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Ozone/membrane hybrid process for arsenic removal in iron-containing water

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ABSTRACT

In this study, the efficiency of arsenic removal by UF and NF membrane after ozonation was investigated. Furthermore, the role of iron in the removal of arsenic was studied. We found that more than 99% of As(III) was oxidized into As(V) with a 1.0 mg/L dose of ozone. The oxidized As(V) was partially removed (20% removal) by UF, and completely removed using NF. The effect of pH on As(V) removal by NF was evaluated. The As(V) was completely removed by NF at pH 9, but the removal rate decreased to 80% at an acidic pH (pH 4). A variation of pH affected the predomination of arsenic species, altering the overall removal rate of NF. The effect of co-existing iron species on arsenic removal was investigated under the condition of pH 7 by adding 5.0 mg/L $FeCl_3$ to the initial concentration of 100 μg/L arsenic. More than 40% of As(V) could be eliminated simply through co-precipitation with the iron precipitate. After UF membrane filtration, up to 99% of As(V) could be removed. The enhanced removal efficiency of As(V) was due to the precipitate As(V) with Fe(III) hydroxide being effectively filtrated onto the UF membrane, which was not observed in the case of the iron-free water.

Keywords: Arsenic; Iron; Membrane; NF; Ozone; UF

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1. Introduction

Arsenic is widely present in the environment such as soils, surface waters, and ground waters due to natural sources, mine effluents, and organoarsenical pesticides [1,2]. The arsenic species occurs in surface and ground waters primarily as a combination of arsenite (As(III)) and arsenate (As(V)) [3]. This form of arsenic is regarded as a highly toxic substance that has become a major human health problem including cancer [4]. WHO recommends that drinking water do not exceed 10 μg/L for arsenic concentration and US EPA also adopted this as a regulatory limit [5,6].

Several technologies of treating water for arsenic removal have been studied such as co-precipitation, adsorption, anion exchange, and membrane filtration. In the case of membrane processes for removing arsenic, although there are differences in removal ratios among the different kinds of membranes, it has been reported that arsenic removing abilities of membranes can be enhanced by oxidizing As(III) into As(V) by applying an oxidizing process as a pre-treatment [7]. In this study, arsenic removing processes using nanofiltration (NF) membranes or ultrafiltration (UF) membranes were tested by applying ozone, a powerful oxidizer, as a pre-treatment. Fe(II) existing in water contaminated with arsenic is also easily oxidized into Fe(III) by ozone in most cases. Fe(III) forms $Fe(OH)_3(S)$ to absorb the arsenic existing in

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the water. In this respect, the purpose of this study was first to assess the efficiency of ozone/membrane hybrid processes in removing arsenic when the processes are applied to underground water where arsenic and iron coexist, and secondly to assess the effect of the process on the membrane fouling.

2. Material and methods

The As(III) and As(V) solutions used in the experiment were prepared at an initial concentration of 100 µg/L by putting $NaAsO_2$ (Fluka, US) and $Na_2HAsO_4·H_2O$ (Sigma-Aldrich, US) into DDI (deionized distilled) water. To make conditions where Fe(II) and Fe(III) iron ions exist in water, 5 mg/L each of Fe(II) and Fe(III) were prepared using $FeCl_2·4H_2O$ and $FeCl_3·6H_2O$ respectively. The pH of the solutions was adjusted using NaOH and HCl to pH 7 in all the experiments, except for the experiments involving arsenic removal effects by pH values. The pH values were measured using a pH meter (Thermo, ORION 3 STAR, US). Supelclean disposable solid phase extraction (SPE) tubes were used to separate and analyze the As(III) and As(V) after oxidization. Each of these tubes contained 2.5 g of an absorbent at pH 4 to pH 9 to selectively absorb only the As(V) while not absorbing the As(III), thereby separating the As(III) and As(V) from each other. The concentration of As(V) arsenic can be seen by deducting the concentration of As(III) from the total arsenic concentration, and through this method the degree to which As(III) is oxidized into As(V) can be seen. The samples used in each experiment were filtered with 0.45 µm syringe filters (PVDF), and the arsenic in the samples was measured using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Varian, 730-ES, US).

