

Study the Remove and Transport Mechanisms of Seleniums in Membrane (UF and NF) Processes

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Abstract

The removal and transport of ionized and non-ionized selenium's were systemically investigated in this study. The charge repulsion between the membrane surface and selenium ions was an important mechanism for the rejection of ions by a charged membrane. In addition, selenium removal was significantly affected by the J_0/k ratio, but was not affected by the cross-flow velocity. Both diffusion and convection are proven to affect the transport of selenium ions transports. The reflection coefficients of both UF and NF membranes increased with increasing the pH, and with the reflection coefficients of selenate are being higher than those of selenite at under the same operating conditions. The spiral-wound type module exhibited slightly higher selenate removal compared to than the flat-sheet type module at under the same operation conditions.

Keywords: Selenium; Diffusion; Convection; J₀/k ratio; Membrane

Introduction

Selenium is an essential element for animal nutrition but there is narrow range of diatery [1]. Selenium has been regulated is regarded as a highly toxic chemical by World health organization(WHO) and EU to recommend maximum selenium concentration in drinking water of 10 ppb while EPA sets limit of 50ppb [2]. There are many processes to for treating selenium, including coagulation, ion exchange resins, and membranes [3]. However, for the removal of seleniums compounds down up to the MCL level of 10 µg/lL, membrane processes is believed to be the only alternative. Selenium exhibits broad toxic properties and complex chemistry characteristics, that which govern the speciation and distribution of its two major oxidation states. Both selenate (Se (VI)) and selenite (Se (IV)) may exhibit different transport phenomena in there natural system, depending on the pH, ionic strength, and oxidation state [4].

Two different mechanisms for the removal of a solute; size and electrostatic exclusions, can be resulted from the solute charge and 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 characterizations in terms of relating to the surface charge and pore size distribution.

Therefore, the objectives of this study were to determine the important transport mechanisms of NF and UF membrane filtrations in terms of the mass transfer coefficients, and diffusivities, of both selenate and selenite ions, to determine the optimum operating conditions for their maximum removal, and to predict the seleniums removal performance of selenium 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[3,5]. 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 (6).

$$J_0 = \frac{Q_p}{A_m} \tag{1}$$

$$k = 1.62 \left(\frac{UD^2}{d_h L}\right)^{0.33} \quad \text{(thin-channel-type module)} \tag{2}$$

Here, Q_p and A_m are the permeate flow rate (cm³/sec) and membrane surface area (cm²), respectively. Equation (2) is derived from the Sherwood number (Sh=kdh/D) with consideration of module configuration (flow regime), where U is the average velocity of the feed fluid (cross-flow velocity (cm/sec));, D is the diffusion coefficient of the solute (cm²/sec) estimated by the Stokes-Einstein relationship, dh 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 this transport characteristics, the solute flux can be expressed by the equation (3) suggested by Kedem and Katchalsky [6], which is based on irreversible thermodynamics considering the membrane is considered as a black box, since the transport mechanisms are not clearly understood.

$$J_s = P_m \left(C_m - C_p \right) + J_v (1 - \sigma) \cdot C^* \tag{3}$$

Here, J_s , P_m , 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 solute), and the logarithmic average concentration ($C^* = (C_m - C_p)/\ln(C_m/C_p)$), respectively. J_v , C_m , and C_p represent solvent flux, solute concentration near membrane, and permeate side solute

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concentration, respectively. The values of C_m and J_v can be obtained from the concentration polarization (CP) relationship, and Js equals the product of J_v and C_p . Using experimentally determined parameters at different J_0/k ratios, including (C_m-C_p) , J_s , J_v , and C^* , P_m and can then be determined by a nonlinear estimation with a three dimensional plot of J_v versus J_v versus C^* .

