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# Adsorption of CECs in the nanofiltration process

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ABSTRACT

Adsorption is one of the main mechanisms of compounds of emerging concerns (CECs) rejection by a membrane process. CECs could be adsorbed not only by membrane but also by suspended solid during membrane filtration. In this study, the adsorption of five CECs by natural organic matter (NOM) and NF270 was investigated by using 96-h bottle and batch tests at 25˚C, respectively. Humic acid (HA), which is the major ingredient of NOM, was added into Milli-Q water as NOM to simulate the natural water. HA added into the solution was found insolubility at pH 7 in this study. Adsorption of CECs by HA was strongly correlated with log $K_{\mathrm{ow}}$ of compound. Adsorption capacity was observed to be maximum with HA followed by NF. The study also found that the removal efficiency of CECs by NF could be affected by NOM present in the water. Micro-pollutants, such as CECs, could be adsorbed by HA and then be removed easily during the membrane filtration. Moderate existence of HA would be contributive for CECs removal, but too much HA would cause fouling phenomenon resulted in a worse removal efficiency.

*Keywords:* Adsorption; CECs; NOM; HA; Nanofiltration

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## 1. Introduction

The influence of water matrix on contaminants rejection by membrane filtration is still unclear. The removal of compounds of emerging concern (CEC) by membrane would be significantly influenced by the properties of water matrix, the membrane properties, and the compound characteristics. However, the phenomenon of adsorption has been always found between contaminants, membrane surface, and also water matrix. CECs could be adsorbed onto different kind of adsorbents, which has been proved in numerous studies. For example, most studies investigated the adsorption of CECs by activated sludge. Clara et al. examined the ability of adsorption of three CECs (bisphenol A, 17β-estradiol, and 17α-ethinylestradiol) by both activated and inactivated sludge [1]. The results indicated that the adsorption of CECs by sludge was significantly increasing with pH. The adsorption ratio of CEC was increasing from 45 to 80%, and there was no difference between the adsorption of CECs onto activated and inactivated sludge. The adsorption of 15 CECs by activated sludge has also been investigated in advance [2]. The study indicated that the increasing tendency of adsorption was occurred in the lower pH condition. The percentage of the adsorption of 15 CECs ranged from 4 to 61%, and endocrine disrupting chemicals had the better adsorption than pharmaceuticals and personal care products

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in the neutral pH condition. Xue et al. also examined the removal efficiency of 19 CECs by the membrane bioreactor [3]. They considered that the adsorption by sludge might be the major mechanism which caused the declination of the concentration of CECs in the water.

The past studies also proved that CECs could be adsorbed by activated carbon. Yang et al. investigated the removal efficiency of CECs by the GAC adsorption unit after membrane filtration of the wastewater reclamation plant [4]. The results showed that the average removal efficiency of 11 CECs (lincomycin—99.54%, levofloxacin—98.61%, dicolofenac—98.34%, ibuprofen—88.12%, trimethoprim—96.34%, ciprofloxacin—85.61%, erythromycin—82.95%, carbamazepine—73.55%, caffeine—44.93%, primidone—19.91%, and dEET—7.85%) is between 7.85 and 99.54%. In addition, the past study also indicated that the adsorption capacity of CECs would decrease over time due to the competition with other organic matters present in the water [5].

Adsorption is one of the main rejection mechanisms of membrane filtration to remove CECs from water. Adsorption between target compounds and membrane was strongly correlated with compound log $K_{ow}$ (Octanol–water partition coefficient) and membrane pure water permeability (PWP), and moderately correlated with compound water solubility [6]. A recent study by McCallum et al. included the investigation of adsorption, desorption, and steady-state rejection of 17β-estradiol (E2) by polyamide thin-film composite NF membranes [7]. The results showed that the adsorption of E2 by the membrane was enhanced during the initial phase of filtration and the desorption of adsorbed E2 to permeate happened when the membrane phase E2 concentration was greater than the equilibrium permeate concentration.

However, in the composition of water matrices, natural organic matters (NOMs) especially have been proved to affect on removal of CECs by membrane. Dolar et al. tested the removal of five CECs (sulfamethoxazole, trimethoprim, ciprofloxacin, dexamethasone, and febantel) in different water samples [8]. The results showed that the rejection of these five CECs was higher in simulated water and tap water than in Milli-Q water. Authors interpreted that the NOM could enhance the adsorption of CECs onto membrane surfaces, which increase both the size exclusion and electrostatic repulsion during the membrane filtration. Agenson and Urase indicated that fouling by NOM led to increased adsorption of CECs, produced narrower membrane pores but caused a higher diffusion of solutes across the membrane [9].