The ozone used in this study was generated with ozone generators (Ozonia®, LAB2B, Switzerland) using highly pure oxygen. Ozone treatment was conducted in a semi-batch type by injecting ozone continuously at a constant rate of 0.5 mg/L-min for 20 min as the ozone contact time. Fig. 1 shows a schematic diagram of the ozone injecting system. The reactor used Pyrex material at 4,000 mL volume. Samples in the reactor were mixed using a stirrer, and the concentrations of the ozone discharged after reactions were measured using KI traps.

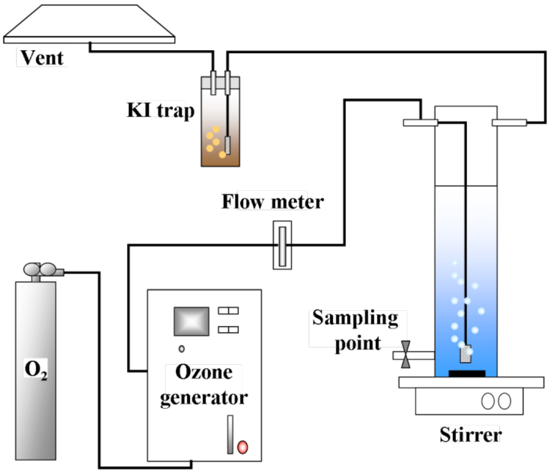
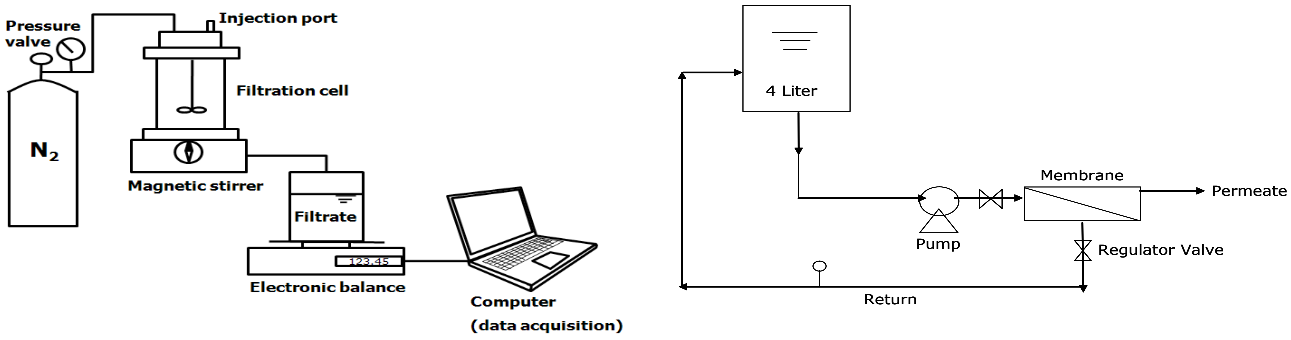


Fig. 1. Schematic diagram of the ozonation system.

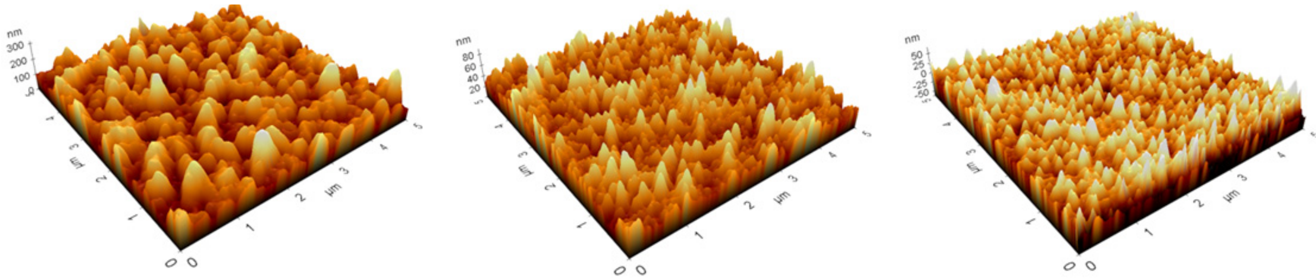
To assess the arsenic removal rate of the bench-scale UF membrane filtration, a process was constructed as shown in Fig. 2a. The membrane filtration device used was a dead-end stirred cell system of Millipore® (model 8010, US), and an 800 mL undercurrent tank was connected to the 75 mL filtration cell. The membrane filtration employed a constant pressure filtration process (3 bar) using nitrogen gas. The amount of the sample permeating the membrane was measured in real time using an electronic balance. The NF membrane filtration system used a cross flow mode constant pressure method of inserting a membrane and a spacer into a plate type, and then filtering, while maintaining the pressure at around 10 bar using a high pressure pump, as schematized in Fig. 2b.

