Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Removal of sulfamethoxazole by nanofiltration membrane*

Su-hua WU†[1,2], Hua-qiang CHU†‡[1], Bing-zhi DONG[1], Jun-ru ZHOU[1], Yu HUANG[1]
([1]*School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China*)
([2]*Shanghai Purge Filtration Technology Co., Ltd., Shanghai 200444, China*)
†E-mail: wusuhua@inbox.com; chq123zl@hotmail.com

Received Oct. 10, 2009; Revision accepted July 6, 2010; Crosschecked Oct. 12, 2010

Abstract: The retention of sulfamethoxazole (SMZ) by nanofiltration (NF) membranes is strongly influenced by the pH value of the solution. The retention of SMZ reaches its peak value when the solution pH rises above its pK_{a2} value as the compound transforms into a negatively charged species. Charge repulsion is the main mechanism involved in SMZ removal by NF membranes. In this study, the removal of SMZ by NF membranes, as a function of solution chemistry, was examined at pH 8.9 to investigate the effect of solution conditions on charge repulsion. The results show that the retention of negatively charged SMZ is relatively independent of SMZ concentration, and an increase in the ionic strength of the solution causes a relatively small reduction in retention. A small effect of humic acid (HA) on SMZ retention was noticed at pH 8.9, which can be explained by a small but insignificant improvement in the zeta potential of the membrane caused by HA at high pH values. However, it was found that SMZ concentration in the feed decreased significantly in solutions containing tannic acid (TA). The Adams-Bohart model was applied to our experimental data and was found to be suitable for describing the initial part of the breakthrough curves. The adsorptive parameters of the membrane were determined.

Key words: Pharmaceutically active compounds (PhACs), Nanofiltration (NF) membrane, Electronic exclusion, Adsorption, Sulfamethoxazole (SMZ)
doi:10.1631/jzus.A0900606 **Document code:** A **CLC number:** TU991.2

1 Introduction

The pollution of drinking water sources by organic micropollutants at very low concentrations is becoming a great concern as the reuse of domestic wastewater for potable drinking water increases in popularity. Among these micropollutants, chemicals categorized as pharmaceutically active compounds (PhACs) have been receiving considerable attention recently because of their widespread occurrence in the aquatic environment. Sulfamethoxazole (SMZ) is an important member of the sulfonamide antibacterial category of PhACs and is probably the most frequently used antibiotic (Heberer, 2002; Kolpin *et al.*, 2002; Lindberg *et al.*, 2004).

The efficiency of removal of SMZ by conventional wastewater and drinking water treatment processes varies greatly (Batt *et al.*, 2007). Intensive efforts have been made to determine the ability of advanced treatment processes, such as membrane filtration and advanced oxidation processes, to remove these organic micropollutants (Andreozzi *et al.*, 2003; Sharma *et al.*, 2006). In view of its high molecular weight (>200 Da), it would be reasonable to consider that nanofiltration (NF) could provide effective control (Yoon *et al.*, 2006; Comerton *et al.*, 2007; Verliefde *et al.*, 2007).

The retention of organics can be attributed to a number of mechanisms, the most common of which are size exclusion, charge repulsion, and adsorption on the membrane surface. Many PhACs are hydrophobic compounds (i.e., log value of noctanol/water partition coefficient logK_{ow}>2) (Kimura *et al.*, 2003) and many high-pressure membranes are considered to

---

‡ Corresponding author

* Project supported by the Key Laboratory of Yangtze Aquatic Environment, Ministry of Education, Tongji University (No. PCRRK-08006)

be hydrophobic, as characterized by their contact angle (Bellona *et al.*, 2004), so hydrophobic adsorption of compounds onto membranes is widely observed and can lead to overestimation of rejection (Nghiem and Schäfer, 2002). However, very few studies have examined the role of electrostatic interactions. The low hydrophobicity of SMZ (0.89) inhibits the hydrophobic adsorption of SMZ molecules by the membrane and facilitates the investigation of electrostatic interactions.

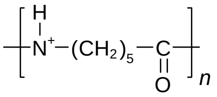
Natural organic matter (NOM) is ubiquitous in any aquatic environment. NOM is a mixture containing a variety of water-soluble organic components, their molecular weight ranging from less than a hundred to several hundred thousand Daltons. Many researchers have found different kinds of NOM in various feed waters. Contaminants like SMZ may bind to organic matter, and their presence can enhance retention and generally determine the fate of compounds. Some fractions of organic matter may compete with SMZ for adsorptive sites. Consequently, this competition may affect retention where adsorption is a dominant factor. Most studies agree that the retention of micropollutants in membrane-based systems tends to be influenced by the presence of NOM. However, the use by various researchers of NOM of different origins, and inadequate information on their physicochemical properties, do not allow comparison of experimental results. Therefore, it is of particular interest to study the relation between the characteristic physicochemical properties of the humic substances that are present in drinking water sources, and the retention performance of NF membranes. To this end, the use of well-defined NOM will aid the better understanding of the mechanisms of NOM-SMZ retention by membranes (Plakas and Karabelas, 2009).

In this paper, the short-term removal of SMZ from synthetic aqueous solution by NF as a function of solution characteristics including SMZ concentration, ionic strength and pH was investigated. Many of the experiments were completed at pH 8.9, a pH level at which both SMZ and the membrane are negatively charged, in order to examine the effects of other solution characteristics on charge repulsion. The effects of the presence of different types of NOMs, represented by humic acid (HA) and tannic acid (TA), were studied. HA is widely used in experiments to represent the dissolved organic loading because it is a major component of the NOM that is present in all natural waters and wastewater (Agbekodo *et al.*, 1996; Schäfer *et al.*, 2006). Also, commercially available TA was used as a type of surrogate NOM for comparison with the results obtained by HA. We applied the Adams-Bohart model to our experimental data to simulate the breakthrough curves. It should be noted that the results presented here do not necessarily show how SMZ could be removed from wastewater in water treatment plants because of the complex composition of natural water.