In view of the above-mentioned research results, it is undoubted that NOM and membranes have the potential to adsorb CECs during membrane filtration processes. Even there is a competition behavior between the NOM and adsorbent or membrane during the adsorption process [10–12]. However, there are few literatures discussing the adsorption of CECs by NOM rather than membranes, as it happens too fast for anyone to observe during the filtration process. In this study, batch reactors were carried out by using NF270 and humid acid (HA) as adsorbents to investigate the influence of adsorption of CECs on membrane filtration processes. HA was added as NOM to simulate the interaction between CECs and NOM in natural water. Five CECs removal efficiencies tested by NF270 in Milli-Q and artificial water samples were also investigated to figure out the real rejection ratio. This study attempts to understand the adsorption behaviors of CECs by NOM and the rejection ratio of adsorption during a NF process. The study also intends to explain the influence of NOM adsorption on CECs rejection by NF270.

## 2. Materials and methods

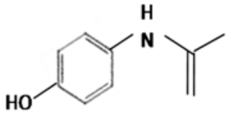
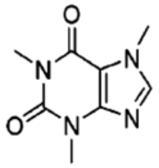
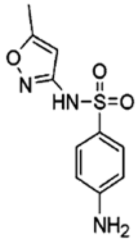
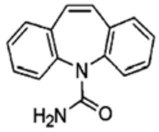
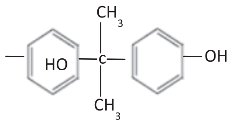
### 2.1. Compound selection and characterization

Five CECs, caffeine (CAF), acetaminophen (AMP), sulfamethoxazole (SFX), carbamazepine (CBZ), and bisphenol A (BPA), were chosen based on its value of log $K_{ow}$ to find the relationship between adsorption abilities and log $K_{ow}$ of CECs. These compounds are commonly found in the aquatic environment all over the world [1,13–18] and also represent different properties which are expected to influence its removal efficiency of membrane. A summary of the CEC physicochemical properties and their structures is presented in Table 1 [6,19–22].

### 2.2. Water selection and characterization

Three artificial water samples were prepared and investigated in this study ($W_1$, $W_2$, and $W_3$). Milli-Q water worked as a base matrix of each filtration test in this study. $W_1$, which was applied not only for the adsorption experiments but also for the filtration test, was only added into these five CECs in the range of 10–200 ng/L. $W_2$ and $W_3$, which were applied only for the filtration test, were added into not only these five CECs but also 4 and 24 mg/L HA, respectively. Characteristics of the $W_1$, $W_2$, and $W_3$ based on the analytical methods in section 2.7 are presented in Table 2. The different concentration of CECs was owing to their trace concentrations and different water solubility of each CECs in the water samples, which resulted in hard quantification and the deviation in

Table 1
Structures and physicochemical properties of the target CECs selected for this study

| CECs | Structure | Molecular Weight | pKa[a] (at 25˚C) | log $K_{ow}$ | Water solubility[a] (mg/L) |
|---|---|---|---|---|---|
| Acetaminophen (AMP) |  | 151.2 | 9.7 [b] (HL-neutral) | 0.46 | $1.4 \times 10^{4}$ |
| Caffeine (CFN) |  | 194.2 | 6.1 (HL-neutral) | −0.07 | $2.16 \times 10^{4}$ |
| Sulfamethoxazole (SFX) |  | 253 | 2.1 (HL-negative) | 0.89 | 610 |
| Carbamazepine (CBZ) |  | 236 | <2 (HB[b]-netural) | 2.45 | 17.7 |
| Bisphenol A (BPA) |  | 228.29 | 10.2 (HB-netural) | 3.32 | 120 |

[a] [6,19–22].

[b] HL = hydrophlic; HB = hydrophobic.

actual measured data, but the concentration of CECs was still in a reasonable range. The similar preparation was also found in the past studies [6].

