

Removal and transport mechanisms of arsenics in UF and NF membrane processes

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ABSTRACT

In this study, the removal and transport mechanisms of ionized and non-ionized arsenics through NF and UF membranes were systemically investigated. The charge repulsion between the membrane surface and arsenic ions was an important mechanism for the rejection of ions by a charged membrane. In addition, the effect of J_0/k ratio was dependent on the membrane and ion charge, but the cross-flow velocity was not significantly affected. Both diffusion and convection are proved to affect the transport of arsenic ions. The reflection coefficients (σ) of both UF and NF membranes increased with increasing pH; the reflection coefficients of arsenate were higher than those of arsenite under the same operating conditions. The spiral-wound module exhibited slightly higher arsenate removal than the flat-sheet module under the same operating conditions.

Key words | arsenic, convection, diffusion, J_0/k ratio, NF, UF

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INTRODUCTION

Arsenic is considered to be a metalloid which occurs in various oxidation states such as -3 , 0 , $+3$ and $+5$. There have been several studies on arsenic occurrence in source drinking waters. Those researches showed that two oxidation states are generally present in drinking water: $+3$ and $+5$ (Chen *et al.* 1994; Clifford & Lin 1991; Davis *et al.* 1994; Frey & Edwards 1997; Roverson 1989). This form of arsenic is regarded as a highly toxic chemical by US EPA; since 1942 it has had a Maximum Contamination Level (MCL) of $50 \mu\text{g l}^{-1}$, which will be reduced to $10 \mu\text{g l}^{-1}$ in 2006 (Chang *et al.* 1994; Pontius 1994).

Several common treatment technologies are used to remove inorganic contaminants including arsenate and arsenite. Large-scale treatment facilities often use conventional coagulation with alum or iron salts followed by sedimentation and filtration to remove arsenic. Lime softening is another common conventional treatment process that can potentially remove arsenic from source waters. Smaller-scale systems and point-of-entry systems often use anion exchange resins or activated alumina. Other arsenic removal technologies include manganese greensand, reverse

osmosis (RO), electro dialysis reversal (EDR), nanofiltration (NF) and adsorption on activated carbon. Various researches have been performed to remove arsenic in water and drinking water. Most arsenic removal processes have focused on removal of As (V) rather than As (III) because better As (V) removal can be achieved under comparable conditions, and As (III) can easily be converted to As (V) using a strong oxidising agent such as chlorine (Hering *et al.* 1996; Sorg 1999). Arsenic has also been removed by up to 60.5% from the source water by coagulation with PACl and alum (Kang *et al.* 2003). However, this conventional process has some limitations with respect to the removal of arsenic. There have been several studies on the removal of arsenic using membrane filtration. More than 75% of As (III) could be removed using NF membrane without any chemical additives, while trivalent arsenic could not be removed by rapid sand. In filtration systems without pre-oxidation of As (III) to As (V), both As (V) and As (III) removal by NF membranes were not affected by source water composition (Sato *et al.* 2002). Rejection of arsenite and arsenate with the RO membrane was over 95%. However, treatment of water

with a high concentration of arsenic might be necessary for the application of the RO process where a 66% recovery was obtained. The behaviour of the membrane is consistent with the extended Nernst-Planck equation model predictions for an uncharged membrane where size exclusion controls ion retention. However, separation of arsenic species was a due to a combination of size exclusion, preferential passage of more mobile ions and charge exclusion (Eric & Waypa 2000).

Since inorganic arsenic behaves as an acid in water, the pH of the system will control the degree of protonation of arsenic and arsenic acids. At moderate pH (pH 5–8), arsenate (As (V)) exists as a mono or divalent anion while arsenite (As (III)) remains as a fully protonated non-charged molecule. Therefore, both arsenate (As (V)) and arsenite (As (III)) may exhibit different transport phenomena in a natural system, depending on the pH, ionic strength and oxidation state (Hem 1992).

Two different mechanisms for the removal of a solute, size and electrostatic exclusions, can result from the solute charge or the charged membrane surface. To demonstrate removal mechanisms in NF and UF membranes, transport phenomena for a solute through the membrane pores should be rigorously investigated, along with membrane characterization relating to the surface charge and pore size distribution. While the mechanisms of fouling and removal of microfiltration (MF) and reverse osmosis (RO) membranes have been rigorously investigated and are well understood, the transport and removal mechanisms of nanofiltration (NF) and ultrafiltration (UF) membranes remain unclear.

