with PAC | 50.04 (±2.4) | 56.11 (±3.2) | 58.54 (±3.6) | –18.83 (±1.2) | 6.5 (±0.6) |
| organic matter treatment with BPAC | 67.37 (±3.5) | 54.31 (±2.0) | 67.89 (±3.4) | –19.07 (±0.5) | 4.2 (±0.5) |

As can be seen from Table 5, the total energy of organic matter in raw water and organic matter after PAC treatment is positive, while BPAC is negative. Studies have shown that the interaction energy of the interface is negative, indicating mutual attraction, while the positive value indicates mutual repulsion, this shows that organic compounds in raw water and organic matter after PAC treatment are not easy to adhere to the surface of the membrane [12]. After BPAC treatment, the organic matter is more likely to stick to the surface of the membrane, causing membrane fouling and speeding up the process of membrane fouling. Furthermore, the organic matter in raw water by BPAC adsorption and degradation, the macromolecule organic matter is transformed into small molecule organic matter, and the proportion of organic matter in water is increased, while small organic matter is more likely to cause pore-blocking pollution, so the



(a) (b)

(c) (d)

Fig. 6. The interfacial energy of organic matter and ultrafiltration membrane: (a) Organic substance in raw water-PVDF, (b) Organic matter treated with PAC-PVDF, (c) Organic matter treated with BPAC-PVDF, (D) $U_{mlf}^{ToT}$

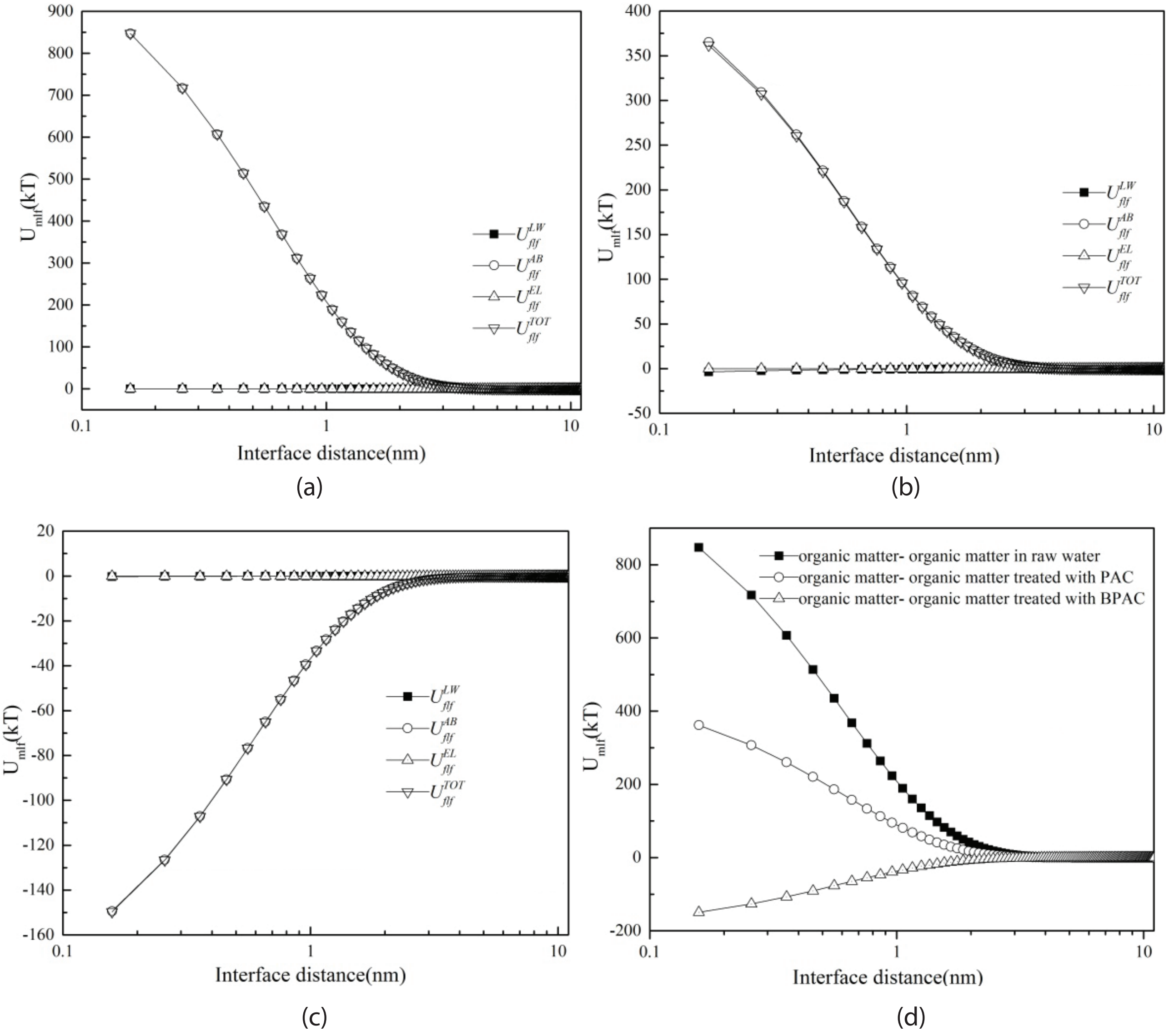
Table 5
The free energy of adhesion between different organic compounds and PVDF films

