

Transportation Characteristics of Bisphenol A Affected by Humic Substances Through Ultrafiltration Membrane with Low Molecule Weight Cut-Off

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Abstract: The hydrophobic interaction properties between bisphenol A (BPA) and humic substances (HS) were investigated using an ultrafiltration (UF) membrane with 1000Da Molecule Weight Cut-off (MWCO). Except for other influences, the Stokes radius of the hydration molecule of the BPA affected by HS was calculated with the hydrodynamic model by simulation of BPA transportation in the membrane. It was found that the rejection efficiencies of BPAs visibly increased in the presence of various HS (humic acid and fulvic acid). Simulation results showed that the effective radius of the hydration molecules was increased accordingly. It is proposed that the HS addition may improve the hydrophobicity and hydration of the BPA hydration molecules, which increased the effective radius of the BPA molecules. This research helps to understand the interaction between hydrophobic molecules and natural organic matters (NOMs) during the removal of emerging hydrophobic contaminants using a membrane with low MWCO.

Keywords: Bisphenol A, Ultrafiltration, Hydration, Humic acid, Fulvic acid.

1. INTRODUCTION

Bisphenol A (BPA) is an organic compound with the chemical formula $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$ belonging to the group of diphenylmethane derivatives and bisphenols, which is a colorless solid that is soluble in organic solvents, but poorly soluble in water [1]. BPA is an endocrine disruptor which can mimic estrogen and has been shown to cause negative health effects [2-9].

As a kind of NOM widely existing in nature, humic substances mainly consist of three groups: humic acid (HA), fulvic acid (FA) and humin. HAs and FAs are the major organic constituents in water sources. A typical difference between HAs and FAs is that when the pH of the solution was adjusted to 1 with hydrochloric acid, HAs can precipitate from solution while FAs are still dissolved in solution [10, 11]. Compared with HAs, FAs have a higher humification degree, containing more oxygen functional groups and aliphatic structures. A previous study has shown that the number of functional groups contributes to physical and chemical properties of FA and HA [12].

Most water sources exhibit a relatively low concentration of BPA and a certain amount of HS. Many treatment technologies such as hydrolysis,

Fenton oxidation, peroxidation, ultrasonication, ozonation and membrane processes have been developed to reduce NOM concentration in water [13]. For instance, Lee *et al.* reported a complete removal of BPA (initial concentration 5-50 mg L⁻¹) during the ozonation of water at 1 mg O₃ L⁻¹ min⁻¹ [14]. Sajiki *et al.* investigated the presence of reactive oxygen species (ROS) to reduce BPA leaching into seawater from plastic debris by degrading it to oxidative metabolites such as BPA-o-quinone [15]. And many researchers reported that combined processes including membrane filtration technology showed high efficiency in removing dissolved components of HS (i.e. a mixture of FAs and HAs) [16-18].

Because of the differences of molecular weight and size between HS and BPA, the two matters were seldom synchronously removed. Thus, the interaction between HS and BPA should be investigated from a new angle.

Ultrafiltration (UF) can also partly remove some organic micro-pollutants, even though the molecular weight of endocrine disruptors is much lower than the molecular weight cut-off of the ultrafiltration membrane. As the pore size ranges of UF and NF overlapped, the mechanism analysis of NF mass transfer process has reference meaning. Yoon *et al.* found that the ultrafiltration membrane of 8 kDa on a variety of endocrine disruptors had a high removal rate of more than 60% and as high as 90% [19]. Shang *et al.*

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studied the tight ceramic UF membrane as RO pre-treatment to remove phosphate and get a better effect in specified conditions [20].

In the filtration process of HS with a UF membrane, membrane fouling is an important focus influenced by the surrounding environment, especially ions. This kind of membrane fouling is both inconvenient and significant. Both Kloster *et al.* [21] and Baalousha *et al.* [22] reported divalent ions effects on the form and solvency of the HA and FA molecules. Moreover, it was reported that the interaction between some organic compounds and humic substances is influenced by calcium ions (Ca^{2+}) present on the membrane [23].

These work show that UF membrane has potential to remove the BPA and HS synchronously. However, most of the researches investigating the removal mechanism and removal efficiency of BPA and HS mainly focus on absorption and solubilization [24-26]. Thus ultrafiltration of MWCO's close to the NF is worth investigation for both micro organic pollutant removal and energy efficiency.