Concerning the effective areas of the two flat membranes, NF and UF were 15 cm², and in the case of the NF membranes, NF 90, NF 70 and NF 40 were used re-



(a) UF (b) NF

Fig. 2. Schematic diagram of the membrane cell system.



(a) NE 90 (b) NE 70 (c) NE 40

Fig. 3. AFM images of (a) NE 90; (b) NE 70; (c) NE 40

Table 1
Properties of the experimental NF membrane

Membrane code	NE 90	NE 70	NE 40
Type	NF (TFC)		
MWCO, Dalton	220-310	350	1000
Contact angle, °C	42	23	24
Zeta potential, pH 7, mV	–36	–46	–16
Roughness	43	11	11

spectively. The materials and other specifications of the NF membranes used are shown in Table 1.

Fig. 3 shows the degrees of roughness of the NF membranes measured by an AFM (atomic force microscope). General MPD membranes show higher roughness than piperazine membranes, which was the case for the two membranes used in this experiment. In the case of UF membranes (polyethersulfone, hydrophilic), whose pores are larger than NF membranes, a total of four different pore sizes (5, 10, 30, and 50 kDa) were used.

3. Results and discussion

3.1. Ozonation

Although As(III) goes through natural oxidation processes by dissolved oxygen or photochemical oxidation, since the kinetic rate of those reactions are low, a process to oxidize As(III) into As(V) by artificially injecting oxidizing agents is necessary for effective treatment. The degrees of oxidation of As(III) into As(V) in cases where ozone oxidation was applied as a pretreatment process of treating water contaminated with arsenic were assessed. Ozone was injected into an As(III) solution at an initial concentration of 100 μg/L, and the oxidation trend for As(III) to be converted into As(V) in relation to the ozone doses consumed was analyzed. As shown in Fig. 4, when the consumed ozone dose was 0.2 mg/L, at least 80% of As(III) was oxidized into As(V), and when the consumed ozone dose was 1.0 mg/L or higher, at least 99% of 100 μg/L As(III) was oxidized into As(V). Given these results, ozonation was identified as being effective in As(III) oxidation.

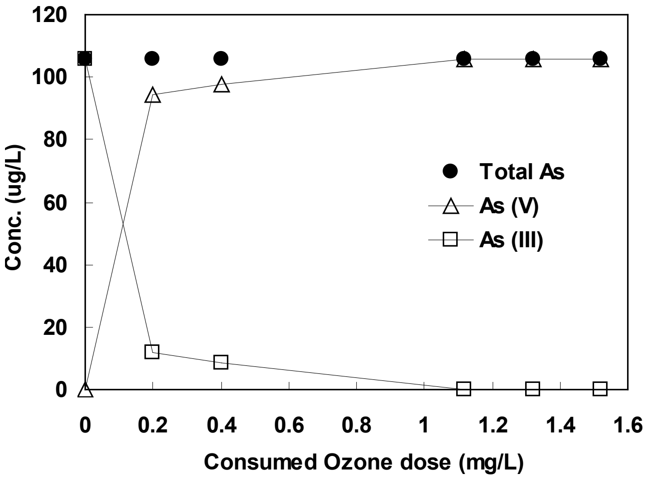


Fig. 4. Arsenic concentrations oxidation by ozone.