2 Materials and methods

2.1 Membrane

The structure of the polyamide membrane surface (Schäfer *et al.*, 2003) and the characteristics of the NF membrane used in this study are summarized in Fig. 1 and Table 1, respectively. The membrane, which is available commercially, was stored at 4 °C. The polyamide contains both carboxylic and amine function groups that can be ionized in an aqueous solution. NF membrane has an isoelectric point at a pH between 3.5 and 4.0 (Nghiem *et al.*, 2005), and hence is negatively charged for most of the time under the conditions in this investigation.



$$\left[\overset{\displaystyle H}{\overset{|}{N^+}} - (CH_2)_5 - \underset{\displaystyle O}{\underset{\|}{C}} \right]_n$$

Fig. 1 Structure of the polyamide membrane surface

Table 1 Characteristics of the NF membranes used in this study

Material	Manufacturer	Salt rejection (2000 mg/L $MgSO_4$)	pH range
Polyamide	Dow-FilmTec (USA)	98%	3–10

2.2 Solution chemistry and chemicals

SMZ was purchased from Sigma-Aldrich (Saint Louis, Missouri, USA) and the stock solution was prepared by adding 100 mg SMZ to 1 L Milli-Q water.

Both HA and TA are typical waterborne components of NOM and were purchased from

Sigma-Aldrich. HA contains a complex and heterogeneous group of many humic molecules, which can be described as a supramolecular colloidal mixture. Their molecular weights are typically above 50 000 Da. TA is a polyphenol, representative of relatively hydrophilic compounds of medium molar mass. It is reported by the supplier to have a mean molecular mass of 1701.18 g/mol with an empirical formula $C_{76}H_{52}O_{46}$, but in fact it contains a mixture of related compounds. The characteristic chemical parameters of HA and TA used in our experiments are summarized in Table 2. In all cases, the organic matter concentration was characterized by total organic carbon (TOC) concentration.

Table 2 Acidity and elemental composition of HA and TA

	Acidity (mequiv·g^{-1}·C)			Elemental composition (%, w/w)				H_2O (%, w/w)[b]
	Carboxylic	Phenolic	Total	C[a]	H	O	N	
HA[c]	3.40	–	–	60	34.5	34.5	0.96	
TA[d]	1.88	9.55	11.4	50	–	–	0	5.8

[a] Elemental composition of a dry, ash-free sample; [b] percentage of H_2O in the air-equilibrated sample; [c] values reported in (Nghiem and Hawkes, 2007); [d] values reported in (Plakas and Karabelas, 2009)

The background electrolyte consisted of 1 mmol/L $NaHCO_3$ and 20 mmol/L NaCl unless otherwise stated. Feed solution was prepared by spiking SMZ stock solution into background electrolyte solution to a certain SMZ concentration. $CaCl_2$, HA and TA were added as required, and the pH was adjusted using 0.1 mol/L NaOH or HCl. In the experiments on the effect of NOM, the solution containing HA or TA and SMZ was prepared and left to stand for 24 h to allow enough contact between HA or TA and SMZ before filtration.

2.3 Filtration system and protocol

Cross-flow tests were carried out to assess the removal efficiency of SMZ by NF membrane. A schematic diagram of the cross-flow membrane filtration setup is shown in Fig. 2. Both permeate and concentrate were recycled to the feed tank except for the sample withdrawn for SMZ concentration measurement. The effective membrane area was 60.0 cm^2. The operating transmembrane pressure was controlled at 0.4 MPa.

A new membrane was used in each experiment. The membrane was soaked in Milli-Q water for a minimum of 24 h prior to use. During this period, the Milli-Q water was replaced every 4–8 h with another new volume of Milli-Q water for membrane stabilization. The dissolved organic carbon (DOC) of the final rinsed water was checked to ensure that it was at a negligible level.

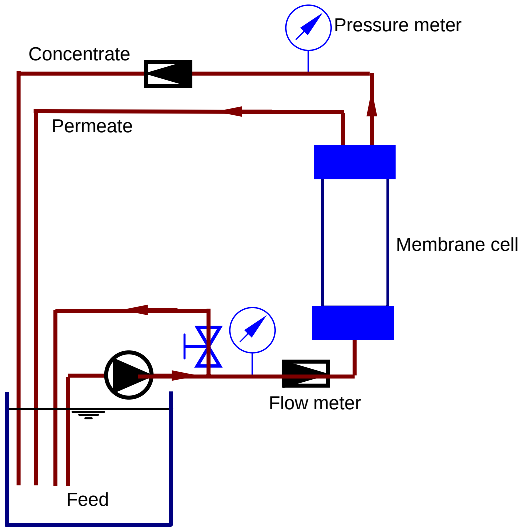


Fig. 2 Schematic diagram of the cross-flow membrane filtration unit

The membranes were compacted for 3 h at 0.4 MPa, prior to the determination of pure water flux with both steps using deionized water. The feed tank was then emptied and refilled with SMZ solution. Each experiment was conducted over a period of 8 h. The corresponding retentate was collected. Flux values (J) were recorded with each sampling. Observed retention rate, R, of SMZ was calculated using $R(\%)=(C_F-C_P)\times100\%/C_F$, where C_F and C_P are the feed and permeate concentrations (μg/L), respectively.

The adsorption breakthrough curves were obtained from the results of experiments performed with a dead-end filtration cell with magnetic stirring. The stirring rate was maintained constant over the experiments. The transmembrane pressure was provided by a compressed N_2 cylinder, with the applied pressure kept at 0.15 MPa. All experiments were performed at pH 3.5 and room temperature ((20±2) °C). For each feed concentration, filtrate samples were collected during filtration at specified time intervals for subsequent analysis.