Therefore, the objectives of this paper were to determine the major transport mechanisms of NF and UF membrane filtrations in terms of the mass transfer coefficients of both arsenate and arsenite ions, to determine the optimum operating conditions for their maximum removal, and to predict the removal performance of arsenic compounds by membranes.

THEORIES

The J_0/k ratio can be used to control hydrodynamic operating conditions. For the same J_0/k ratio, it is hypothesized that solute removal, and flux decline trends, for a given

solute-membrane pair are almost identical (Cho *et al.* 2000a, b). J_0 (the initial pure water permeation flux (Equation 1) and k (the back-diffusional mass transfer coefficient) can be calculated from the following equations (Mulder 1996).

$$J_0 = \frac{Q_p}{A_m} \quad (1)$$

$$k = 1.62 \left(\frac{UD^2}{d_h L} \right)^{0.55} \quad (\text{thin-channel-type module}) \quad (2)$$

Here, Q_p and A_m are the permeate flow rate ($\text{cm}^3 \text{s}^{-1}$) and membrane surface area (cm^2), respectively. Equation (2) is derived from the Sherwood number ($Sh = kd_h/D$) with consideration of module configuration (flow regime), where U is the average velocity of the feed fluid (cross-flow velocity (cm s^{-1}); D is the diffusion coefficient of the solute ($\text{cm}^2 \text{s}^{-1}$) estimated by the Stokes-Einstein relationship, d_h is the equivalent hydraulic diameter (cm), and L is the channel length (cm).

The non-equilibrium thermodynamic equation takes into account two driving forces (convection and diffusion). To describe these transport characteristics, the solute flux can be expressed by the equation suggested by Kedem and Katchalsky (1958) (Equation 3), which is based on irreversible thermodynamics where the membrane is considered as a black box, since the transport mechanisms are not clearly understood.

$$J_s = P_m(C_m - C_p) + J_v(1 - \sigma) \cdot C^* \quad (3)$$

Here, J_s , P_m , σ and C^* represent the solute flux, the solute permeability (the diffusive transport of the solute through the membrane pores), the reflection coefficient (which is a measure of the selectivity of a membrane for a particular solute), and the logarithmic average concentration ($C^* = (C_m - C_p)/\ln(C_m/C_p)$), respectively. The values of C_m and J_v can be obtained from the concentration polarization (CP) relationship, and J_s equals the product of J_v and C_p . Using experimentally determined parameters for different J_0/k ratios, including $(C_m - C_p)$, J_s , J_v and C^* , P_m and σ can then be determined by a nonlinear estimation with a three dimensional plot of J_s versus J_v versus C^* .

HYPOTHESES

Ion removal by the membrane may be affected by the charge of the membrane and ion. To demonstrate this hypothesis, NF and UF membranes were tested, and arsenite and arsenate were used as target ions. To change membrane and ion charge, the pH of the feed solution was changed, and arsenite and arsenate were used to demonstrate ion charge effect.

The removal of arsenic compounds by NF and UF membranes can be substantially affected by electrostatic exclusion. It is hypothesized that arsenate and arsenite exhibit different transport characteristics, which are pH dependent. Arsenic rejection is hypothesized to increase at higher pHs and the higher oxidation state. Transport of arsenic compounds during the operation can be affected by both membrane pore sizes and charges. In addition, operating conditions, in terms of J_0/k ratios, are important in arsenic transportation. It is also hypothesized that the transport characteristics of arsenic compounds may vary with different types of membrane or J_0/k ratio.

In addition, the Natural Organic Matter (NOM) functional group can affect ion removal through the membrane. A positively ionizable functional group (e.g. amine group) may enhance ion removal due to binding ion and NOM, but a negatively ionizable functional group (e.g. carboxyl and hydroxyl group) may not affect ion removal.

MATERIALS AND METHODS

Two different bench-scale units, a spiral-wound module and a flat sheet membrane, were tested under various hydrodynamic operating conditions determined from J_0/k ratios. The initial test J_0/k ratios were obtained with deionized (DI) water, prior to the actual tests with arsenic-containing feed

waters. A particular J_0/k ratio was adjusted by varying J_0 (controllable with trans-membrane pressure valve) for a fixed value of k (changeable by cross-flow velocity control), or vice versa. Based on these pre-determined J_0/k ratios, membrane filtration tests were performed with feed water and membranes. All of the filtration experiments were conducted in the recycle mode.

