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Evaluation of manganese removal by adsorption for prevention of membrane fouling

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ABSTRACT

In the membrane-applied water treatment process, residual manganese often generates a significant problem because scaling of oxidized manganese can lead to irreversible membrane fouling. For the membrane process to operate effectively, advanced treatment process should be considered for manganese removal. In this study, an adsorption process utilizing a newly developed magnetite-coated adsorbent was adopted to overcome manganese fouling in ultrafiltration (UF) applications, particularly during chemically enhanced backwashing. Typical manganese-coated sand (i.e., Ferox) was also evaluated simultaneously for comparison. These adsorbents were assessed for basic performance in a fixed bed adsorption column test under various operating conditions. With the addition of chlorine dosing, the efficiency of manganese removal was improved dramatically. Specifically, magnetite column was effective to prevent flux decline in typical UF applications even with an empty bed contact times of 1 min, while severe fouling was observed with no such pretreatment, suggesting it as a promising technology for the control of fouling caused by manganese.

Keywords: Membrane fouling; Ultrafiltration; Manganese removal; Manganese adsorption; Magnetite adsorbent

1. Introduction

To ensure safe drinking water supply, the importance of monitoring and treating various contaminants, including pathogenic microorganisms, pharmaceuticals, endocrine disrupting chemicals and arsenic, has been magnified [1–4]. Manganese is one of such contaminants to be rejected as soluble manganese causes black water with its oxidized state and exacerbates taste and odor problems [5]. In addition, several studies reported that high concentration of manganese induces neurotoxicity and hepatotoxicity when exposed for a long period [6,7]. For this reason, the World Health Organization (WHO) has established the recommended guideline of 0.4 mg/L [8], and the US Environmental Protection Agency (EPA) limited it up to 0.05 mg/L for drinking water [9].

Manganese ions naturally exist in groundwater [10] and appear in the anoxic zone of reservoirs as a result of turning over occurred during seasonal change [11,12]. In conventional water treatment plants, the removal of manganese was achieved with oxidation methods such as chlorination, ozonation, aeration and potassium permanganate dosing. When manganese ions precipitate as an oxidized form, they could be removed by clarification and sand filtration [13]. However, as membrane technology is increasingly adopted in recent water treatment plants, manganese emerged as a new troublesome object which lowers the efficiency of plant.

Membrane processes are applied in a number of water treatment plants from drinking water production to high salinity water treatment [14–16]. In particular, microfiltration (MF) and ultrafiltration (UF) have been widely used as these processes are effective to remove

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suspended solids, turbidity, microorganisms and viruses [17–19]. Meanwhile, membrane fouling remains as a significant obstacle of its cost-effective operation, which reduces water permeability severely [20,21]. Manganese in particular is a major problem in this respect, leading to irreversible fouling due to its abnormal oxidation characteristics [22,23].

Manganese fouling often occurs during periodic membrane backwashing, where oxidants are added to enhance the removal of foulants. The oxidizing chemicals are dosed with the purpose of membrane performance recovery, but, ironically, it induces severe manganese fouling. Due to the dosed oxidants, the oxidation of manganese ions is progressed; as the oxidation kinetics of manganese is slow, the oxidation happens while the ions pass through the membrane [23,24], which results in irreversible fouling. Irreversible fouling occurred by manganese requires intensive membrane cleaning to recover its performance, which increases the maintenance cost significantly. Therefore, additional treatment process should be considered with manganese-rich feedwater.

This study suggested the adsorption of manganese during membrane backwashing in order to mitigate irreversible fouling derived by manganese. The feasibility of adsorption prior to the backwashing was investigated with two adsorbents under various operating conditions. For the adsorption column test, manganese concentrations, empty bed contact times (EBCTs), and sodium hypochlorite dosage were varied to determine the optimal operating conditions of manganese adsorption. The UF following backwashing step combined with adsorption was performed, and then consequent membrane performance was monitored to verify fouling reduction with newly adopted process.

2. Materials and methods

2.1. Preparation of adsorbents

Two adsorbents with differing characteristics were evaluated in this study. Magnetite-coated adsorbent is developed for removal of heavy metals, and manganese-coated adsorbent (Ferox) is used for removal of iron and manganese. Prior to evaluation, pretreatment was conducted to remove silt and surplus chemicals. In case of magnetite-coated type, ethanol washing was carried out combined with deionized (DI) water washing. Detailed information about the pretreatment methods for each type of adsorbent is summarized in Table 1.