2.4 SMZ characteristics

The physicochemical characteristics of SMZ are summarized in Table 3. With a logK_{ow} value of 0.89, it is noteworthy that SMZ has low hydrophobicity in its neutral form, and consequently low hydrophobic adsorption to the membrane. From the speciation of SMZ as a function of pH, it can be seen that SMZ exists in positive, neutral, as well as negative forms as it has two ionizable amine groups.

Adsorption can also depend on several factors related to the membrane properties including the nature of the polymeric membrane material, membrane hydrophobicity (represented by contact angle) and membrane surface roughness (Nghiem and Hawkes, 2007).

2.5 Analytical methods

SMZ concentration was analyzed using a 1200 Series High Performance Liquid Chromatography (Agilent, USA). Separation of SMZ was achieved on a ZORBAX Eclipse Plus C18 column (4.6 mm× 150 mm, 5 μm, Agilent, USA) with a mobile phase composed of 25% acetonitrile and 75% formic acid (0.1%, v/v), delivered at a constant flow rate of 1.0 ml/min. Detection was carried out using a fluorescence detector at an excitation wavelength of 270 nm and an emission wavelength of 344 nm. The injection volume was 50 μL and the total run time for each analysis was 8 min. A typical quantification limit for SMZ under these conditions was about 1 μg/L.

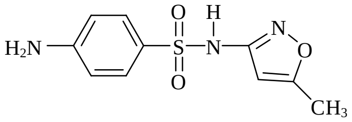
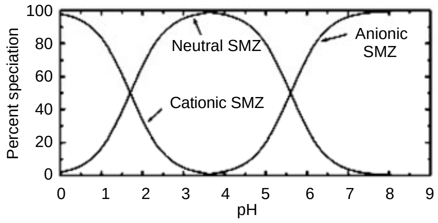
TOC was measured using a Shimadzu TOC-VCSH analyzer (Japan). All samples were filtered through 0.45 μm membrane prior to TOC measurement. Thus, the TOC values obtained here are, in fact, DOC values.

2.6 Modeling dynamic adsorption on the membrane

The performance of packed beds is described using the concept of the breakthrough curve. In dead-end filtration experiments, we can consider the membrane as a short column, so the concept of the breakthrough curve was applied in the filtration of SMZ solution by NF membrane.

The breakthrough curves show the loading behavior of SMZ to be removed from the solution

Table 3 Physicochemical properties of sulfamethoxazole (SMZ)

Parameter	Description
Molecular formula	$C_{10}H_{11}N_3O_3S$ (Clara *et al.*, 2005)
Molecular weight (g/mol)	253.3
Molecular size (nm)	Molecular width *X*: 0.526, molecular height *Y*: 0.587, molecular length *Z*: 1.031 (Nghiem and Hawkes, 2007)
Acid dissociation constant	pK_{a1}=1.4, pK_{a2}=5.8 (Nghiem and Hawkes, 2007)
Octanol/water partition coefficient	0.89 (Nghiem and Hawkes, 2007)
Dipole moment (D)	5.4 (Schäfer *et al.*, 2003)
Henry's law coefficient (atm m^3/mol)	6.42E−13 (Kimura *et al.*, 2004)
Water solubility at 293 K (mg/L)	600 (Schäfer *et al.*, 2003)
Structure	 (Schäfer *et al.*, 2003)
pH dependence of SMZ speciation	 (Qiang and Adams, 2004)

passing through a membrane and are expressed in terms of a normalized concentration, defined in this study as the ratio of effluent SMZ concentration to inlet SMZ concentration (C/C_0) as a function of time.

There are several kinetic models to simulate the breakthrough curves. In this study, we used the fundamental equations established by Adams and Bohart (Aksu and Gönen, 2004) to describe the relationship between C/C_0 and t in a flowing system. This model assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the sorbing species. The Adams-Bohart model was used for the description of the initial part of the breakthrough curve.

The mass transfer rates of the Adams-Bohart model obey the following equations:

$$\frac{\partial q}{\partial t} = -k_{\mathrm{AB}} C_{\mathrm{b}} q, \tag{1}$$

$$\frac{\partial C_{\mathrm{b}}}{\partial Z} = \frac{-k_{\mathrm{AB}}}{Z C_{\mathrm{b}} q}, \tag{2}$$

where q is the SMZ concentration in the membrane (μg/L) at any time t (min), k_{AB} is the kinetic constant (L/(μg·min)), C_{b} is the bulk SMZ concentration in the solution flowing through the membrane (μg/L), and Z is the thickness of the membrane (cm). The following equation is obtained with parameters k_{AB} and N_0 when the differential equations are solved:

$$\ln(C/C_0) = k_{\mathrm{AB}} C_0 t - k_{\mathrm{AB}} N_0 Z / U_0, \tag{3}$$

where N_0 and U_0 are the saturation concentrations in the Adams-Bohart model (mg/L) and the superficial velocity (cm/min), respectively. In this study, we change the equation to a more practical form:

$$Q\ln(C/C_0) = k_{\mathrm{AB}} C_0 V - 1000 k_{\mathrm{AB}} q_0 M, \tag{4}$$

where q_0 is the maximum adsorption capacity of the membrane (μg/cm^2), M is the amount of adsorbent (15.2 cm^2 in this experiment), V is the filtered volume downstream (ml), and Q is the flow rate with the fixed value of 1 ml/min in this investigation. From this equation, values describing the adsorptive characteristic parameters of the membrane can be determined from a plot of $Q\ln(C/C_0)$ against V at a given Q.