| | $\Delta G_{mlf}^{LW}$ | $\Delta G_{mlf}^{AB}$ | $\Delta G_{mlf}^{EL}$ | $\Delta G_{mlf}^{TOT}$ |
|---|---|---|---|---|
| Organic matter in raw water | –0.0051 | 18.84 | –7.79 | 11.04 |
| Organic matter treated with PAC | 0.51 | 7.00 | –3.96 | 3.55 |
| Organic matter treated with BPAC | 0.16 | –11.83 | –4.01 | –15.68 |

raw water after BPAC treatment of organic matter is more likely to cause membrane fouling. Therefore, after different treatment, the fouling of UF membrane caused by organics is in turn: organic matter treated with BPAC > organic matter treated with PAC > organic substance in raw water. This is consistent with the previous contact angle analysis.

### 3.3.2. The interfacial action at the later stage of UF

By the end of the experiment, organic matter accumulates in the membrane surface, and gradually formed the cake layer, then the interaction between the organism and the UF membrane is gradually weakened, the interface interaction between the organic and the cake layer gradually exposed, produce the cohesion stage. Fig. 7 shows the interaction energy between the organic compounds and the cake layer with the change of interface distance in the three process solutions.



(a) (b)

(c) (d)

Fig. 7. Interfacial interaction energy between organic matter and interfacial distance: (a) Organic matter- organic matter in raw water, (b) Organic matter-organic matter with PAC, (c) Organic matter-organic matter treated with BPAC, (D) $U_{mlf}^{ToT}$

As can be seen from Fig. 7, the tendency of interfacial interaction energy in the viscous phase is consistent with the trend of adhesion in Fig. 6; in the interfacial interaction energy, the role of AB is dominant, while the role of AB and EL in the micro range of 0.1–10 nm is not obvious. At the same time, it is observed in Table 6 that the interfacial energy of BPAC organics remains attractive, consistent with the total free energy previously analyzed, this shows that the organic compounds adsorbed by BPAC are more likely to accumulate on the surface of the membrane to form the cake layer, small molecules are more likely to cause membrane hole plugging, so the film fouling of the filter cake layer is the most serious.