The membrane rejection of pollutants depends primarily on a mass transfer process of pollutants in the membrane. Building a theoretical model for the mass transfer process is an effective method to study the mechanism of membrane rejection.

In the rejection mechanism of porous membranes (MF, UF and NF), the most classic and widely used model of mass transfer is pore model, also known as the pore transfer model, pore diffusion model or hydrodynamic model.

As few research has explained BPA retention affected by HS clearly, a new mechanism and phenomena of HS influence on soluble BPA would be investigated and simulated in this study. BPA retention properties of ultrafiltration would be studied. And it is the first time that pore model was applied to investigate the interaction between BPA and HS. This research can make up the theoretical insufficiency of the effect of HS on the transportation of soluble BPA.

2. MATERIALS AND METHODS

2.1. Theory

In order to investigate the mass transfer of the model substance in the ultrafiltration membrane, this literature aims to build a membrane rejection model for

organic materials based on the pore model and the concentration polarization model. [27-35]

The hydrodynamic solute transport model is based on the widely accepted understanding that UF membranes have pores. In this study, these pores are assumed to be capillary tubes in shape and to have a uniform pore radius, r_p . The model pollutant BPA is assumed to be a spherical substance whose radius is r_s (stokes radius of the solute).

From the pore model and the concentration polarization model, there is a relationship between trans membrane pressure ΔP and J_V :

$$J_V = 145\Delta P \times 6 \times 10^{-8} \quad (1)$$

The including equations and models above were used to create a new M-file. Using the M-file in the Matlab, input values of r_s , r_p and substituting P for R , which is the theory of rejection rate R . (R_{obs})

2.2. Membrane

Retention experiments were carried out with a regenerated cellulose acetate UF membrane produced by Millipore Corporation (America). The front of the membrane is made of cellulose acetate while the back of the membrane is made of glass fibre. The molecular weight cut-off of the ultrafiltration membrane in this study is 1000Da and the thickness of the membrane is 0.1 mm. During the filtration process, the effective area of the membrane is approximately 28.7 cm².

2.3. Chemicals

BPA was prepared at a concentration of 5 mg/L in each step. To study the effect of HS, mixed BPA/HS were prepared with guarantee reagent HA and FA. The HS concentrations in these mixed-solute solutions were fixed at 1, 5 and 10 mg/L. HA and FA were provided by Mudanjiang Fengda Chemical Corporation (China).

The concentrations of BPAs in both feed and permeate solutions were determined using ultraviolet-visible spectrophotometer. Through spectrum scanning, the absorption wavelength of BPA was selected on the absorption peak (276 nm). The concentrations of BPAs adsorbed by HS were identified by high performance liquid chromatograph (HPLC) and then determined using ultraviolet-visible spectrophotometer. We prepared a series of concentrations of BPA solutions. Thus the absorbance could be determined directly and the working curve

could be also drawn. The response observed was linear over a limited range.

2.4. Filtration Experiments

Filtration experiments were carried out under dead end conditions with an ultrafiltration cup. The ultrafiltration membrane was at the bottom of the cup and fitted the cross profile of the cup strictly. The solution was put into the ultrafiltration cup. The magnetic stirring apparatus inside the ultrafiltration cup made the solution reach turbulent flow conditions.

At the same time, N_2 from a pressure cylinder was filled into the ultrafiltration cup. Rejection efficiencies were measured as a function of the transmembrane pressure (ΔP) by varying the transmembrane pressure from 0.1×10^6 Pa, 0.15×10^6 Pa, 0.2×10^6 Pa, 0.25×10^6 Pa and 0.3×10^6 Pa. The filter liquor in each filtration process was gathered in a glass tube, respectively. And the flow rate was measured by a liquid flow meter (shown in Figure 1).

A sample of the permeate solution was taken after a 30-min filtration run. A 30 minute time period was found to be sufficient to reach constant filtration performance. The automatic control system was used to show the pH and liquid level of the solutions. All experiments were

carried out at room temperature of $20 \pm 2^\circ\text{C}$. Figure 1 shows the whole ultrafiltration and data collection system.