3 Results and discussion

3.1 Effect of pH on SMZ retention

It is known that the solution pH value can affect the chemical speciation of dissociable compounds as well as the charge characteristics of membranes. Therefore, pH was expected to affect the rejection efficiency of SMZ. In this section, we will analyze and discuss the experimental observations on the rejection of SMZ by NF membrane at different pH levels. Considering the pH limitations of the NF membrane and the pump, the pH range 3.5–8.9 was adopted in the experiments. Within this range SMZ was expected to show variation in negatively charged and neutral speciation.

The dependency of SMZ rejection by NF membrane on solution pH value is shown in Fig. 3. At all pH levels except pH 8.0 and 8.9, SMZ concentration in the feed decreased remarkably with filtration time and had still not stabilized after 4 h (Fig. 3a). There were notable differences in the feed concentration across the pH range 3.5–6.5. This phenomenon could be attributed directly to the adsorption of SMZ onto the membrane. At pH 8.0 and 8.9, nearly all SMZ molecules in the initial feed water were dissociated and negatively charged (Table 3). The electrostatic repulsion between dissociated SMZ molecules and the highly negatively charged NF membrane significantly decreased the proximity of SMZ to the membrane surface and thus reduced the adsorption of SMZ onto the membrane. The rate of decline in SMZ concentration in the feed varied directly in relation to the ratio of neutral and negatively uncharged SMZ molecules which was proportional to the pH values. For example, at pH 3.5 the SMZ concentration in feed decreased by 73.2% (from an initial 88.2 to 23.6 μg/L at the end of experiment). That decline was nearly double the 38.8% reduction (from 94.7 to 57.9 μg/L) shown at pH 5.5.

It has been widely observed that the retention of a variety of chemicals by NF membrane or loose reverse osmosis membrane is dependent on solution pH values (Kimura *et al.*, 2004). The most surprising observation from our study compared with previous studies (Nghiem *et al.*, 2004; Hu *et al.*, 2007) was the way in which the objective micropollutant concentration in the permeate changed over time. For example,

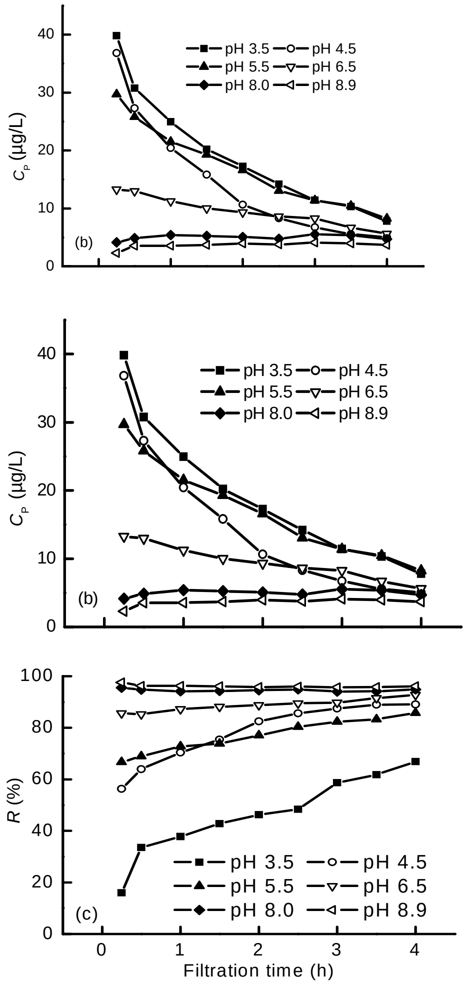


Fig. 3 Effect of solution pH values on SMZ concentrations in the feed (a) and permeate (b) and on the retention (c) of SMZ by NF membrane (cross-flow filtration; feed solution: 100 μg/L SMZ, 1 mmol/L $NaHCO_3$, 20 mmol/L NaCl, pH varied from 3.5 to 8.9)

at pH 4.5, the SMZ concentration in the permeate dropped dramatically from 36.8 to 5.0 μg/L after 4 h (Fig. 3b), whereas in other investigations the concentration in the permeate increased from a low value to a much higher value as shown by the breakthrough curves (Aksu and Gönen, 2004; Kimura *et al.*, 2004; Qiang and Adams, 2004) or remained stable with filtration processing (Nghiem *et al.*, 2006). Retention of trace organics is often explained by the solution diffusion model. According to this model, solute transport across the membrane is a two-step process: first, the solute is adsorbed or dissolved by the membrane; second, it migrates across the membrane by diffusion or convection (Nghiem and Schäfer, 2002; Nghiem *et al.*, 2002). The separation process in such cases would be subject to the differential diffusion coefficient between water and SMZ, the concentration gradient, and also the thickness of the membrane skin layer. After more than 20-h filtration at pH 3.5 with all SMZ molecules uncharged, it can be seen from Fig. 4 that the permeate concentration is equal to the feed concentration and the value is close to the detection limit, showing that all the SMZ molecules can be adsorbed on or into the membrane after sufficient filtration. It indicates that the transport mechanism of SMZ across this NF membrane can be characterized as convection dominated and only an adsorptive mechanism is effective in retaining SMZ. Further investigation of the adsorption saturation of SMZ on NF membrane is needed.