3.2. NF membrane filtration

3.2.1. Arsenic removal efficiency

The rates of removal of As(III) and As(V) at an initial concentration of 100 μg/L by NF membrane filtration are shown in Fig. 5. NE 90 NF membranes with the smallest pores showed an As(III) removal rate of around 50% and an As(V) removal rate of around 90%. NE 70 NF membranes showed an As(III) removal rate of around 35% and an As(V) removal rate of at least 90%. Finally, NE 40 NF membranes with the largest pores showed an As(III) removal rate of 15% and an As(V) removal rate of at least 90%. In general, the NF membranes' As(III) removal rates were shown to be lower than their As(V) removal rates. It is known that a major mechanism of arsenic removal by membrane filtrations is size exclusion [8]. However, in addition to size exclusion, in the case of negatively charged As(V), a Donnan exclusion removal mechanism also works, since membrane surfaces are also negatively charged [9]. Therefore, it was considered that the As(V)

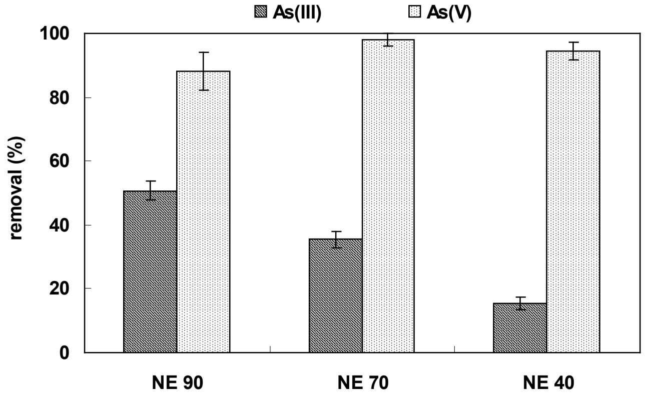


Fig. 5. Effects of NF membrane type on arsenic removal.

removal rates were higher than As(III) because As(V), which is negatively charged, was removed by not only size exclusion but also by Donnan exclusion. Thus, it was considered that oxidation processes are essential to effectively remove the As(III) that mainly exists in nature.

3.2.2. *The effect of pH on arsenic removal efficiency*

Since pH is an important factor in water treatment processes, and arsenic exists in diverse oxidized sates depending on pH, the effects of changes in pH on As(III) and As(V) removal rates were examined. As shown in Fig. 6, As(V) removal rates were higher than As(III) removal rates regardless of pH, and arsenic removal rates increased as pH increased from pH 4 to pH 7 and to pH 9.

In the experimented range of pH (pH 4, 7, and 9), As(V) mostly exists in ionized states — as $H_2AsO_4^-$ or $HAsO_4^{2-}$ — as shown in Eqs. (1)–(3) [10–12]. On the other hand, As(III) sometimes exists in a neural state as H_3AsO_3 in the experimented range of pHs [Eqs. (4)–(6)]. In addition, As(V) exists as monovalent anions $HAsO_4^{2-}$ at pH 7 or lower pH values, while it exists as divalent anions $HAsO_4^{2-}$ at pH 7 or higher pH values. There are larger repulsion reactions between divalent anion materials and negatively charged NF membrane surfaces than in the case of monovalent anion materials [13]. Therefore, it could be seen that, as pH values become higher, the removal rates will become higher because of the state of As(V) existence and the ion repulsion on membrane surfaces.

Arsenate [As(V)]

$$AsO_4^{3-} + H+ \Leftrightarrow HAsO_4^{2-} \qquad pKa = 11.6 \tag{1}$$

$$HAsO_4^{2-} + H+ \Leftrightarrow H_2AsO_4^- \qquad pKa = 6.7 \tag{2}$$

$$H_2AsO_4^- + H+ \Leftrightarrow H_3AsO_4 \qquad pKa = 2.2 \tag{3}$$

Arsenite [As(III)]