2.2. Preliminary evaluation of the adsorbents in a batch test

Experiments were conducted to observe the basic performance of the adsorbents and to select the optimal adsorbent for manganese removal. Manganese adsorption was carried out with a batch test at room temperature (20°C–25°C) using an aqueous solution. The solution was prepared with manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$ [98%]; Junsei, Japan) and UF-treated water obtained from a drinking water treatment plant located in Gyeonggi province, Korea. As the concentration of manganese in the raw water was negligible (a level of non-detected), therefore, manganese was spiked to adjust the target concentration. The manganese concentrations were varied from 0.1 to 10 mg/L, representing groundwater or the case of an abrupt spill [25,26]. The samples were periodically collected at $t = 0$, 1, 5, 10, 20 and 30 min during adsorption experiment. The pH value of solutions was adjusted at pH 7 with hydrochloric acid and sodium hydroxide. For chlorination, sodium hypochlorite (NaOCl [8%]; Junsei, Japan) was prepared at 5 mg/L for manganese oxidation. The experiments were carried out in media bottles with 100 mL of sample and 1 g of adsorbent dosage. In order to ensure regular contact, an orbital shaker (C-SK-6, Changshin Scientific Co., Korea) was used at a 200-rpm equivalent stirring rate. The analysis of manganese concentration was performed with a DR5000 Ultraviolet-visible spectrometer (Hach Company, Germany). The wavelength for analysis was conducted at 525 nm for high range manganese and 560 nm for low range manganese. Entire experiments were performed in triplicate, and the analysis of manganese concentration was conducted in duplicate to increase reliability.

2.3. Fixed bed adsorption column experiments

A fixed bed column for adsorption was manufactured with a glass tube 1 cm in diameter and 30 cm in length, with the volume of packed adsorbent 20 cm^3. Glass wool and beads were placed at both ends of the column to prevent the escape of the adsorbents. The manganese and sodium hypochlorite solutions were injected into the adsorption column separately in order to avoid pre-oxidation before inflow into the column (Fig. 1). A Masterflex peristaltic pump (Cole-Parmer, Vernon Hills, IL, USA) was used to inject each stream into the adsorption column. Prior to the experiments, DI water was passed through the adsorbent-packed column for 12 h to remove impurities and air. The manganese and NaOCl solutions were passed through the column in two streams for 20 min before the beginning of the experiments to stabilize the adsorption process. Effluent samples for analysis were collected at $t = 0$, 1, 2, 4, 8 and 12 h.

Table 1
Adsorbents used for the evaluation of manganese removal

Type	Manufacturer	Model	Size	Pretreatment
Magnetite coated	"A" company	Under development	0.4– 0.84 mm	Ethanol washing 30 min, 5 times DI washing, 2 h Drying in desiccator
Manganese-coated sand	Tohkemy	Ferox	1.0–2.5 mm	DI washing, 12 h Drying in desiccator

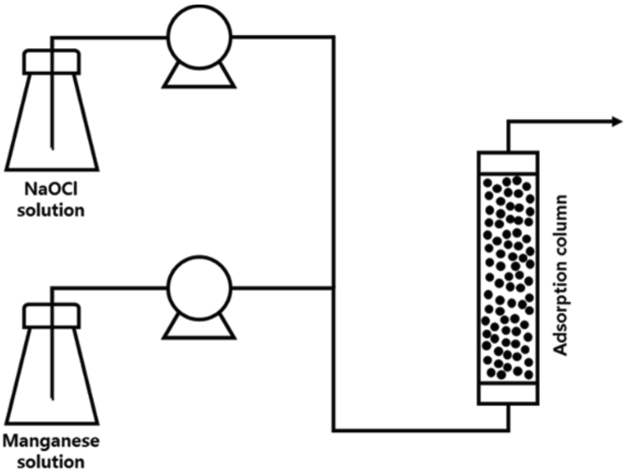

Fig. 1. Schematic description of the adsorption column test.

Table 2
Specific information of UF membrane and mini module

Fiber specification			Mini module specification	
Average pore size (μm)	Outer diameter (μm)	Inner diameter (μm)	Number of fiber (ea)	Surface area (m^2)
0.04	1,360	698	3	0.023

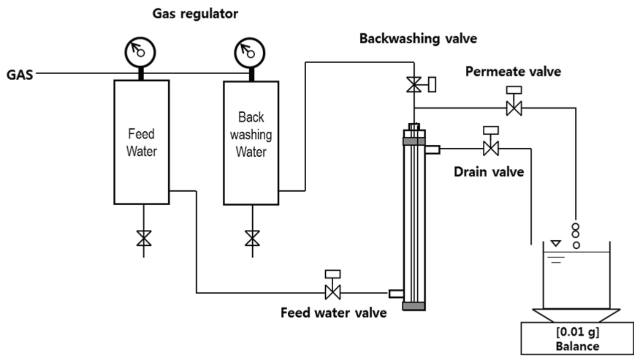

Fig. 2. Schematic description of the UF membrane system.