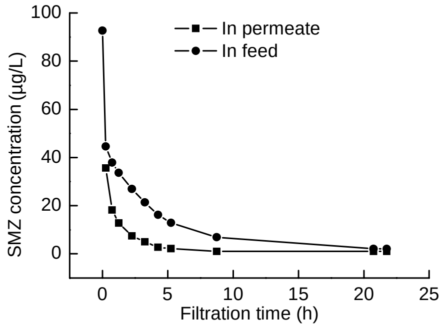


Fig. 4 Adsorption balance of SMZ on NF membrane (cross-flow filtration; feed solution: 100 μg/L SMZ, 1 mmol/L $NaHCO_3$, 20 mmol/L NaCl, pH 3.5)

The Adams-Bohart sorption model was applied to the dead-end filtration experimental data for the description of the initial part of the breakthrough curve. This approach was focused on the estimation of the characteristic parameters q_0 and k_{AB} from the Adams-Bohart model. After applying Eq. (4) to the experimental data for variable inlet SMZ concentrations, a linear relationship between $\ln(C/C_0)$ and V was obtained for the relative concentration region up to 0.5, i.e., up to 50% breakthrough (Fig. 5) for all breakthrough curves (R^2>0.900). Respective values of q_0 and k_{AB} calculated from the $\ln(C/C_0)$ versus V plots at all inlet SMZ concentrations studied, are presented in Table 4 together with the correlation coefficients.

It should be noted that the mechanism driving adsorptive retention at the membrane surface is still

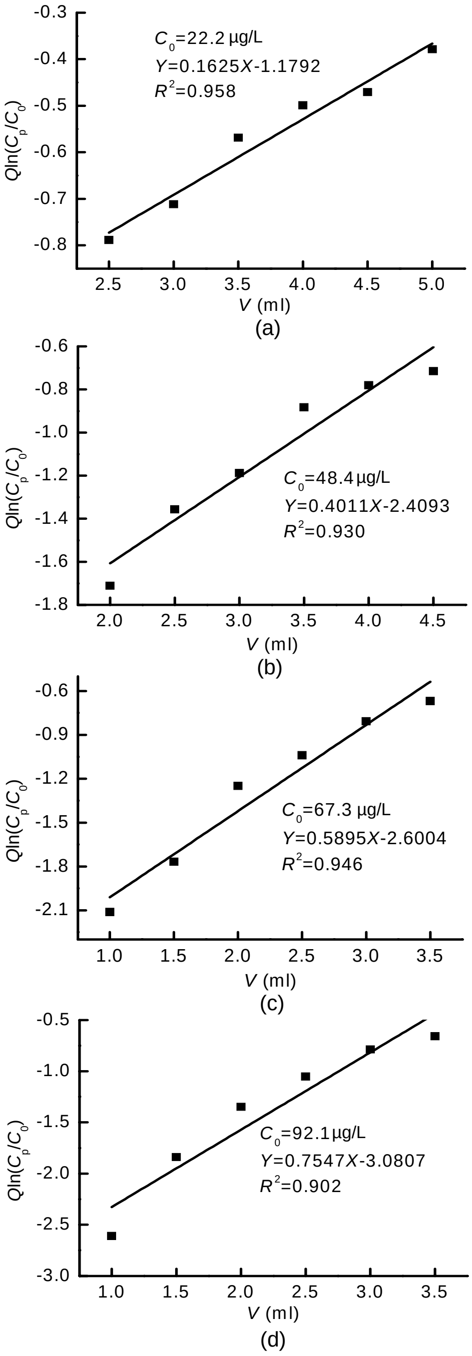


Fig. 5 Fit of Eq. (4) to breakthrough data in the range of 0–0.5 (dead-end filtration; feed solution: 1 mmol/L NaHCO$_3$, 20 mmol/L NaCl, pH 3.5)

Table 4 Parameters predicted from the Adams-Bohart model at different inlet SMZ concentrations (dead-end filtration; feed solution: 1 mmol/L NaHCO$_3$, 20 mmol/L NaCl, pH 3.5)

C_0 (μg/L)	k_{AB} (L/(min·μg))	q_0 (μg/cm^2)	R^2
22.2	0.0073	0.0106	0.958
48.4	0.0083	0.0191	0.930
67.3	0.0087	0.0195	0.946
92.1	0.0082	0.0247	0.902

unclear, but it may reflect hydrophobic partitioning to the organic membrane surface or be related to more specific interactions such as hydrogen bonding. The major adsorptive effects for SMZ seen in this investigation could be mediated by hydrogen bonding between SMZ and the membrane because of the limited hydrophobic adsorption, i.e., SMZ has low hydrophobic potential because of its low logK_{ow} value (Table 3). Therefore, the differences in the trend of SMZ concentration variation in the permeate may be due to the different characteristics of SMZ compared with other chemicals investigated in other studies. First, without charge repulsion, SMZ molecules can easily penetrate through the NF membrane and exist in the permeate. Thus, with the filtration processing, more and more SMZ molecules are adsorbed onto the membrane as they pass through it. However, desorption from the membrane is quite difficult under this specific interaction. Hence, the decreasing concentration in the permeate is caused by the depletion of SMZ molecules in the feed as a result of more efficient adsorption with filtration.

The stable SMZ concentration in the feed and its lowest value in the permeate guarantee a stable retention rate (>94.0%, Fig. 3c) at pH 8.9 by the charge repulsion mechanism. Thus, experimentation with pH 8.9 appears to be justified to examine the influences of other factors on charge repulsion and retention.