### 2.3. Membrane characterization

NF270 (Dow Chemical Co., Filmtec NF270-400, Midland, MI) was applied in this study. The characteristics of NF270 are presented in Table 3. PWP and molecular weight cutoff (MWCO) associated with NF270 were determined by using a commercially available stainless steel cross-flow membrane filtration unit (GE OSMONICS). PWP provides an indication of the maximum flux that can be achieved by the membrane and was determined by taking the slop of the average flux of Milli-Q water through the membranes as measured over a range of feed pressure. The MWCO of a membrane represents the molecular weight of a molecule that is rejected at 90% and was estimated using the solute transport technique described by Singh et al. via rejection tests using solutions containing polyethylene glycol molecules (87976, Sigma–Aldrich, Oalville, ON) of varying molecular weights (200, 400, 600, 1,000, 2,000 Da) but at a constant solute concentration of 10 ppm by weight [23].

Membrane zeta potential was measured by using a SurPass electrokinetic analyzer (Anton Paar, Graz, Austria) following streaming current methodology described by Childress and Elimelech [24], which can be determined the charge of the membrane surface. Membrane contact angle is an index of the hydrophilic/hydrophobicity of a membrane. A contact angle less than 90˚ indicates that the membrane surface is hydrophilic, whereas the membrane surface is hydrophobic if a contact angle above 90˚. Thus, the hydrophobicity increases with the increase in the contact angle of membrane. The static contact angle of dry membrane samples was measured in triplicate via the

Table 2
Initial characteristics of the water samples

| Feed water samples | pH | Conductivity (μS/cm) | TOC (mg/L) | DOC (mg/L) | UV254 ($cm^{-1}$) | SUVA (L/m/mg) | CEC concentration (ng/L) |
|---|---|---|---|---|---|---|---|
| $W_1$ | 7.3 ± 0.2 | 2.3 ± 0.2 | 0.41 ± 0.22 | 0.02 ± 0.01 | 0.003 ± 0.00 | 0.0015 ± 0.00 | BPA:131.5<br>SFX:24.4<br>CAF:161<br>CBZ:194<br>AMP:81 |
| $W_2$ | 6.8 ± 0.2 | 107.4 ± 0.2 | 4.11 ± 0.22 | 0.27 ± 0.01 | 0.21 ± 0.04 | 0.078 ± 0.04 | BPA:174.9<br>SFX:48.8<br>CAF:125.4<br>CBZ:188.2<br>AMP:47.6 |
| $W_3$ | 6.8 ± 0.2 | 113.3 ± 0.2 | 23.97 ± 0.22 | 2.08 ± 0.01 | 0.71 ± 0.04 | 0.025 ± 0.04 | BPA:163.2<br>SFX:37.4<br>CAF:133.4<br>CBZ:138.1<br>AMP:75.8 |

sessile drop technique, described by Chen and Wada [25], with Milli-Q water (drop volume of approx. 10 μL) by using a first 10 Angstroms dynamic contact angle analyzer (FTA200, Folio Instruments Inc., Kitchener, ON).

### 2.4. Adsorption experiments

NF270 and NOM were used as the adsorbents in this study. Equilibrium adsorption experiments have been carried out to evaluate the adsorption capacity of NF270 and NOM. The 96 h batch and basin tests were performed to estimate the extent of mixed compounds adsorption for NOM and NF270, respectively. The batch adsorption of mixed CECs was studied in 100 mL amber vials containing 50 mL of $W_1$ with 0.2 mg NOM added. Reaction proceeded for 96 h at 25°C with shaking (200 rpm) in an incubator.

Bottle tests were performed in triplicate to estimate the extent of mixed CECs adsorption for NF270. A whole new NF270 coupon (19 × 14 cm), cut into small pieces (approx. 5 × 5 cm), was stuck on a piece of styrofoam (6 × 6 cm) with pins and floated on the sample water ($W_1$) in a close basin to estimate the adsorption capacity of NF270 surface. The experiments error control included consisting of $W_1$ and any potential compound losses due to adsorption on the basin wall.

The contacting time with 96 h was sufficient for equilibrium to be attained in the experiment [26]. And each water sample was completely contacted with targeted adsorbents for 96 h, then the suspension was sampled at 1, 8, 24, 48, 72, and 96 h, respectively. All samples were filtered through a 0.45-μm cellulose acetate membrane filter (MFS), subsequently extracted by a solid-phase extraction (SPE) procedure and analyzed by a LC/MS/MS system. All experiments were performed in duplicate, and the samples were analyzed triplicate for CECs by LC/MS/MS.