3. RESULTS AND DISCUSSION

3.1. Effect of HS Addition on the Water Flux of Membrane

The main factors influencing the retention on the membrane in this experiment are r_s and r_p . The membrane fluxes of the pure BPA solution (5mg/L) and mixed-solute (BPA 5mg/L and HA/FA 10 mg/L) solution were tested in order to study whether inorganic salts could affect the variation of r_p . The filtration process in Figure 2 and Figure 3 was conducted under 0.1 MPa.

As shown in Figure 2, the variations of mean water flux ratio in filtration and backwashing experiments affected by pure HA and FA solutions were investigated. During the whole filtration/backwashing experiments, only slight variations of the water flux were observed after filtering FA solutions. The filtration and recovery of water flux affected by FA was nearly better than that affected by HA. During the initial period (1st and 2nd filtering times), the variations of the water flux affected by HA and FA were similar. Nevertheless, as filtering times increased (3rd and 4th filtering times), water flux affected by HA decreased sharply and water

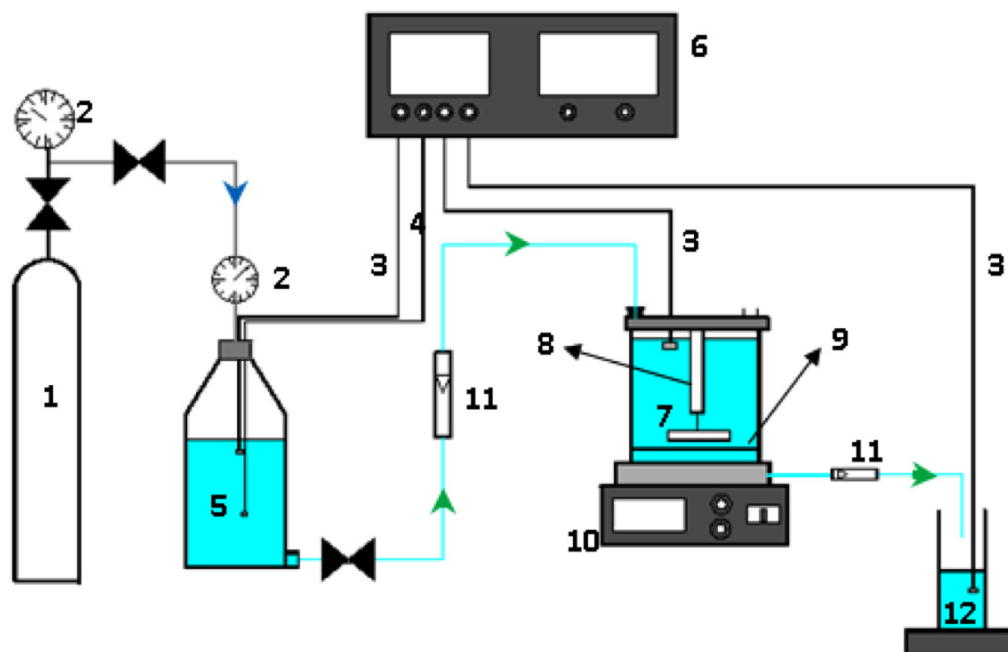


Figure 1: The whole ultrafiltration and data collection system.

Note*: 1.The nitrogen pressure bottle, 2. Pressure gauge, 3. Liquid sensor, 4. pH sensor, 5. Fluid reservoir, 6. Automatic control system, 7. Ultrafiltration cup, 8. Magnetic stirrer, 9.Ultrafiltration membrane, 10. Controller of magnetic stirrer, 11. Liquid flowmeter, 12. Cuvette.