Arsenic removal measurements were conducted on one NF membrane (ESNA, Hydronautics, USA) and two UF membranes (PW and GM, Desal. Osmonics, USA). The membrane properties, in terms of Molecular Weight Cut Off (MWCO), charge, and pure water permeability (PWP), are listed in Table 1, and Figure 1 shows the results of the zeta potential of membranes.

Synthetic solutions were used to perform bench-scale membrane tests. These solutions were prepared with pure water, and spiked with $100 \mu\text{g l}^{-1}$ of either arsenate (As (V)) or arsenite (As (III)) as a pure component, at various pH values (4, 7 and 10). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were added to the synthetic solutions to adjust the pH. Arsenic concentrations were measured by continuous hydride generation (Perkin Elmer FIAS 400) using atomic adsorption spectroscopy (AAS, Perkin Elmer 5100ZL). The limit of detection for arsenic was $4 \mu\text{g l}^{-1}$.

This study comprised four main experiments: Experiment I included the characterization of the membrane in terms of surface charge and pore size distribution. Experiment II included the evaluation of the ion removal efficiencies by changing various chemical and hydrodynamic operating conditions. Experiment III included the determination of transport coefficients, including the solute permeability (P_m) and the reflection coefficient (σ), using modified Kedem and Katsky models; the modified models

Table 1 | Membrane properties

Membrane	Material	MWCO (Da)	Zeta Potential (mV) @ pH 7.0	PWP (l/day-m ² -kPa)	Contact angle (°)
GM (UF)	Polyamide TFC	8,000	-45.09	4.34	61.0
PW(UF)	Polyethersulfonate	10,000	-29.11	28.22	73.9
ESNA (NF)	Polyamide TFC	250	-9.90	2.35	63.0

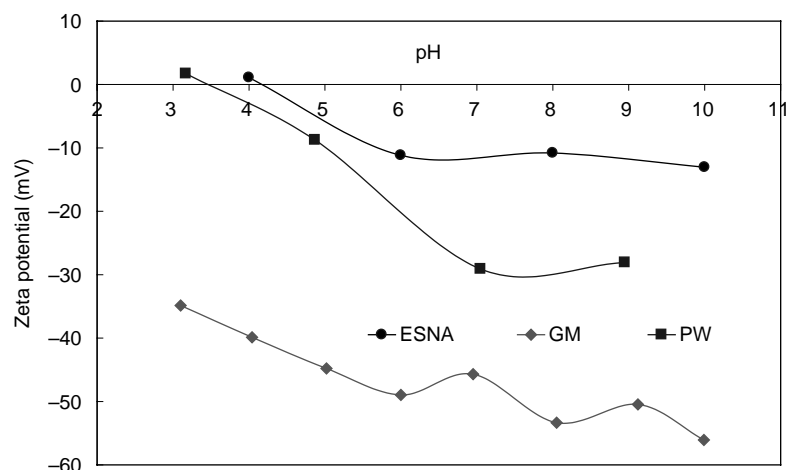


Figure 1 | Zeta potential of membranes.

used implied convection and diffusion transport terms, and transport coefficients (k); the reflection coefficient was determined in the constant cross-flow velocity mode. Experiment IV included the effect of the NOM structure on arsenic removal. Using dialysis bag (MWCO 3500 Dalton, Spectra, USA) and XAD 8/4 resins, NOM was isolated into colloidal organic matter (COM), hydrophobic NOM (HP-NOM), transphilic NOM (TL-NOM), and hydrophilic NOM (HL-NOM). Among these structures, we used only COM, HP-NOM and TL-NOM spiked with arsenic for experiment IV (Leenheer *et al.* 2000).