$$AsO_3^{3-} + H+ \Leftrightarrow HAsO_3^{2-} \qquad pKa = 13.4 \tag{4}$$

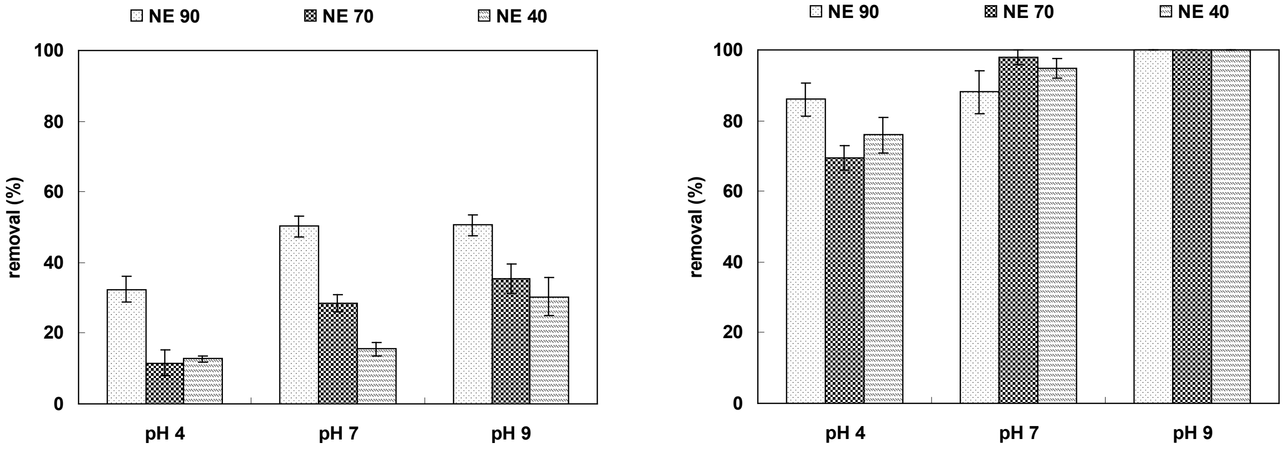
$$HAsO_3^{2-} + H+ \Leftrightarrow H_2AsO_3^- \qquad pKa = 12.1 \tag{5}$$

$$H_2AsO_3^- + H+ \Leftrightarrow H_3AsO_3 \qquad pKa = 9.2 \tag{6}$$

3.3. *Ozone/membrane hybrid process*

3.3.1. *Arsenic removal efficiency of single UF membrane filtration process*

Arsenic removal rates of UF membranes with diverse pore sizes (1, 5, 10, and 30 kDa) are shown in Fig. 7. To review the results, both As(III) and As(V) with initial concentrations of 100 μg/L showed low removal rates — 20% or lower. Since UF membranes have relatively larger pores than NF membranes, it was identified that arsenic was not removed in membrane filtration by only size exclusion, which is a major arsenic removal mechanism.



(a) As(III)

(b) As(V)

Fig. 6. Effect of pH on the removal of arsenic.

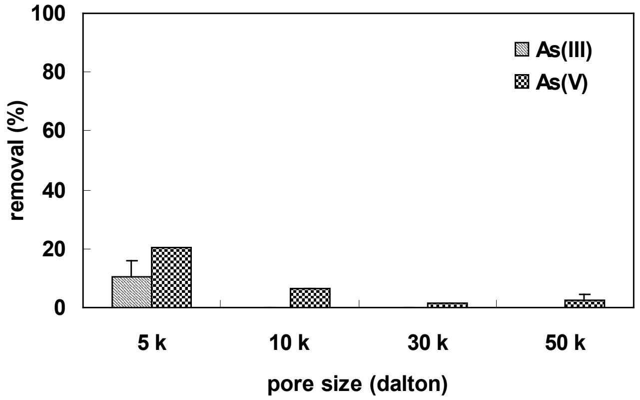


Fig. 7. Effects of UF membrane type on arsenic removal.