### 2.5. Filtration test

A cross-flow filtration apparatus with a flat-sheet of membrane cell which made by GE was used for all filtration tests. The surface area of the membrane was 140 $cm^2$ (14.6 cm (L) × 9.5 cm (W)), and the cross-sectional area was 1.9 $cm^2$ (9.5 cm (W) × 0.2 cm (H)). A new membrane (membrane sheets were stored in 1.5% of sodium meta-bisulfite ($Na_2S_2O_5$) to avoid oxidation and keep it wet) was used in each experiment. It was rinsed with Milli-Q water carefully and then conditioned by filtering with Milli-Q water for 24 h straight until the stable pure water permeate flux was established before starting the filtration tests. Following the initial step, pure water was replaced by each water sample in each run. And each water sample was filtrated for 96 h, then the permeate was sampled at 1, 8, 24, 48, 72, and 96 h, respectively, for analyzing. All experiments were operated in recycle mode, i.e. both permeated water and retention were recycled back to the feed reservoir. The water in the feed reservoir was about 10 L, which was enough to sample during the whole run. Operation conditions of filtration test were

Table 3
Characterization of NF270 used in this study

| Membrane | Material | MWCO (Da) | NaCl retention (%) | Average pore diameter (nm) | Zeta potential (mV) | Thickness (μm) | Contact angle (°) | Roughness ($R_{rms}$) (nm) | Pure water permeability ($L/m^2/h/kPa$) |
|---|---|---|---|---|---|---|---|---|---|
| NF-270 | Polyamide thin-film composite (TFC) | 300 | 40.0 | 0.84 | −22 (at pH 7) | 135 | 26 (clean membrane) | 1.279 (clean membrane) | 0.16 |

constant of which filtrating pressure was 70 psi, flow rate was 0.4 L/min, and temperature was controlled at 25 ± 2℃.

### 2.6. Solubility of humid acid

Humid acid is the major component part of NOM. It is necessary to understand the solubility of HA in the pH range of natural water environment to prove the hypothesis of this study, which is that CECs could be adsorbed on the NOM and removed by NF easily through rejection. The solubility of HA tested in this study was investigated at pH of 3, 7, and 10, respectively. One L Milli-Q water was added into 4 mg HA and then adjusted pH with sulfuric acid or sodium hydroxide. The pH adjusted water samples were prepared and stayed at 25℃ for 24 h. The completely mixed water samples were filtered through a 0.45-μm fiberglass membrane filter and then dried at 105℃ for 24 h for weighting to compare with the initial added weight to calculate the solubility of HA in different pH conditions.

### 2.7. Analytical method

All water samples for CECs analysis had been vacuum-filtered through a 0.45- and 0.22-μm cellulose acetate membrane filter, acidified to pH 4.0 by using sulfuric acid (2 N), and was stored at 4℃ until analysis. Oasis HLB cartridges (500 mg, 6 mL, Waters, Milford, MA, USA) used for SPE were preconditioned with 6 mL of methanol and 6 mL of deionized (DI) water. Aliquots of 400 mL water samples were spiked with $^{13}C_6$-sulfamethazine (employed as a surrogate) and loaded to the cartridge with flow rate of 3–6 mL/min. After sample passage, cartridges were rinsed with 6 mL DI water to remove excess EDTA-2Na and dried with a flow of nitrogen gas. After drying, analyte was eluted with 4 mL of methanol and 4 mL of methanol–diethylether (50:50, v/v). The elutes were collected, evaporated to dry with nitrogen stream, and reconstituted to 0.4 mL with 25% aqueous methanol. Final solutions were filtered through a 0.45-μm PVDF membrane filter.

CECs were analyzed by following the method which was developed by National Taiwan University (NTU) and conducted repeatedly for three times [27]. All analyses were conducted at NTU laboratory using an Applied Biosystem LC/MS/MS system (Sciex API 4000) with an Agilent 1200 LC (Agilent Technologies, Palo Alto, CA, USA), equipped with a

Phenomenex Luna $C_{18}$ column (150 × 4.6 mm, 5 μm). The method detection limits (MDLs) of these compounds are from 1 to 10 ng/L. Total organic carbon (TOC) was analyzed by using TOC Analyzer (O.I. Analytical Model 1010, Texas) with auto-sampler (O.I. Analytical Model 1051) for raw water samples, following the NIEA W532.51C (Taiwan Environment Analysis Laboratory, 2000). The MDLs for DOC were 0.22 mg/L.