Materials and Methods

Two different types of bench-scale units; including a spiralwound and a flat sheet membrane module were tested under various hydrodynamic operating conditions in terms of determined from J_0/k ratios. The initial test J_0/k ratios tests were performed obtained with deionized (DI) water, prior to the actual tests with selenium containing feed waters containing selenium. A particular J_0/k ratio was adjusted by controlling varying J_0 (controllable with trans-membrane pressure valve) and 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.

Selenium removal measurements were conducted on one NF membrane (ESNA (Hydraunautics)) and two UF membranes (PW (Desal.) and GM (Desal.)). The membrane properties, in terms of MWCO, charge, and pure water permeability, are listed in Table 1.

Synthetic solutions were used to perform bench-scale membrane tests. These solutions were prepared with pure water, and spiked with either 100 μ g/L of selenate (Se (IV)) or selenite (Se (VI)) was spiked as a pure component, at various pHs conditions (4, 7, and 10). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were added to the synthetic solutions to adjust solution the pH. Selenium concentrations were measured with continuous hydride generation (PERKIN ELMER FIAS 400) using an Atomic Adsorption Spectroscopy (AAS, PERKIN ELMER 5100ZL).

Membrane	Material	MWCO (Dalton)	Zeta Potential (mV) @ pH 7.0	PWP (l/day-m²- kPa)	Contact angle (^O)
GM (UF)	Polyamide TFC	8000	-45.09	4.34	61.0
PW(UF)	Polyethersulfonate	10000	-29.11	28.22	73.9
ESNA (NF)	Polyamide TFC	250	-9.90	2.35	63.0

Table 1: Membrane properties.



Figure 1: The results of selenium $% \left({{\rm{S}}_{\rm{P}}} \right)$ ions removal by the spiral wound type module with the NF membrane.



This study was comprised of three main experiments. Experiment I included the characterization of the membrane characterizations in terms of surface charge and pore size distribution. Experiment II included the evaluation of the ion removal efficiencies of ions by changing various chemical and hydrodynamic operating conditions. Experiment III included the determinations of transport coefficients, including the solute permeability (P_m) and the reflection coefficient (σ), with using the modified Kedem and Katalsky [6] models; the modified models used implied convection and diffusion transport terms, and transports coefficients (k), and with the reflection coefficient were being determined at the constant cross-flow velocity mode.

Hypothesis

The removal of seleniums compounds removal by NF and UF membranes can be substantially affected by electrostatic exclusion. It is hypothesized that selenate and a selenite exhibit different transport characteristics, which are pH and oxidation state depending on pH and oxidation state. Selenium rejection is hypothesized to increase at higher pHs and in the higher oxidation state. Transports of selenium compounds during the operation can be affected by both membrane pore sizes and charges. In addition, operating conditions, in terms of J_o/k ratios, is also important to selenium transportations. It is also hypothesized that the transport characteristics of selenium compounds may exhibit differently with different types of membrane type and J_o/k ratios.

Results and Discussions

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

Figure 1 presents shows the results of selenite ions rejection by the spiral-wound type module of the NF membrane.

The removal of selenite increased with increasing pH value due to the charge repulsion. The relationship between selenite removal and pH was also investigated. The removals of selenite ions in the pH range of 7 to 10 were much higher than for those in the pH range of 4 to 7. This is because the pKa value of selinite is approximately 9.2, so in the latter pH range selenite ions are still are non-charged species in pH range of $4 \sim 7$.

The J_o/k ratio also affected selinite removal. Without charge repulsion (pH 4 and 7), the maximum value of selinite removal was

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found for a J_o/k ratio of approximately 1.0. That means the major transport mechanism changed from diffusion to convection at a J_o/k ratio of 1.0. But tThe removal of selinite increased with increasing values of J_o/k ratio at pH 10. Unlike pH and J_o/k ratio, the cross-flow velocity (U) did not affect significantly the removal of selinite. The same experiments were performed for selenate. However, selenate exhibited high removal values (above 0.92) due to electrostatic interaction between the negatively-charge membrane and ionized selenate ions.