2.4. Membrane filtration experiments

A UF membrane filtration was performed to investigate the effect of manganese adsorption on membrane fouling. A hollow fiber membrane in a mini-module (HSF-CP75, Hyosung Corporation, Korea) was used, and specific information was presented in Table 2. The membrane modules were stored in 10 mg/L NaOCl solution and rinsed using DI water. The bench scale UF system shown in Fig. 2 was operated at a constant pressure using N_2 gas. Filtration was conducted under 0.5 Mpa, and backwashing was performed at 0.75 Mpa. In order to focus on backwashing, the process was operated automatically with a protocol of 3-min permeation and 1-min backwash. The feedwater and the backwashing water were prepared separately. The spiking of the manganese and sodium hypochlorite solutions was adjusted for three different experimental treatments (Table 3). UF-treated water test was conducted as a baseline where manganese was not added. Here, membrane fouling caused by oxidation due to residual NaOCl after backwashing as well as complexation of natural organic matter (NOM) and manganese were avoided. The feedwater and backwashing water in the pressurized vessel were replaced every 20 min in order to prevent any further oxidation. During the operation of UF membrane system, permeate was continuously monitored using a digital balance and recorded in real time with a laboratory computer.

3. Results and discussion

3.1. Selection of adsorbents by batch test

In conventional water treatment process, manganese concentration was controlled by oxidation process. However, it often fails to decrease manganese effectively since manganese oxidation is a slow reaction. The characteristics of oxidation kinetics were presented in Fig. 3 which was progressed with hypochlorite, typically used oxidant in water treatment plant. The experiments were operated with two concentrations, 0.1 mg/L and 10 mg/L, representing general condition and abrupt spill, respectively. Fig. 3 shows only a slight decrease in manganese concentration with 30 min oxidation, with reduction rates of 14% and 20% for each low and high concentration. Several previous researches also reported relatively low manganese oxidation kinetics [24,27,28], in accordance with our results, indicating that an additional process may be required for efficient manganese removal.

Table 3
Composition of feedwater and backwashing water for each treatment

Experiment	UF filtered water		Mn^{2+} 1 mg/L + Column		Mn^{2+} 1 mg/L	
	Feedwater	Backwashing water	Feedwater	Backwashing water	Feedwater	Backwashing water
Manganese spiking (1 mg/L)	X	X	O	O	O	O
NaOCl spiking (5 mg/L)	X	O	X	O	X	O
Adsorption column treatment	X	X	X	O	X	X

Current study suggested a combined process of oxidation and adsorption process in order to reduce manganese concentration. First, basic performance of adsorbents was assessed to select the optimal adsorbent and operating conditions. Newly developed magnetite-coated adsorbent was compared with typical manganese-coated sand (Ferox). Their removal efficiencies are presented in Figs. 4(a) and 4(b). The magnetite-coated adsorbent generally showed higher removal rates compared with Ferox. In addition, adsorption process with sodium hypochlorite dosing was performed which simulates the synergetic effect of oxidation and adsorption. Figs. 4(c) and 4(d) show significantly improved removal for both low and high concentrations; in particular, the removal rate was more than 76% under the low manganese concentration for magnetite. In the case of Ferox, the manganese concentration increased at initial period. This could be explained as a result of the elution at the surface of Ferox which is coated with manganese. However, the concentration of manganese gradually decreased with adsorption and eventually showed decreased concentration after 30-min operation. Therefore, stable behavior could be expected for longer period of operation.

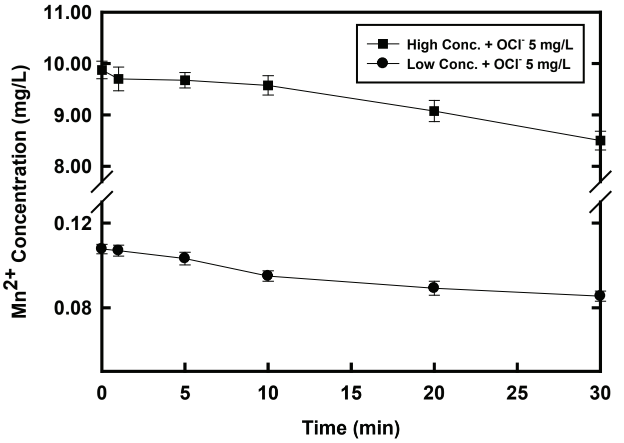

Fig. 3. Manganese removal by sodium hypochlorite (5 mg/L OCl$^-$) in high and low manganese concentrations (high concentration of Mn^{2+}: 9.875 ± 0.2 mg/L; low concentration of Mn^{2+}: 0.108 ± 0.002 mg/L).