## 3. Results and discussion

According to the results of both 96 h adsorption and filtration tests, five samples from the suspension or effluent of each run were taken at 1, 8, 24, 48, 72, and 96 h, and then the CECs concentration of samples was continuously measured in triplicate. Finally, the measured values were averaged from each run to obtain the average treated concentration. Removing efficiency of targeted compounds of each sample by both adsorption and NF rejection was calculated by Eq. (1):

$$R\ (\%) = \left(1 - \frac{C}{C_0}\right) \times 100\% \tag{1}$$

C symbolizes the concentration of CECs in water sample on the specific experiment time. $C_0$ is the initial concentration of the CECs spiked into each raw sample. Therefore, a $C/C_0$ value of 1.0 indicates no removal by the membrane or adsorbent, whereas a value of 0 indicates complete removal by the membrane or adsorbent.

### 3.1. Effect of pH on NOM solubility

The solubility of NOM at pH of 3, 7, and 10 presented in Table 4 obviously shows that the solubility of the HA used in this study is equal to zero both at acid and neutral environment. Therefore, it means that the NOM are insoluble in nature water and could be as absorbents for CECs adsorption. The observations of NOM at different pH have a significant difference, which are worthily mentioned and shown in Fig. 1. The color of solution with HA at pH of 3 is deeper than that at pH of 7 and 10. In addition, the cake on the filters surface could be easily observed the differences. The color of the cake also became deeper with the decrease of solution pH. Therefore, the phenomenon indicated that the solubility of HA in the solution was increasing with an increase of pH.

Table 4
The solubility of NOM at different pH

| pH | Solubility (mg/L) |
|---|---|
| 3.03 | 0 |
| 6.88 | 0 |
| 10.31 | 31.5 |

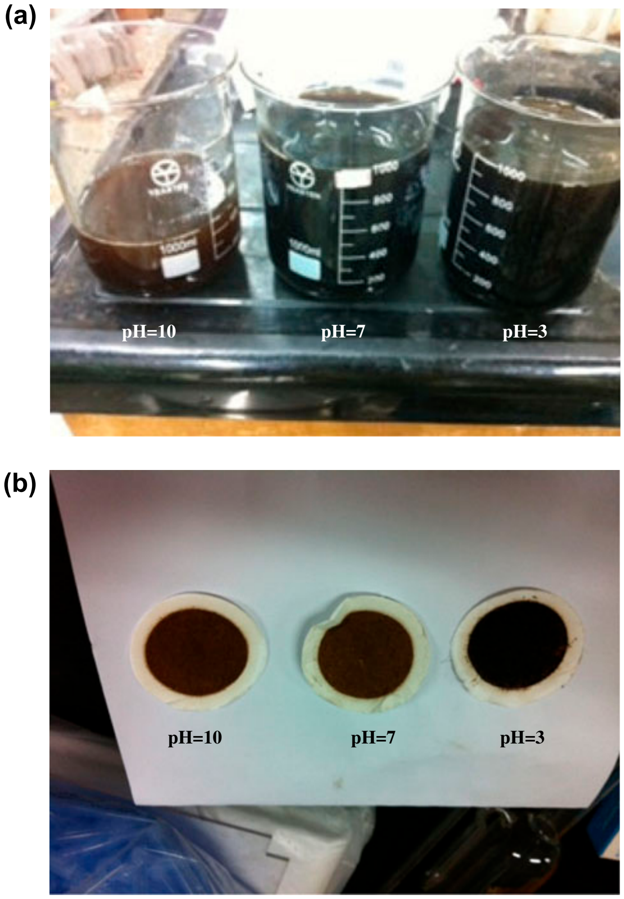


Fig. 1. Observation of (a) NOM and (b) membrane surface at different pH.

### 3.2. Influence of NOM concentration on CECs filtration

In order to clarify that whether CECs could be adsorbed on NOM and then removed together with NOM by NF270. Averaged rejection of samples with different NOM (HA) concentrations (TOC = 0.41, 4.11, and 23.97 mg/L) by NF270 is shown in Fig. 2. Generally, it could be found that the BPA has the highest rejection with different NOM concentrations. The rejection of CECs with the same NOM concentration (TOC = 4.11 mg/L) followed the order of BPA > CBZ > CAF > AMP ≒ SFX. The results also showed that different NOM concentrations in water samples had a great