Table 6
The free energy of adhesion between organic matter and organic matter in cake layer

| | $\Delta G^{LW}_{flf}$ | $\Delta G^{AB}_{flf}$ | $\Delta G^{EL}_{flf}$ | $\Delta G^{TOT}_{flf}$ |
|---|---|---|---|---|
| Organic matter in raw water | –0.00011 | 51.13 | –16.74 | 34.39 |
| Organic matter treated with PAC | –1.14 | 30.53 | –4.68 | 24.71 |
| Organic matter treated with BPAC | –0.11 | –15.39 | –4.80 | –20.30 |

## 4. Conclusion

(1) The normalized membrane flux of reclaimed water treated by three different processes decreases in different degrees. Adding appropriate amount of PAC/BPAC (PAC 10 mg/L, BPAC 40 mg/L) can increase the membrane flux of PAC/BPAC-UF combined process and alleviate membrane fouling. At the optimum dosage, the irreversible membrane fouling resistance of the BPAC-UF process increases most

slowly and is lower than that of direct UF and PAC-UF process with the filtration cycle.

(2) PAC-UF combination process is superior to UF and BPAC-UF in the removal of DOC. BPAC-UF combination process is superior to PAC-UF and UF in the EEM detection of two stage effluent, and the emergence of soluble microbial metabolite fluorescence Peak II confirms the importance of BPAC biodegradation. Microorganisms such as *Burkholderiales*, *Cytophagales*, *Sphingobacteriales*, *Planctomycetales*, and so on which growing on the surface of BPAC can enhance the degradation and removal of organic compounds in water.

(3) Combining x-DLVO theory to analyze the whole process of membrane fouling, the polar force plays a leading role in the whole membrane fouling process. The interaction force between organics which are in raw water or treated with PAC and UF membrane is repulsive, but the interaction force between organics treated with BPAC and UF membranes is attractive. Therefore, membrane fouling caused by organic compounds which are adsorbed and degraded by BPAC in raw water is the most serious.

## Acknowledgments

This work was supported by the Funds for the National Natural Science Foundation of China (Grant no.: 51678027).

## References

[1] A.D. Benetti, Water reuse: issues, technologies, and applications, Eng. Sanit. Ambient, 13 (2007) 247–248.

[2] A. Takashi, D.L. Audrey, Wastewater reclamation, recycling and reuse: past, present, and future, Water Sci. Technol., 33 (1996) 1–14.

[3] H. Wang, F. Qu, A. Ding, H. Liang, R.B. Jia, K. Li, L.M. Bai, H.Q. Chang, G.B. Li, Combined effects of PAC adsorption and in situ, chlorination on membrane fouling in a pilot-scale coagulation and ultrafiltration process, Chem. Eng. J., 283 (2016) 1374–1383.

[4] S.L. Xia, Y.N. Liu, X. Li, Drinking water production by ultrafiltration of Songhuajiang River with PAC adsorption, J. Environ. Sci., 19 (2007) 536–539.

[5] J.Y. Hu, R. Shang, H.P. Deng, Evaluation of PAC Effect in Integrated PAC/UF System for Surface Water Treatment, International Conference on Bioinformatics and Biomedical Engineering, ICBBE, 2010, pp. 1–4.

[6] L.J. Xie, W.Y. Li, J. Chen, Q. Chen, B. Dong, Study on removal characteristics of PAC-UF integrated process for MCs., Technol. Water Treat., 7 (2010) 92–95, 99.

[7] M. Zhang, C. Li, M.M. Benjamin, Y. Chang, Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment, Environ. Sci. Technol., 37 (2003) 1663–1669.

[8] B.Z. Dong, J. Feng, Y. Chen, N.Y. Gao, Effect of properties of organics on ultrafiltration membrane flux, J. Tongji Univ. (Nat. Sci.), 35 (2007) 356–360.

[9] S.J. Lee, Fouling characteristics of ceramic microfiltration and ultrafiltration membranes during surface water treatment, Georgia Institute of Technology, 2013.

[10] F.G. Meng, H.M. Zhang, F.L. Yang, L.F. Liu, Characterization of cake layer in submerged membrane bioreactor, Environ. Sci. Technol., 41 (2007) 4065–4070.