RESULTS AND DISCUSSION

Arsenic removal by the spiral-wound module of the NF membrane

Figure 2 shows the results of arsenite ion rejection by the spiral-wound module of the NF membrane. The removal of arsenite increased with increasing pH due to the charge repulsion. The relationship between arsenite removal and pH was also investigated. The removal of arsenite ions in the pH range 7 to 10 was much higher than for those in the pH range 4 to 7. This is because the pKa value of arsenite is

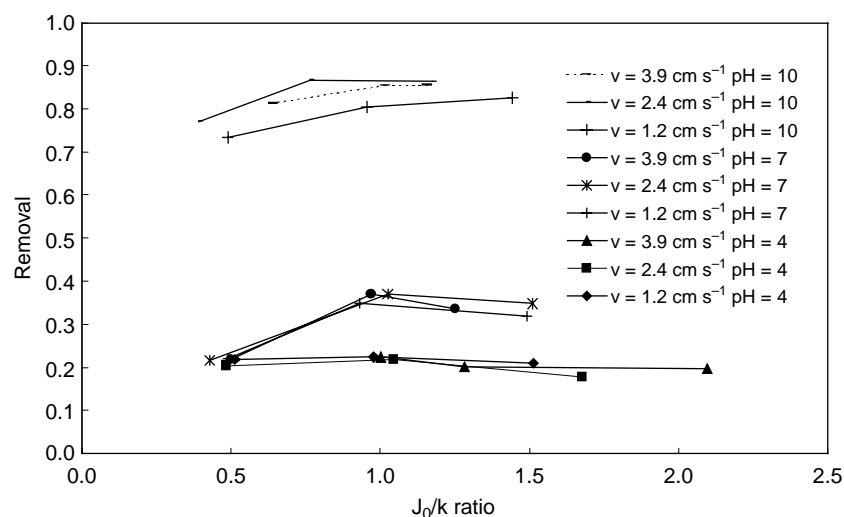


Figure 2 | Results of arsenite ion removal by the spiral-wound module with the NF membrane.

approximately 9.2, so in the latter pH range arsenite ions are still non-charged species.

The J_0/k ratio also slightly affected arsenite removal. Without charge repulsion (between pH 4 to 7), the maximum value of arsenite removal was found for a J_0/k ratio of approximately 1.0. That means the major transport mechanism changed from diffusion to convection at a J_0/k ratio of 1.0. The removal of arsenite increased with increasing values of J_0/k ratio at pH 10. Unlike pH and J_0/k ratio, the cross-flow velocity did not significantly affect the removal of arsenite. The same experiments were

performed for arsenate. However, arsenate exhibited high removal values (above 0.92) due to electrostatic repulsion between the negatively charged membrane and arsenate ions (data not shown in this paper).

Arsenic removal by flat-sheet module with the NF and UF membranes

Figures 3 and 4 show the removal behaviours of arsenite and arsenate ions using the flat-sheet module with the NF (ESNA) and UF (GM) membranes, respectively. At the

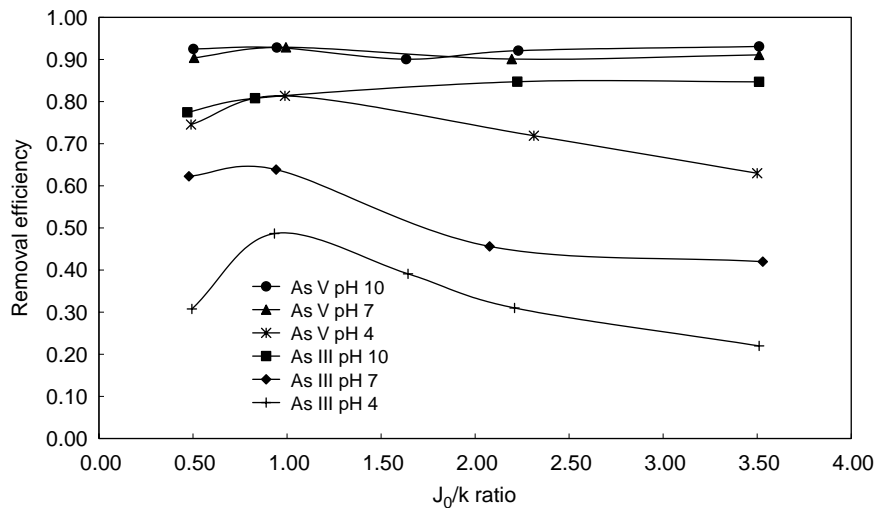


Figure 3 | Removal behaviour of arsenite and arsenate ions by the NF membrane.