3.2 Effect of SMZ concentration

Fig. 6 shows that the effect of SMZ concentration between the range from 100 to 500 μg/L is minimal, when retention values are compared. The

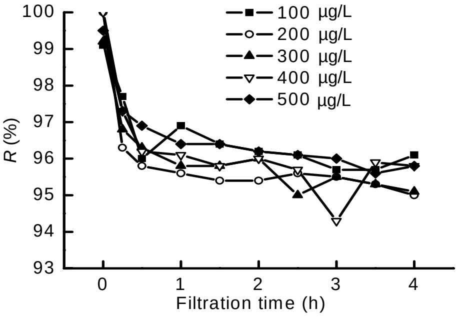


Fig. 6 Effects of concentration on SMZ retention (cross-flow filtration; feed solution: 1 mmol/L NaHCO$_3$, 20 mmol/L NaCl, pH 8.9, and SMZ concentration varied from 100 to 500 μg/L)

same result was obtained in previous researches (Nghiem *et al.*, 2005; Zhang *et al.*, 2006), in which the phenomenon was explained by the suggestion of a constant partition coefficient for the objective micropollutants between membrane and bulk solution. However, it should be noted that the main mechanism in this experiment is charge repulsion because all SMZ molecules and the NF membrane are negatively charged at pH 8.9. In previous investigations, experiments were often carried out under the condition that adsorption was expected to dominate the interaction between membrane and objective micropollutants.

3.3 Ionic strength effects on retention

The presence of counterions in the solution may partially screen the charge associated with the molecular functional groups and thus reduce the apparent "size" of the molecules. Similarly, the ionic strength may shield the electrostatic potential generated by the membrane surface functional groups and thus reduce electrostatic repulsive effects. Both phenomena would be expected to influence the solute retention in similar ways and cannot easily be separated.

The effect of increasing $CaCl_2$ concentration is shown in Fig. 7. A slight decrease in retention at the higher calcium concentrations could be the result of the ability of Ca^{2+} to decrease the charge repulsion since both the membrane and SMZ are negatively charged at pH 8.9, but the effect is too minor to draw any firm conclusions. The relatively small effect on retention reduction at high $CaCl_2$ concentration is consistent with the results obtained from other investigations (Nghiem *et al.*, 2004; Nghiem *et al.*, 2005) even though the main interaction between the membrane and the objective micropollutants under the experimental conditions was different. A possible reason is that the $CaCl_2$ concentration was still too low to have an apparent effect on the charge repulsion.

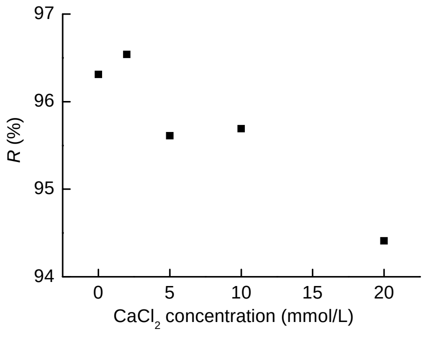


Fig. 7 Effects of $CaCl_2$ concentration on SMZ retention (cross-flow filtration; feed solution: 100 μg/L SMZ, 1 mmol/L $NaHCO_3$, 20 mmol/L NaCl, pH 8.9, Ca^{2+} concentration varied from 0 to 20 mmol/L)

3.4 Effect of NOM on SMZ retention

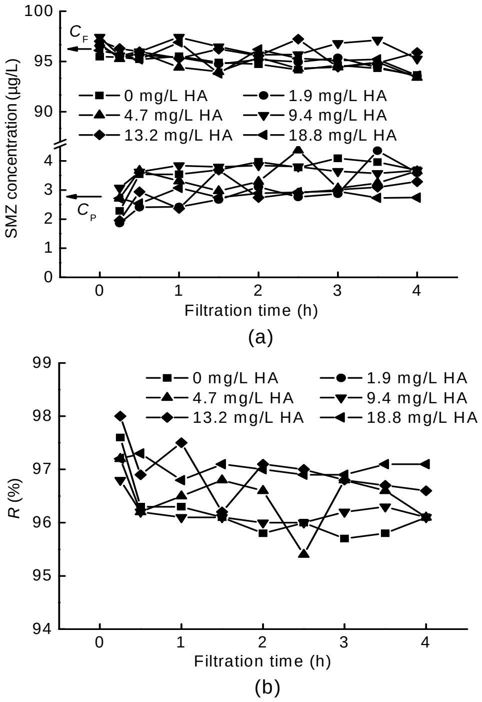
1. HA

The effect of HA on the retention of SMZ is illustrated in Fig. 8. It can be seen that the variation in rejection under different HA concentrations is too small and uncertain to draw any conclusions. Various papers have reported the effect of NOM on retention of pollutants. In some cases, retention was raised with the presence of NOM (Agbekodo *et al.*, 1996; Nghiem *et al.*, 2004) and in others, NOM independence was observed (Zhang *et al.*, 2006).

From experiments on the effect of HA on the zeta potential of membrane as a function of pH, it is claimed that a dramatic increase in the effect of HA on the membrane surface charge is most apparent at low pH and diminishes as the pH increases, becoming very small at high pH values (Childress and Elimelech, 1996). So added HA improved charge repulsion only slightly at pH 8.9 within this experiment compared with more significant improvements found in previous studies at lower pH values. The formation of a fouling layer (a brown layer attached to the membrane surface) by HA was observed at the end of the experiments, but no drop in permeate flux was observed and the brown layer could be removed very easily by rinsing. So it can be concluded that added HA had no impact on the size exclusion by the membrane selectively rejecting SMZ, and the adsorption of SMZ onto HA molecules was negligible, while the enhanced removal rates in other studies can be explained by the more effective size exclusion after pollutants become absorbed onto HA. From the above explanations, it can be concluded that different effects shown by HA result from differences in the solution chemistry and in the main removal mechanisms involved.