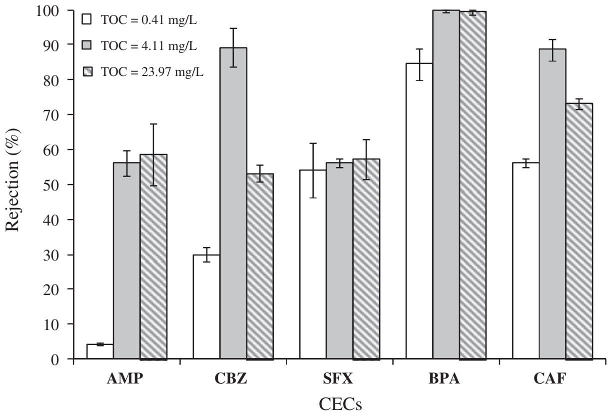


Fig. 2. Removal efficiency of CECs with different NOM concentrations by NF270.

impact on filtration rejection for the studies CECs (except for SFX). The CECs rejection significantly increased as the concentration of TOC was increased to 4.11 mg/L in the solution. As the content of HA was moderately existed in water samples, the interaction between CECs and organic matters frequently occurred, which made hydrophobic adsorption as the critical mechanism. However, as the NOM concentration in water sample was higher than a specific level, fouling phenomenon occurred easily, which resulted in a worse rejection than the moderate NOM existed in water sample. The result is similar to a previous study which suggested fouling cause a decline of bulk electricity by the double electric layer compression [28]. This could also be resulted from concentration polarization [23] or decreasing adsorption sites of NF270 [6]. Besides the above mentioned, the similar studies also concluded that the HA at a concentration of 1 mg/L increased the adsorption of pharmaceuticals on NOM, whereas 10 mg/L of HA decreased the adsorption [29].

In accordance with the results of filtration, there is a strong correlation between the NOM concentration and rejection. The past studies also interpret that four types of functional groups, including carboxyl, amino, hydroxyl, and phosphate groups, were identified as the most important moieties in adsorption of organic matters [29,30]. The existence of these functional groups is favorable to the adsorption of CECs. In addition, the results show that log $K_{ow}$ values have significant impact on adsorption of CECs. CBZ (log $K_{ow} = 2.45$) and BPA (log $K_{ow} = 3.32$) with relative high log $K_{ow}$ have higher removal efficiency than other compounds. This conclusion is also in accordance with the past studies [6]. However, CAF with low $K_{ow}$ also has higher removal efficiency might due to its high electronegativity of functional group, which can combine with the functional groups of NOM through adsorption via H-bond [31]. The decrease of CECs adsorption could be attributed to an association among CECs and NOM, which could be formed via hydrophobic interactions and hydrogen bonding [29].

### 3.3. Adsorption performance of CECs on NF

Owing to the CECs would also be adsorbed by the membrane, the contribution of CECs adsorption on NF270 was also investigated in this study. Fig. 3 shows the results about the adsorption performance of CECs on NF270. After the 96 h contacting time, the five CECs were adsorbed onto the membrane and reached the equilibrium state around 24 h. The adsorption efficiency was in the order of CBZ > BPA > CAF > AMP > SFX. Although the initial concentration of CECs was different, we think that the major impact factor for adsorption was still the properties of CECs. In addition, all of the adsorption capacity was lower than 10%; the results indicated that the adsorption of membrane indeed contributed small part of removal capacity during the CECs filtration process. The CECs (CBZ and BPA) with higher log $K_{ow}$ also have higher adsorption capacity than other CECs.

### 3.4. Adsorption performance of CECs on HA

In order to understand the contribution in the removal of CECs by the organic matter adsorption, the adsorption performance of CECs was also evaluated in this study. The adsorption efficiency of CECs onto HA at different contacting time is shown in Fig. 4. From the results, it could be found that the adsorption efficiency of CECs after contacting time of

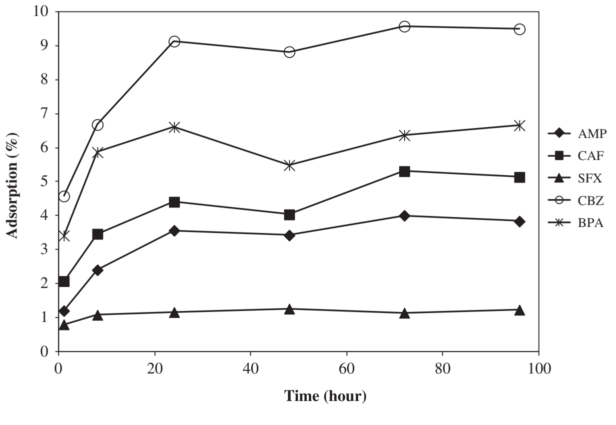


Fig. 3. CECs adsorption onto NF270 with different contacting time.