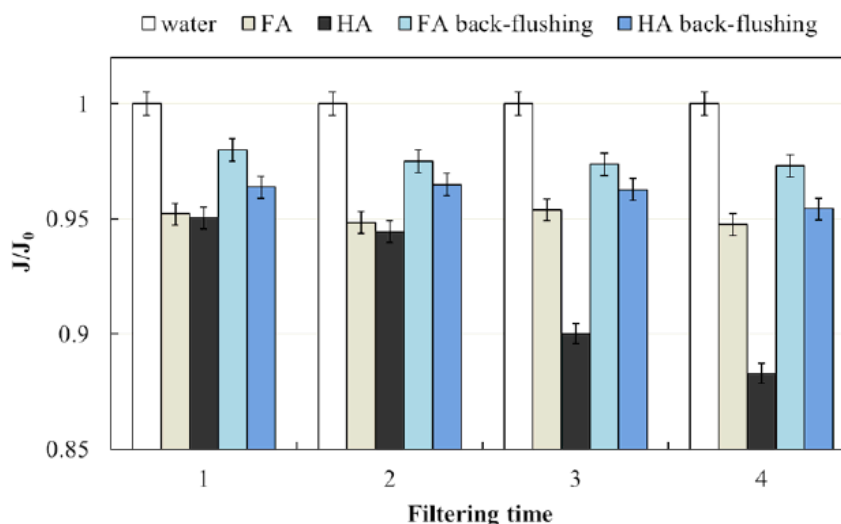


Figure 2: The mean water flux ratio vs. various filtration times of each pure solution.

recovery was also restrained. It was indicated that membrane fouling affected by HA or FA is slight at the beginning of the filtration process. It is reported that the FA is hydrophilic and easily soluble in water while the HA is hydrophobic [11]. Thus, compared to the FA, it is more easily for the HA to deposit on membrane surface and cause the sharp decrease of the water flux. The membrane used in the experiment was 1000 Da MWCO and removal efficiencies of FA and HA were 95% and 98%, respectively. It was indicated that the particle sizes of HA and FA colloids [10] were larger than the pore size of the membrane. Therefore, membrane fouling affected by HS mainly acted on membrane surface and could be washed out easily. Hence it can be concluded that the presence of HS does not affect the pore size of the membrane significantly during the filtration process.

As shown in Figure 3, the whole filtration processes (in 60 minutes) were stable and steady. And the fluctuation of BPA flux in pure solution and mix-solute solutions were slight and nearly constant. Therefore, the membrane pore radius, r_p changes only slightly in pure and mix-solute solutions and can be considered as a constant parameter.

3.2. Effect of HS Addition on the Rejection of BPA by Membrane

When the r_p is identified at a constant value, the change of r_s would directly affect the variation of the solute rejection efficiency.

Figure 4 shows the observed rejection efficiency of BPA in pure BPA solutions and mixed-solute solutions versus transmembrane pressure for HA and FA at various concentrations (1, 5 and 10 mg/L). The rejection efficiency R_{obs} was defined as follows:

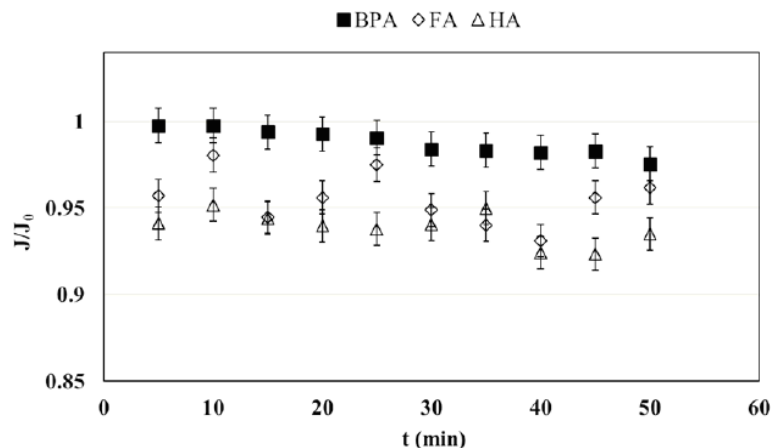


Figure 3: Filtration time vs. the flux ratio of the pure BPA solution and mix-solute solutions.