2. TA

Fig. 9 shows the influence of TA on SMZ concentration in the feed and permeate and the rejection behavior of the NF membrane. We observed that SMZ concentration in the feed decreased continuously over

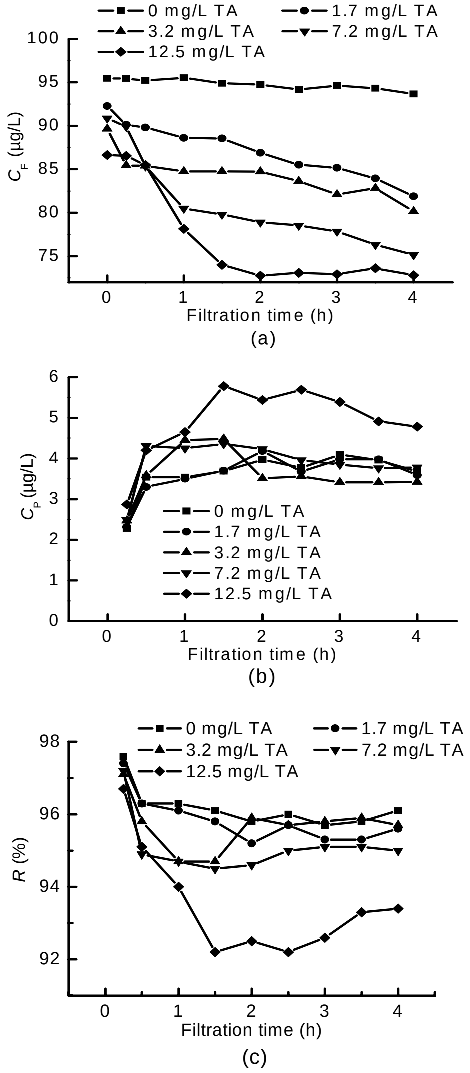


(a)

(b)

Fig. 8 Effect of HA on the feed and permeate concentrations of SMZ (a) and on the rejection of SMZ (b) by NF membrane (cross-flow filtration; feed solution: 100 μg/L SMZ, 1 mmol/L $NaHCO_3$, 20 mmol/L NaCl, HA concentration varied from 0 to 18.8 mg/L)

the filtration time for TA-containing solutions compared with a stable concentration for TA-free solutions. Moreover, higher concentrations of TA led to a slightly more pronounced decrease in SMZ concentration in the feed. In TA-containing solutions, SMZ concentration in the feed decreased from an initial 90.9 to 75.2 μg/L after 4 h of filtration and had still not stabilized. Thus, saturation had not been reached and more SMZ would be adsorbed onto the membrane after longer filtration. This implies that addition of TA may encourage the partitioning of SMZ molecules from water to membrane. A possible explanation is that the formation of an extra layer of organic matter (TA) on the membrane surface led by concentration polarization during the nanofiltration process, decreased the charge repulsion between the membrane and SMZ molecules and thus increased the adsorption of SMZ on the membrane or on the extra layer of TA.



(a)

(b)

(c)

Fig. 9 Effect of TA on the feed concentration (a) and permeate concentration (b) and on the rejection (c) of SMZ by NF membrane (cross-flow filtration; feed solution: 100 μg/L SMZ, 1 mmol/L $NaHCO_3$, 20 mmol/L NaCl, TA concentration varied from 0 to 12.5 mg/L)

The evolution of SMZ concentrations in the permeate during filtration shows that added TA accelerated SMZ desorption from the membrane (Fig. 8b), especially when a high TA concentration was used. Fig. 9c shows the corresponding removal rate after TA was added. The occurrence of a more significant decrease of SMZ concentration in the feed and an increase in concentration in the permeate can be well explained by the influence of so-called cake enhanced concentration polarisation (Lee *et al.*, 2005), whereby the fouling cake layer hinders back diffusion of solutes from the membrane surface into the bulk solution. The buildup of solutes at the membrane surface results in a higher solute concentration gradient across the membrane and thus, a greater solute transport through the membrane and a lower observed solute rejection.

The different effects of HA and TA on SMZ removal are most likely attributable to the different characteristics of different types of NOM. Further study of the effect of NOM on the removal of micropollutants is necessary.

4 Conclusions

The retention of ionizable SMZ is strongly influenced by solution pH. Solution pH governs the speciation behavior of the compound and therefore the retention mechanisms. With the low hydrophobic adsorption potential on the membrane, the main mechanism in SMZ removal is charge repulsion. SMZ retention peaks as solution pH increases above its pK_{a2} value, as the compound transforms into a negatively charged species. Ionic strength screens the molecule and membrane charges and therefore reduces the effectiveness of electrostatic repulsion as a major retention mechanism in NF membranes. However, such a reduction is relatively small.

The finding of no apparent improvement in the zeta potential of membrane by HA at pH 8.9 supports the small effect of HA on SMZ concentration in the feed and permeate, and consequently on retention rate. Decreasing SMZ concentration in the feed with filtration time for TA-containing solution shows that the addition of TA may encourage the partitioning of SMZ molecules from water to membrane, while the impact of TA on SMZ concentration in the permeate and retention is not as significant as in the feed. The different effects shown by HA and TA need to be further investigated in terms of the characteristics of NOM.

The Adams-Bohart model was applied to experimental data obtained from dead-end filtration studies to predict the breakthrough curves and to determine the membrane adsorptive kinetic parameters. The results show that the initial region of the breakthrough curve was well defined by the Adams-Bohart model at all inlet SMZ concentrations.