[11] Y. Zhang, J.Y. Tian, J. Nan, S. Gao, H. Liang, M. Wang, G. Li, Effect of PAC addition on immersed ultrafiltration for the treatment of algal-rich water, J. Hazard. Mater., 186 (2011) 1415–1424.

[12] J.A. Brant, A.E. Childress, Assessing short-range membrane–colloid interactions using surface energetics, J. Membr. Sci., 203 (2002) 257–273.

[13] J.A. Brant, A.E. Childress, Membrane-colloid interactions: comparison of extended DLVO predictions with AFM force measurements, Environ. Eng. Sci., 19 (2002) 413–427.

[14] D. Jermann, W. Pronk , S. Meylan , M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res., 41 (2007) 1713–1722.

[15] L. Gourley, M. Britten, S.F. Gauthier, Y. Pouliot, Characterization of adsorptive fouling on ultrafiltration membranes by peptides mixtures using contact angle measurements, J. Membr. Sci., 97 (1994) 283–289.

[16] S.D. Yao, X.Y. Gao, B.N. Guo, H.J. Xie, S. Liang, Reverse osmosis membrane fouling by humic acid using XDLVO approach: effect of calcium ions, Environ. Sci., 33 (2012) 1884–1890.

[17] Y.Q. Wang, W.Y. Lu, D.J. Tan, Z.Y. You, Study on membrane fouling control with activated carbon, Water Wastewater Eng., 33S1 (2007) 131–134.

[18] W. Wang, C.Z. Yang, W.H. Pu, H.B. Liu, Treatment of domestic wastewater using PAC-DMBR, Environ. Sci. Technol., 30 (2007) 64–65.

[19] Y.Z. Li, Y.L. He, Y.H. Liu, S.C. Yang, G.J. Zhang, Comparison of the filtration characteristics between biological powdered activated carbon sludge and activated sludge in submerged membrane bioreactors, Desalination, 174 (2005) 305–314.

[20] Z. Li, Y.H. Gao, L. Cai, H.P. Deng, J. Shi, A comparative study of PAC-MBR and BPAC-UF process on treatment of micro-polluted raw water, Technol. Water Treat., 42 (2016) 92–95.

[21] P.Q. Fu, C.Q. Liu, F.C. Wu, Three-dimensional excitation emission matrix fluorescence spectroscopic characterization of dissolved organic matter, Spectrosc. Spectral Anal., 25 (2005) 2024–2028.

[22] L.L. Yao, X. Tu, H.B. Yu, D.Y. Xu, L. Han, Y.H. Song, Evaluation of dissolved organic matter removal in municipal wastewater based on fluorescence regional integration, Chin. J. Environ. Eng., 7 (2013) 411–416.

[23] M. Hashino, K. Hirami, T. Ishigami, I.Y. Ohmuka, T. Maruyama, N. Kubota, H. Matsuyama, Effect of kinds of membrane materials on membrane fouling with BSA, J. Membr. Sci., 384 (2011) 157–165.

[24] T. Carroll, S. King, S.R. Gray, N.A. Booker, The fouling of microfiltration membranes by NOM after coagulation treatment, Water Res., 34 (2000) 2861–2868.

[25] Y.W. Liu, X. Li, Y.L. Yang, D.Z. An, J.W. Ren, Z.W. Zhou, R.B. Jia, W.C. Song, Effect of raw water and sedimentation effluent on fouling control of PAC/UF integrated process, J. Harbin Inst. Technol., 2012.

[26] Y.X. Zhao, R.Q. Zong, X.Y. Gao, H.J. Xie, Y.Q. Yin, S. Liang, Fouling behavior of sodium alginate during microfiltration at various ionic compositions: XDLVO approach, Environ. Sci., 35 (2014) 1343–1350.

[27] W. Gao, H. Liang, G.B. Li, Interface effect of three organic matters on ultrafiltration membrane fouling, China Water Wastewater, 29 (2013) 66–69.