3.3.2. Ozonation of iron-containing water

Based on the results of the experiment mentioned above, it was identified that arsenic removal rates of UF membranes were remarkably low. However, since it is known that iron ions usually also exist in water contaminated with arsenic, and iron oxide $Fe(OH)_3(S)$ removes arsenic by absorbing it, we assessed the arsenic removal rates of processes that use UF membrane filtration following ozonation in cases where iron and arsenic exist together. In general, iron ions existing in water exist as Fe(II) [14], and arsenic exists as As(III). Therefore, we expected that if Fe(II) if oxidized into Fe(III) oxide and As(III) into As(V) by ozone, arsenic removal rates would be increased.

Fig. 8 shows the results of experiments conducted to assess the consumption of ozone when Fe(II) and As(III) are simultaneously oxidized by ozone. Compared to the ozonation where only 100 μg/L As(III) existed, as shown in the earlier experiment (Fig. 4), larger amounts of ozone were necessary when oxidizing a solution containing both As(III) in the same concentration and 5 mg/L Fe(II). To review the necessary amounts of ozone, the ozone dose needed to oxidize 50% of As(III) into As(V) was around 2.5 mg/L, while the ozone dose needed to oxidize 100% was around 3.8 mg/L. Therefore, it was identified that ozone consumption in solutions containing both As(III) and Fe(II) was relatively higher compared to solutions containing only arsenic, because the injected ozone was consumed due to reactions between irons and arsenic existing in water as shown in Eqs. (7) and (8).

$$\text{As(III)}\ (H_3AsO_3) + O_3 \rightarrow \text{As(V)} \quad k = 5.5(\pm 0.1)\times 10^5\ \text{M}^{-1}\text{s}^{-1} \tag{7}$$

$$\text{Fe(II)} + O_3 \rightarrow \text{Fe(III)} \quad k = 8.2\times 10^5\ \text{M}^{-1}\text{s}^{-1} \tag{8}$$

Therefore, in order to efficiently use the ozone process as a pre-treatment process for water contaminated with arsenic, background matters existing in water should be examined to determine the optimum ozone dose.

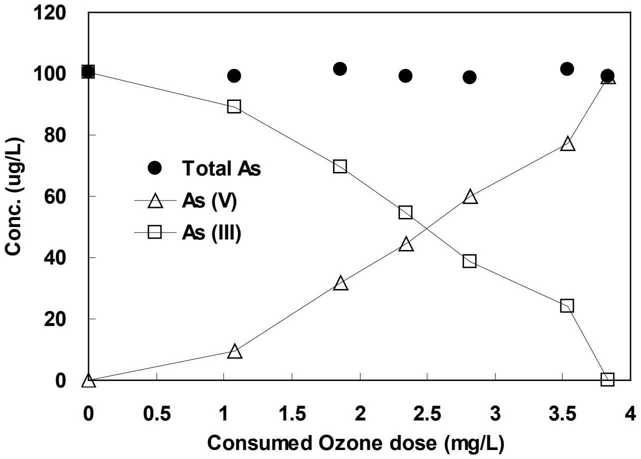


Fig. 8. Arsenic and iron(II) chloride concentrations oxidation by ozone.

3.3.3. Arsenic removal by ozone/UF hybrid process

The As(V) removal rates of UF membrane filtration following ozonation (consumed ozone dose = 3.8 mg/L) when used on samples that contained both 100 μg/L As(III) and 5 mg/L Fe(II) were compared with the removal rates of an independent UF membrane filtration process and an independent iron oxide absorption process when used on As(V) solutions with an initial concentration of 100 μg/L (Fig. 9). The As(V) removal rates of the independent UF membrane filtration process are the same as the results shown earlier in Fig. 7, and an arsenic absorption experiment using iron oxide was conducted by spiking 5 mg/L Fe(III) into a 100 μg/L As(V) solution, shaking the solution for two hours at 20°C and analyzing the As(V) removal rates afterward.