References

Agbekodo, K.M., Legube, B., Dard, S., 1996. Atrazine and simazine removal mechanisms by nanofiltration: influence of natural organic matter concentration. *Water Research*, **30**(11):2535-2542. [doi:10.1016/S0043-1354(96)00128-5]

Aksu, Z., Gönen, F., 2004. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochemistry*, **39**(5):599-613. [doi:10.1016/S0032-9592(03)00132-8]

Andreozzi, R., Raffaele, M., Nicklas, P., 2003. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere*, **50**(10):1319-1330. [doi:10.1016/S0045-6535(02)00769-5]

Batt, A.L., Kim, S., Aga, D.S., 2007. Comparison of the occurrence of antibiotics in four full-scale wastewater treatment plants with varying designs and operation. *Chemosphere*, **68**(3):428-435. [doi:10.1016/j.chemosphere.2007.01.008]

Bellona, C., Drewes, J.E., Xu, P., Amy, G., 2004. Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review. *Water Research*, **38**(12):2795-2809. [doi:10.1016/j.watres.2004.03.034]

Childress, A.E., Elimelech, M., 1996. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*, **119**(2):253-268. [doi:10.1016/0376-7388(96)00127-5]

Clara, M., Strenn, B., Gans, O., 2005. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Research*, **39**(19):4797-4807. [doi:10.1016/j.watres.2005.09.015]

Comerton, A.M., Andrews, R.C., Bagley, D.M., Yang, P., 2007. Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds. *Journal of Membrane Science*, **303**(1-2):267-277. [doi:10.1016/j.memsci.2007.07.025]

Heberer, T., 2002. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. *Journal of Hydrology*, **266**(3-4):175-189. [doi:10.1016/S0022-1694(02)00165-8]

Hu, J.Y., Jin, X., Ong, S.L., 2007. Rejection of estrone by nanofiltration: Influence of solution chemistry. *Journal of Membrane Science*, **302**(1-2):188-196. [doi:10.1016/j.memsci.2007.06.043]

Kimura, K., Amy, G., Drewes, J., Watanabe, Y., 2003. Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection. *Journal of Membrane Science*, **221**(1-2):89-101. [doi:10.1016/S0376-7388(03)00248-5]

Kimura, K., Toshima, S., Amy, G., Watanabe, Y., 2004. Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *Journal of Membrane Science*, **245**(1-2):71-78. [doi:10.1016/j.memsci.2004.07.018]

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zuggg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. *Environmental Science & Technology*, **36**(6):1202-1211.

Lee, S., Cho, J., Elimelech, M., 2005. Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling. *Journal of Membrane Science*, **262**(1-2):27-41. [doi:10.1016/j.memsci.2005.03.043]

Lindberg, R., Jarnheimer, P.A., Olsen, B., Johansson, M., Tysklind, M., 2004. Determination of antibiotic substances in hospital sewage water using solid phase extraction and liquid chromatography/mass spectrometry and group analogue internal standards. *Chemosphere*, **57**(10):1479-1488. [doi:10.1016/j.chemosphere.2004.09.015]

Nghiem, L.D., Schäfer, A.I., 2002. Adsorption and transport of trace contaminant estrone in NF/RO membrane. *Environmental Engineering Science*, **19**(6):441-451.

Nghiem, L.D., Hawkes, S., 2007. Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size. *Separation and Purification Technology*, **57**(1):176-184. [doi:10.1016/j.seppur.2007.04.002]

Nghiem, L.D., Schäfer, A.I., Waite, T.D., 2002. Adsorptive interactions between membranes and trace contaminants. *Desalination*, **147**(1-3):269-274. [doi:10.1016/S0011-9164(02)00550-7]

Nghiem, L.D., Manis, A., Soldenhoff, K., 2004. Estrogenic hormone removal from wastewater using NF/RO membranes. *Journal of Membrane Science*, **242**(1-2):37-45. [doi:10.1016/j.memsci.2003.12.034]

Nghiem, L.D., Schäfer, A.I., Elimelech, M., 2005. Pharmaceutical retention mechanisms by nanofiltration membranes. *Environmental Science & Technology*, **39**(19):7698-7705. [doi:10.1021/es0507665]

Nghiem, L.D., Schäfer, A.I., Elimelech, M., 2006. Role of electrostatic interactions in the retention of pharmaceutically active contaminants by a loose nanofiltration membrane. *Journal of Membrane Science*, **286**(1-2):52-59. [doi:10.1016/j.memsci.2006.09.011]

Plakas, K.V., Karabelas, A.J., 2009. Triazine retention by nanofiltration in the presence of organic matter: The role of humic substance characteristics. *Journal of Membrane Science*, **336**(1-2):86-100. [doi:10.1016/j.memsci.2009.03.020]

Qiang, Z.M., Adams, C., 2004. Potentiometric determination of acid dissociation constants (pK_a) for human and veterinary antibiotics. *Water Research*, **38**(12):2874-2890. [doi:10.1016/j.watres.2004.03.017]

Schäfer, A.I., Nghiem, L.D., Waite, T.D., 2003. Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. *Environmental Science & Technology*, **37**(1):182-188. [doi:10.1021/es0102336]

Schäfer, A.I., Nghiem, L.D., Oschmann, N., 2006. Bisphenol A retention in the direct ultrafiltration of greywater. *Journal of Membrane Science*, **283**(1-2):233-243. [doi:10.1016/j.memsci.2006.06.035]

Sharma, V.K., Mishra, S.K., Ray, A.K., 2006. Kinetic assessment of the potassium ferrate (VI) oxidation of antibacterial drug sulfamethoxazole. *Chemosphere*, **62**(1):128-134. [doi:10.1016/j.chemosphere.2005.03.095]

Verliefde, A.R.D., Heijman, S.G.J., Cornelissen, E.R., Amy, G., van der Bruggen, B., van Dijk, J.C., 2007. Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water. *Water Research*, **41**(15):3227-3240. [doi:10.1016/j.watres.2007.05.022]

Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C., 2006. Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *Journal of Membrane Science*, **270**(1-2):88-100. [doi:10.1016/j.memsci.2005.06.045]

Zhang, Y., Causserand, C., Aimar, P., Cravedi, J.P., 2006. Removal of bisphenol A by a nanofiltration membrane in view of drinking water production. *Water Research*, **40**(20):3793-3799. [doi:10.1016/j.watres.2006.09.011]