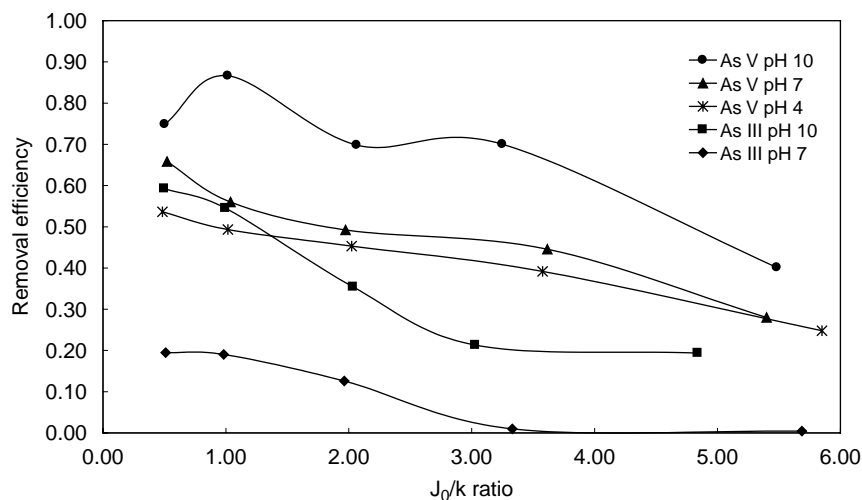


Figure 4 | Removal behaviour of arsenite and arsenate ions by the UF membrane.

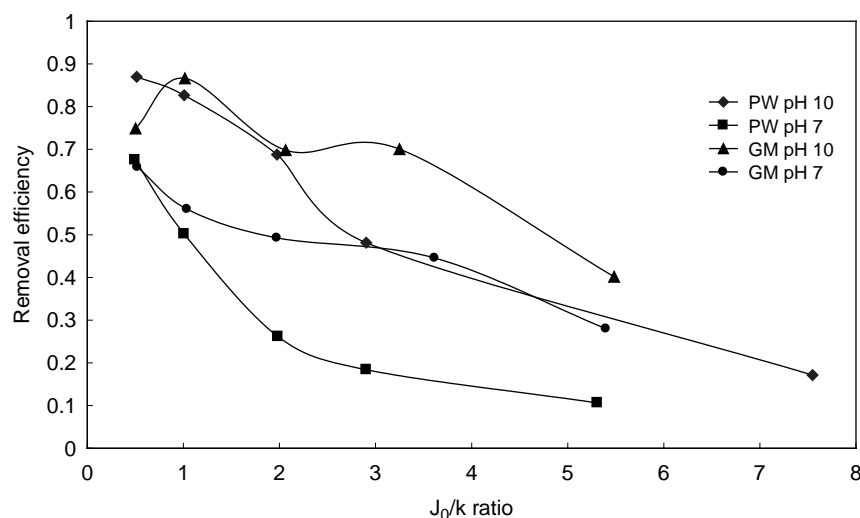


Figure 5 | Arsenate removal at pH 7 and 10 with two different UF membranes (PW and GM).

same pH and concentration of ions, the removal of arsenic compounds by the NF membrane was higher than by the UF membrane due to size exclusion. However, the UF membrane has the potential to remove arsenic compounds up to 0.87. Diffusion is the major transport mechanism for the removal of charged arsenate and arsenite ions by the NF membrane because the removal efficiencies of those charged arsenic ions increased with increasing J_0/k ratio. The major transport mechanism for uncharged arsenate and arsenite changed from diffusion to convection at a J_0/k ratio of approximately 1 because the removal efficiency of arsenic ions showed the maximum value at J_0/k ratio of approximately 1. Conversely, the major transport mechanism of arsenate and arsenite with the UF membrane was convection, with the exception of highly charged arsenate (i.e. arsenate at pH 10).

Arsenic removal by flat-sheet types of two different UF membranes

Figure 5 shows the removal behaviour of arsenate ions at pH 7 and 10, by two different UF membranes (GM and PW). The major transport mechanism of the PW membrane is always convection even in conditions of high pH (pH = 10), but the major transport mechanism of the GM membrane, for highly charged arsenate, changed from diffusion to convection at J_0/k ratio of approximately 1.0. It is believed that the pore size of the GM membrane

(MWCO of 8,000 Da) is slightly larger than that of the PW membrane (MWCO of 10,000 Da).

In addition, arsenate removal by the GM membrane was slightly higher than that by the PW membrane.