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

Figures 2 and 3 show the removal behaviors of selinite and selenate ions conducted by using the flat-sheet type module of with both the NF (ESNA) and UF (GM) membranes. At the same pH and concentration of ions, the removal of selenium compounds removals by the NF membrane was higher than those by the UF membrane due to size exclusion. However, the UF membrane has the potential to remove selenium removal up to 0.87. The Diffusion is always the major transport mechanism for the removal of selenate and charged selinite ions by the NF membrane was always diffusion, but the major transport mechanism of uncharged selinite changed from diffusion to convection at J_o/k ratio of approximately 1. On the other hand conversely, the major transport mechanism of selinate and selenite



Figure 3: The removal behaviors of selinite and selenate ions by the UF membrane.



	Membrane	Module	pН	σ	P _m (cm/sec)
Selenate	ESNA	Spiral-wound	10	0.85	7.1×10 ⁻⁶
	ESNA	Spiral-wound	7	0.82	6.8×10 ⁻⁶
	ESNA	Spiral-wound	4	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
Selenite	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

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Table 2: Estimated transport coefficients.



with the UF membrane was convection, with the exception for highlycharged selenate (i.e. selenate at pH of 10).

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

Figure 4 shows the removal behaviors of selenium ions removal at two different pHs conditions (pH =of 7 and 10,) by two different UF membranes (GM and PW). The major transport mechanism of the PW membrane is always convection in spite of even in conditions of high pH condition (pH = 10), but the major transports mechanism of the GM membrane, for highly charged selenate, changed from diffusion to convection at J_o/k ratio above approximately 1.0 It is believed that pore size of the GM membrane (MWCO of 8000) is slight larger than that of the PW membrane (MWCO of 1000).

In addition, the selenate removal by the GM membrane was slightly higher than that of the PW membrane. However, the water permeability of the PW membrane is quite significantly higher than that of the GM membrane, thus the PW membrane is believed to be more efficient in the case of selenate at a higher pH conditions than the GM membrane based on the operation condition (especially low J_0/K ratio value)

Determination of Transport Coefficients from the Benchscale Membrane Tests

Using equation (3), transports coefficients were estimated. Table 2 lists the detail transport coefficients

From table 2, it was found that membrane pore sizes, as well as charge solute properties y solute, and the feed solution chemistry were affected membrane transport. Both diffusion and convection are proven to affect the ion transports of ions,. However, in the case of the NF membrane, diffusion is the most dominant transport mechanism over convection, but whereas convection is more dominant mechanism in case for the UF membrane, convection is more dominant transport mechanism over diffusion. The reflection coefficients (σ) for both the UF and NF membranes were increased with increasing the pH values, and the reflection coefficients (σ) of selenate were being higher than those for selenites, which can both results can be explained by the charge repulsion.

Effect of Module Type on selenium Removal (Spiral-Wound Type vs. Flat-Sheet Type)

Figure 5 shows the effects of module type on selenium removal. Selinate removal, under both neutral and basic conditions (pH 7 and 10), was evaluated. From the results, the spiral-wound type module showed slightly higher selinate removal than the flat sheet module, type membrane under for both pHs conditions.

Conclusions

From bench-scale membrane tests, electrostatic interactions are an

important mechanism for the removal selenium ions by both UF and NF membranes. Membrane transports were affected by membrane pore size, and the charge repulsion between selenium ions and the charged membrane. The reflection coefficients (σ) of the NF membrane were higher than those of UF membrane. However, some experiments (NF membrane: uncharged selenium ion, UF membrane: highly charged a selenium ions) exhibited indicate that the major transport mechanism was changed by the J₀/k ratio. Therefore, the J₀/k ratio can be used as an important operating parameter during the operation of both UF and NF membranes operations. In addition, it is possible that the UF membrane can be applied to remove selenium ions efficiently, through control of operating conditions without any additional treatment.

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