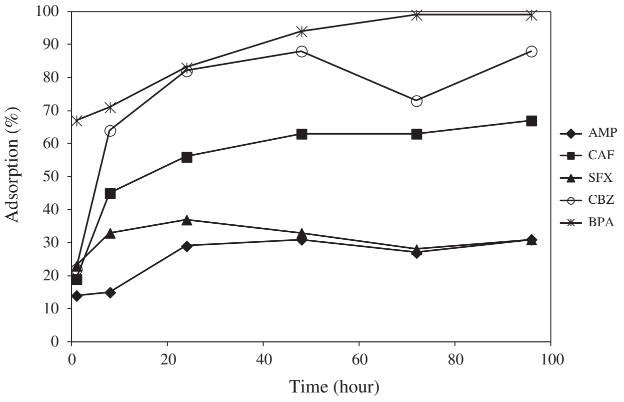


Fig. 4. CECs adsorption onto HA with different contacting time.

96 h was in the order of BPA > CBZ > CAF > AMP ≒ SFX. In general, HA would not used as an adsorbent for removing CECs, but the experimental results undoubtedly appear that CECs could be adsorbed onto HA.

### 3.4.1. Adsorption kinetics

In this study, both pseudo-first-order kinetic model (as Eq. (2) [32]) and pseudo-second-order kinetic models (as Eq. (3) [32]) were applied to find out the potential rate-controlling step involved in the process of adsorption of CECs on NOM.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$1/(q_e - q_t) = 1/q_e + k_2 t \tag{3}$$

where $q_e$ (mg/g) is the amount of each CECs adsorbed on NOM in equilibrium and $q_t$ (mg/g) is the amount of each CECs absorbed at any time. $k_1$ (min$^{-1}$) and $k_2$ (g/(mg min)) are the rate constants of Eqs. (2) and (3), respectively.

Kinetic parameters are calculated from the intercepts and slops of the linear relationships expressed in Eqs. (2) and (3). All the parameters of the pseudo-first-order and pseudo-second-order model are summarized in Table 5. The results show that the correlation coefficient and agreement between the calculated and experimental $q_e$ values of the pseudo-first-order kinetic model are higher than those of the pseudo-second-order kinetic model, except for CAF. However, the low correlation coefficient of AMP, SFX, and CBZ shows that the adsorption behavior of these three compounds did not obey the pseudo-first-order or pseudo-second-order model. Therefore, it is assumed that the chemisorption or other mechanisms are involved in the adsorption process [33]. The results also indicate that the adsorption process of BPA can be better described by the pseudo-first-order kinetic model and CAF can be better described by the pseudo-second-order kinetic model.

### 3.4.2. Adsorption isotherm

Adsorption isotherm was used to describe the interaction between the NOM and HA at a specific temperature in this study. In the equilibrium state, Langmuir Eq. (4) and Freundlich Eq. (5) isotherm models were used to fit the experimental data.

$$1/q_e = 1/q_m + 1/bq_m C_e \tag{4}$$

$$\ln q_e = \ln K_f + \ln C_e/n \tag{5}$$

where $q_m$ (mg/g) is the maximum amount of CECs adsorbed. $C_e$ (mg/L) is the concentration of CECs in the solution in equilibrium. $b$ (L/mg) is the constant of Langmuir model related to the energy or net enthalpy of adsorption. $K_f$ and n are the Freundlich constants which are related to the adsorption capacity and adsorption intensity of the adsorbent, respectively.

Table 5
Kinetics constants for adsorption of CECs on NOM

| | | Pseudo-first-order | | | Pseudo-second-order | | | Measured |
|---|---|---|---|---|---|---|---|---|
| CECs | Initial concentration (ng/L) | $k_1$ (min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | $k_2$ (g/mg min) | $q_e$ (mg/g) | $R^2$ | $q_{e,\text{exp}}$ (mg/g) |
| CAF | 223 | 0.0151 | 0.0147 | 0.8720 | 3.938 | 0.0243 | 0.9541 | 0.021 |
| AMP | 187 | 0.0112 | 0.0102 | 0.6612 | 2.462 | 0.0078 | 0.6306 | 0.018 |
| SFX | 230 | 0.0155 | 0.0223 | 0.7832 | 2.706 | 0.0229 | 0.7186 | 0.032 |
| CBZ | 197 | 0.0111 | 0.0114 | 0.5047 | 2.122 | 0.0071 | 0.4352 | 0.036 |
| BPA | 265 | 0.0190 | 0.0424 | 0.9582 | 3.428 | 0.0265 | 0.8193 | 0.059 |