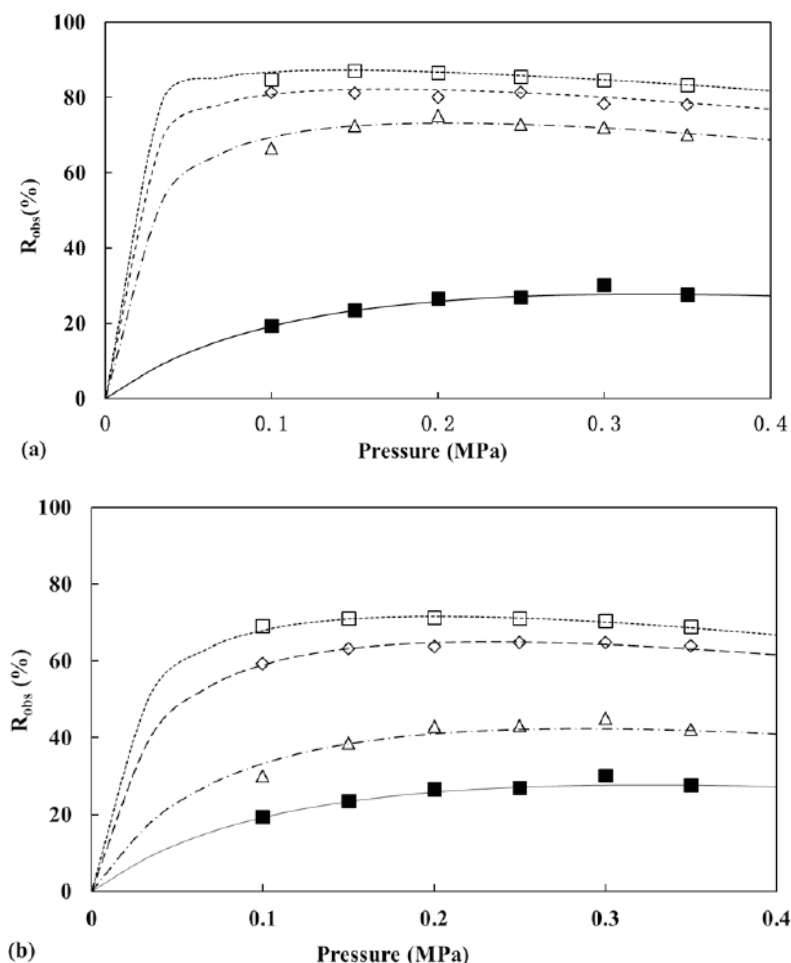


Figure 4: Observed rejection efficiencies of BPA vs. transmembrane pressure for single-solute solutions.

Note*: BPA feed concentration: 5 mg/L; symbols: experimental data; full lines: intrinsic rejection coefficients computed from theory section; added humic substance (HS): HA (a), FA (b). (■) No salt added; (△) [HS] = 1 mg/L; (◇) [salt] = 5 mg/L; (□) [HS] = 10 mg/L.

$$R_{obs} = 1 - \frac{c_1 + c_2}{c_0} \quad (2)$$

where c_0 was the concentration of BPA in the feed solution, c_1 was the concentration of BPA in permeate and c_2 was the concentration of BPA absorbed by HS (which was identified by HPLC). The rejection efficiency of BPAs is higher in mixed-solute solutions than in the pure BPA solutions. Additionally, the rejection efficiency increases as the HS concentration increases regardless of the kinds of HS used. A similar phenomenon has been reported in previous research in which the removal efficiency of BPA increased in the presence of HA [36]. But the mechanism of the interaction between BPA and HS mostly only attributes to absorption [24-26]. In this experiment, for the first time we observe that HS can cause the higher retention efficiency of the hydrophobic solute by enhancing its hydrophobic interaction with water.

Actually, the mechanism of such an effect is seldom discussed. In this research, it is proposed that the hydration effects may help to explain the variation of the retention of solutes by the membrane in a solution in the presence of HS. It is known that when an ionic or polar compound (e.g. Na^+ or sugar) enters water, it is surrounded by water molecules (Hydration). Water molecules can form a hydration shell surrounding the compounds which would result in covalent bonds or hydrogen bonds with each other. This shell can be several molecules thick and depend on the polar regions of the compound. Recently, dynamic, global hydration around proteins has been directly mapped and analyzed by other researchers [37, 38].

Similarly, hydrophobic compounds (e.g. BPA) can also attract water molecules with a van der Waals force which is weaker than covalent bonds or hydrogen bonds. These compounds (e.g. BPA) can disperse and

dissolve in water with a hydration shell when the attracted water molecules are enough to overcome the inter-molecule force among the hydrophobic compounds. The effective size of BPA with the hydration shell can affect the retention efficiency by membrane. There is a large number of hydrophobic groups on HS surround them (free states) [39]. When HS are added in the solution, hydrophobic groups will preferentially interact with BPA by stronger attractive forces [40], leading to a larger effective size of BPA molecule and a thicker hydration shell. As a result, the retention efficiency of BPA by membrane can be increased.