As shown in the results, around 40% of arsenic was absorbed and removed by iron oxide. When this treated water was filtered by UF membranes, the arsenic removal rates were shown to be 96%, 94%, 100%, and 100% when the pore sizes used in the experiment were 5, 10, 30, and 50 kDa respectively. Therefore, the additional arsenic removal rates achieved by UF membranes after absorption by iron oxide were 56%, 44%, 60%, and 60% when the pore sizes were 5, 10, 30, and 50 kDa respectively. Since the removal rates of As(V) by independent UF membranes without any absorption processes were maximum 20%, UF membrane filtration in the presence of iron ions had a synergy effect of around 30–40% increases in arsenic removal rates. Therefore, it was identified that in processes for treating water contaminated with arsenic, if iron exists in the water and an ozone process is applied as a pre-treatment process, arsenic can be sufficiently removed by UF membrane filtration.

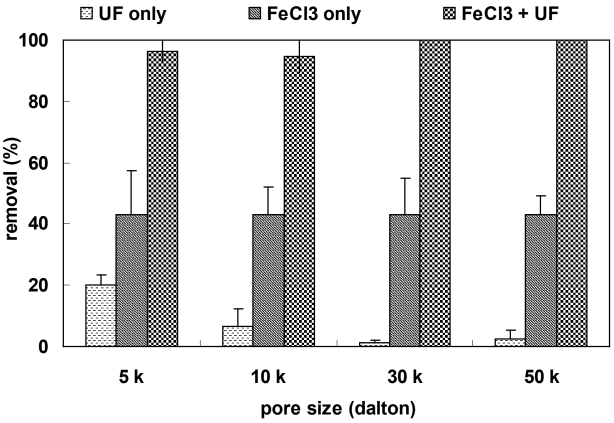


Fig. 9. Arsenic removal by UF membrane after ozonation with iron.

3.3.4. *Assessment of fouling on UF membranes*

Fig. 10 shows resistance values calculated in steps after fouling assessments. Total membrane resistance, R_t could be calculated by sum of R_m, R_f, and R_c values. R_c which is resistance caused by cake layer formation, existed only at a very low level in the cases of 5 and 10 kDa, and hardly appeared in the cases of 30 and 50 kDa. R_f resistance, which indicates irreversible resistance like absorption, existed at higher levels compared to R_c, as the levels were 1.1 m^{-1} on average and showed similar tendencies in all samples. In the case of UF membranes helped by iron oxide, R_f resistance was shown to be around two times higher than R_c resistance. Therefore, it could be said that a major resistance in this experiment was irreversible fouling caused by pore blocking due to absorption rather than membrane fouling determined by particle sizes.

4. Conclusions

As(III) was oxidized effectively into As(V) with ozonation, and As(V) removal rates were higher than As(III) because As(V), which is negatively charged, was removed by not only size exclusion but also by Donnan exclusion. Thus, it was considered that oxidation processes are essential to effectively remove the As(III) that mainly exists in nature. UF membrane filtration in the presence of iron ions had a synergy effect of around 30–40% increases in arsenic removal rates. Therefore, it was identified that in processes for treating water contaminated with arsenic, if iron exists in the water and an ozone process is applied as a pre-treatment process, arsenic can be sufficiently removed by UF membrane filtration. In the case of UF membranes helped by iron oxide, R_f resistance was shown to be around two times higher than R_c resistance, and thus it could be seen that a major cause of fouling was irreversible fouling caused by absorption rather than membrane fouling determined by particle sizes.

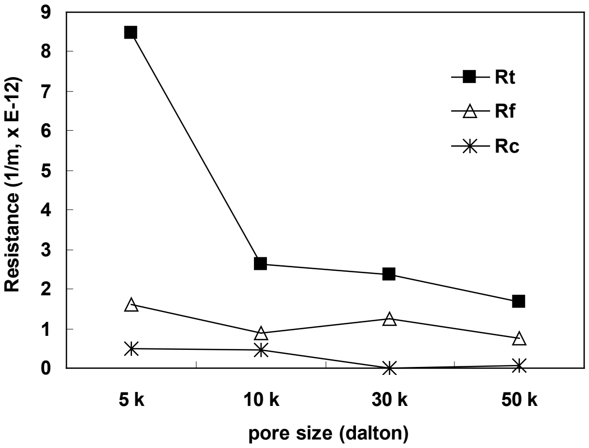


Fig. 10. Membrane resistance.

Acknowledgement

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