Table 2 | Estimated transport coefficients

	Membrane	Module	pH	σ	P_m (cm s ⁻¹)
Arsenate	ESNA	Spiral-wound	10	0.85	7.1×10^{-6}
	ESNA	Spiral-wound	7	0.82	6.8×10^{-6}
	ESNA	Spiral-wound	10	0.84	6.9×10^{-6}
	GM	Flat-sheet	10	0.62	2.3×10^{-4}
	GM	Flat-sheet	7	0.43	2.2×10^{-4}
	GM	Flat-sheet	4	0.19	2.0×10^{-4}
	PW	Flat-sheet	10	0.51	1.7×10^{-3}
Arsenite	ESNA	Spiral-wound	10	0.80	7.0×10^{-6}
	ESNA	Spiral-wound	7	0.61	6.9×10^{-6}
	ESNA	Spiral-wound	4	0.31	6.9×10^{-6}
	GM	Flat-sheet	10	0.31	2.2×10^{-4}
	GM	Flat-sheet	7	0.13	2.2×10^{-4}
	PW	Flat-sheet	10	0.11	1.7×10^{-3}

Table 3 | Summary of major transport mechanism of arsenic

	Charged arsenic	Non-charged arsenic
NF membrane	Diffusion	Diffusion to convection
UF membrane	Diffusion to convection	Convection

However, the water permeability of the PW membrane is significantly higher than that of the GM membrane, thus the PW membrane is believed to be more efficient in the case of arsenate at higher pH conditions than the GM membrane based on the operation condition (especially the low J_0/K ratio value).

Determination of transport coefficients from the bench-scale membrane tests

Using equation (3), transport coefficients were estimated (listed in Table 2). From Table 2, it was found that membrane pore sizes, as well as charge solute properties and the feed solution chemistries affected membrane transport. Both diffusion and convection are proven to affect the transport of ions; however, in the case of the NF membrane, diffusion is the most dominant transport mechanism, whereas convection is the more dominant mechanism for the UF membrane. The reflection coefficients (σ) for both the UF and NF

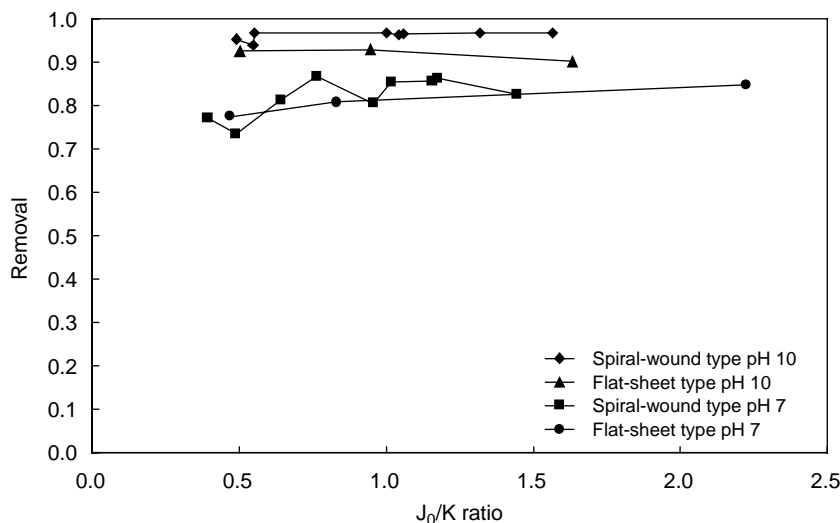
membranes were increased with increasing pH, while the reflection coefficients of arsenates were higher than those for arsenites; both can be explained by the charge repulsion. Table 3 shows the summary of major transport mechanisms in terms of ion charge and membrane type. In the case of the NF membrane, the major transport mechanism of charged ions was diffusion but that of non-charged ions changed from diffusion to convection at J_0/k of approximately 1. Conversely, in the case of the UF membrane, the major transport mechanism of charged ions changed from diffusion to convection at approximately $J_0/k = 1$, but that of non-charged ions was convection.

Effect of module type on arsenic removal (spiral-wound type vs. flat-sheet type)

Figure 6 shows the effects of module type on arsenic removal. Arsenate removal, under both neutral and basic conditions (pH 7 and 10), was evaluated. From the results, the spiral-wound module showed slightly higher arsenate removal than the flat-sheet module, for both pH values.