It is worth mentioning that the observed results cannot be ascribed to concentration polarization effects since rejection efficiencies are compared at identical volume fluxes (Figure 3). And the stirring intensity was enough to keep the solutions turbulent. So with the same volume fluxes and osmotic pressure conditions, the parameter caused by the concentration polarization effect is held a constant.

In addition, the procedure used in this study is designed to take the concentration polarization effects into consideration. That is to say the influence of concentration polarization effects could be measured in a more accurate way.

Moreover, the membrane used in this study was hydrophilic to avoid the adsorption of the hydrophobic solute molecules. Every set of data had been observed after filtration for three times, so the possibility of membrane adsorption which may influence the BPA observed rejection can be excluded.

3.3. Estimation of the Effective Size Under Different

HS Concentrations

The hydrophobic BPA molecules behave as solutes with a larger effective size and lead to higher rejection efficiencies by membrane. In order to investigate the effect of the HS nature on the hydration and hydrophobicity, the effective size of BPA are estimated with the addition of different HS (HA and FA) by calculating its dynamic Stokes radius, fitting the model to the experimental data.

The mean value of the r_p is $1.05 \pm 0.02 \text{ nm}$. Then the Stokes radius of the BPA molecules as an adjustable parameter in the different solute/HS solutions can be calculated. It is worth mentioning that the parameters r_p and r_s are adjusted at the same time in order to make the R_{app} fit the R_{obs} . Then the correlation coefficient of each set of the data has been up to 95%.

From Figure 5, it can be observed that the effective size of the BPA molecule increases with the increasing concentration of each HS. More HS can provide more free hydrophobic groups and interact with BPA, which lead to the increased Stokes radius. It is also found that at the same concentration, the effective size varies with the variation of the HS types. HA can do more to increase the effective size of BPA than FA. It is found that when 10 mg/L of HA is added to the raw solution, the effective size increases from 0.47nm to 0.725nm. We propose that HA molecules with more hydrophobic groups have a greater ability to compete for BPA than FA molecules.

Results obtained in this study show that the hydration and hydrophobicity of solutes plays a significant role in the ultrafiltration process of pollutant removal.

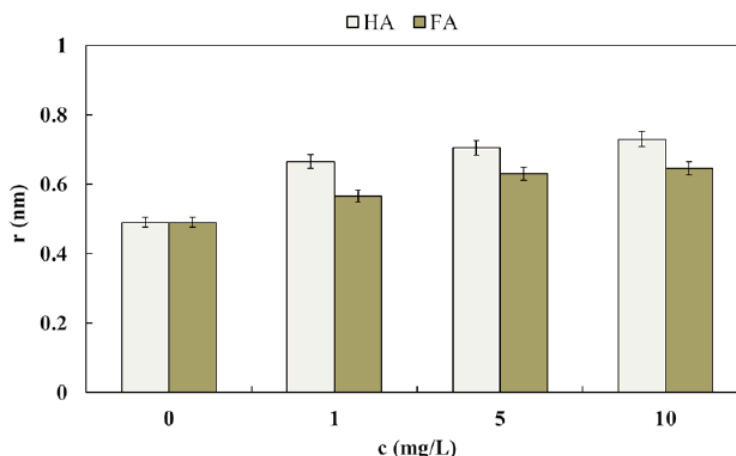


Figure 5: Variation of the Stokes radius of BPA vs. the humic substances concentration in the various mixed-solute solutions.

4. CONCLUSIONS

The influence of HS on the retention of BPA by an UF membrane with low molecular cut-off was investigated in this study. Both HA and FA effects could improve the retention of BPA. It is proposed that in mixed BPA/HS solutions, not only the absorption effect, but also the hydrophobicity of BPA affected by HS could influence the removal efficiency of BPA. The interaction with free hydrophobic groups caused increased effective size (i.e. the Stokes radius) of BPA.

It is suggested that hydration and hydrophobic effects should be considered when studying the transportation characteristics of hydrophobic solutes, and emerging contaminants (ECs) through an ultrafiltration membrane.

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NOMENCLATURE

C0	solute concentration in the feed solution [mole/m ³]
C1	permeate concentration [mg/L]
C2	solute concentration by HS absorption [mg/L]
JV	overall solvent flux [L/m ² /s or m/s]
P	trans membrane pressure [Pa]
Rapp	apparent rejection

Robs	observed rejection
rp	pore radius of membrane
rs	Stokes radius of the solute

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