Table 6
Langmuir and Freundlich isotherm constants for adsorption of CECs

| | Langmuir equation | | | Freundlich equation | | |
|---|---|---|---|---|---|---|
| CECs | $b$ | $q_m$ (mg/g) | $R^2$ | $n$ | $K_f$ (mg/g) | $R^2$ |
| CAF | 0.1011 | 0.1020 | 0.7240 | 0.0052 | 4.8E-188 | 0.8985 |
| AMP | 0.1777 | 1.0039 | 0.8402 | 0.0503 | 8.76E-13 | 0.8815 |
| SFX | 0.1081 | 2.3952 | 0.9834 | 0.1079 | 7.6E-07 | 0.8283 |
| CBZ | 0.1652 | 7.5988 | 0.5199 | 0.2430 | 0.4216 | 0.8571 |
| BPA | 0.5776 | 149.25 | 0.1253 | 0.7675 | 1219.6 | 0.5004 |

Table 7
Averaged removal contribution of CECs by adsorption in the NF process

| | Averaged removal contribution of CECs (%) | | | | |
|---|---|---|---|---|---|
| Removal behaviors | CAF | AMP | SFX | CBZ | BPA |
| Membrane adsorption | 7.29 | 25.98 | 1.09 | 32.58 | 16.66 |
| HA adsorption | 27.03 | 27.89 | 47.57 | 55.04 | 82.88 |
| Total rejection | 88.7 | 56.2 | 56.1 | 89.3 | 99.82 |

All of the parameters of the two models to the experimental data are listed in Table 6. The correlation coefficient of the Freundlich model was higher than that of the Langmuir model, except for SFX, which indicates that the former gives a better fit than the latter for CAF, AMP, CBZ, and BPA. The results also indicate that the Freundlich isotherm is the better fitting isotherm for adsorption of CAF, AMP, CBZ, and BPA onto HA. However, the low correlation coefficient of BPA shows that the adsorption behavior of BPA did not obey the Langmuir or Freundlich model.

### 3.5. The contribution of adsorption on CECs rejection by NF

From the results of CECs adsorption onto NF270 and HA, it could be deduced that the total removal efficiency of CECs during the filtration process includes three different removal behaviors: membrane adsorption, HA adsorption, and membrane rejection. The averaged removal contribution of CECs in the $W_2$ filtration process is displayed in Table 7. The results clearly show that the different removal behaviors caused different contribution for different CECs. For example, the major removal mechanism during the total filtration process for BPA, CBZ, and SFX is HA adsorption, but for CAF is membrane rejection. High ratio of removal efficiency by HA adsorption shows that most of CECs would be adsorbed onto HA first and then filtrated by the membrane indirectly. The past study indicates that the molecular width and length of BPA was slightly smaller than the pore size of NF270 [34], which cause the low rejection efficiency of BPA by membrane directly. The experimental result about low membrane rejection of BPA in this study also validates this phenomenon. Comparing with CECs, the large and complicated molecular structure of HA would be more easily removed by filtration. Therefore, the removal of CECs would be increased because of the existence of HA and the adsorption behavior of CECs onto HA in the solution. But too much HA existed in the solution would also cause fouling phenomenon of membrane, which resulted in a decreased rejection. Although past studies also found similar phenomena or results [6,29,34], the detailed removal mechanisms have not been thoroughly discussed yet. Finally, it could be concluded that the moderate existence of NOM in the solution would be contributive to the removal of CECs during the filtration process.

## 4. Conclusions

This study shows that CECs could be adsorbed not only by membrane but also by NOM during membrane filtration. Generally, BPA and CBZ had better adsorption efficiency than other CECs at certain NOM concentration. Adsorption of CECs by HA was also strongly correlated with log $K_{ow}$ of compounds. The study also found that the adsorption process of BPA can be better described by the pseudo-first-order kinetic model and CAF can be better described by the pseudo-second-order kinetic model. In addition, the Freundlich isotherm is the better fitting isotherm for adsorption of CAF, AMP, CBZ, and BPA onto HA. Finally, the results confirmed that the removal efficiency of CECs by NF could be affected by the organic matter present in the water. CECs would be adsorbed by HA first and then be removed easily during the membrane filtration. The removal efficiency of CECs would be increased because of the moderate existence of HA in the solution. However, as the NOM concentration was higher than a certain level, fouling phenomenon occurred easily, which resulted in a worse rejection than the moderate NOM existed in the solution.

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