Effect of NOM structure on arsenic removal efficiency

Figure 7 shows the effect of NOM structure on arsenic removal. During fractionation, we used 0.1 HCl and 0.1

**Figure 6** | Effects of module type on arsenic removal.

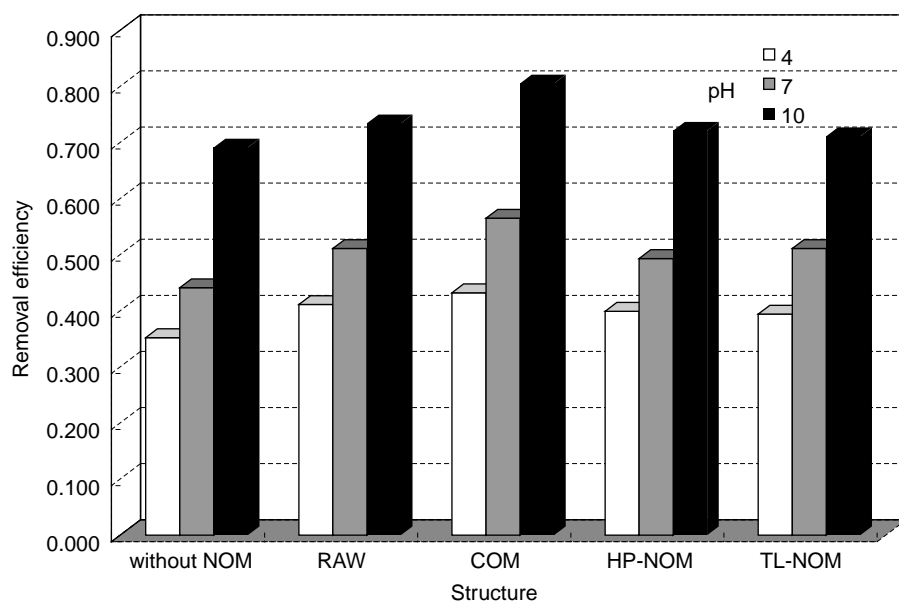


Figure 7 | Effect of NOM structure on arsenic removal efficiency.

NaOH, so each fractionated NOM had a different ionic strength. To give the same ionic strength effect and the same organic loading, we adjusted the ionic strength of all fractionated samples to $1,400\text{--}1,600\ \mu\text{S cm}^{-1}$ using NaCl and applied $5\ \text{mg l}^{-1}$ of fractionated samples based on DOC (dissolved organic carbon). The GM membrane was used and J_0/k ratio was adjusted to approximately 1. As shown in [Figure 7](#), the removal efficiency of arsenic without NOM slightly decreased compared with the non-ionic strength adjusted test due to compaction of the double layer near the membrane surface (see [Figures 4 and 7](#)). Removal efficiencies of arsenic with NOM fractions were higher than without NOM fractions. COM showed the most positive effect on arsenic removal as we described in the hypotheses. It is believed that a positively ionizable functional group of COM (e.g. amine group) may enhance ion removal due to binding ion and NOM. However, the removal efficiencies of arsenic with HP-NOM and TL-NOM were also slightly higher than that without NOM. This may be not caused by the functional group of NOM because, generally, HP-NOM and TL-NOM have a negatively ionizable functional group (e.g. carboxyl and hydroxyl group). It is likely that these HP-NOM and TL-NOM adsorbed or concentrated near the membrane surface may interrupt arsenic transport through the membrane.

CONCLUSIONS

From the bench-scale membrane tests, electrostatic interactions are an important mechanism for the removal of arsenic ions by both UF and NF membranes. Membrane transport was affected by membrane pore size, and the charge repulsion between arsenic ions and the charged membrane. The reflection coefficients (σ) of the NF membrane were higher than those of the UF membrane. However, some experiments (NF membrane: uncharged arsenic ion; UF membrane: highly charged arsenic ions) indicate that the major transport mechanism was changed by the J_0/k ratio. Therefore, the J_0/k ratio can be used as an important operating parameter during the operation of both UF and NF membranes. In addition, it is possible that the UF membrane can be applied to remove arsenic ions efficiently, through control of operating conditions without any additional treatment. All the NOM structures showed positive effects on the removal of arsenic due to the ionizable functional group and adsorption of the NOM structure on the membrane surface.

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