Our results proved the synergetic effect of NaOCl dosing with adsorption for effective manganese removal. The improved performance could be explained with the change of oxidation state and subsequent adsorption mechanism. With no chlorine oxidation, the manganese ions are removed only by adsorption (Fig. 5). However, under hypochlorite dosing, they are removed by more complex mechanism of oxidation by hypochlorite and reaction with manganese dioxide (MnO_2) at the surface of adsorbent (Fig. 5) as follows:

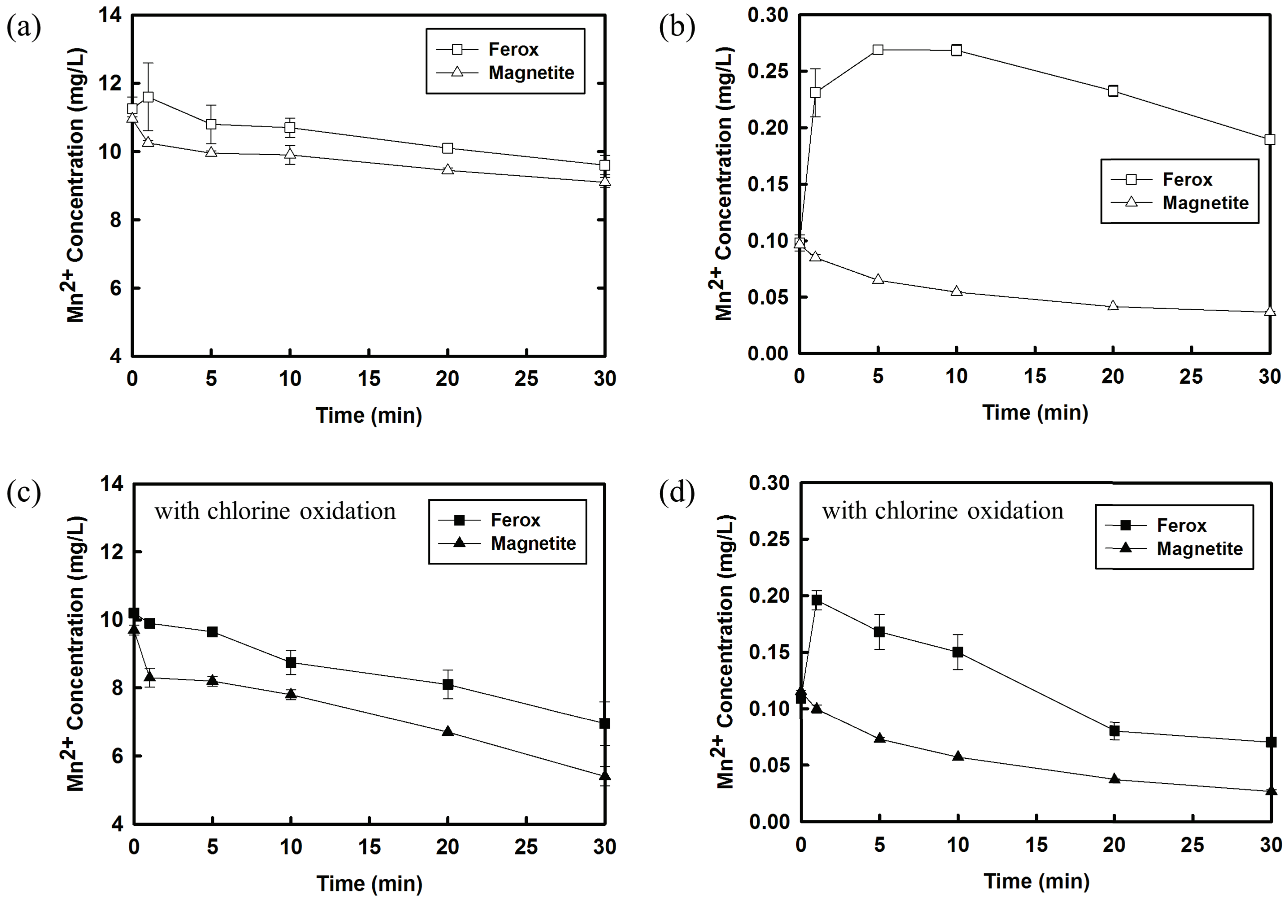

Fig. 4. Adsorption performance for (a) high concentration of Mn^{2+} (11.15 ± 0.25 mg/L), (b) low concentration of Mn^{2+} (0.0963 ± 0.003 mg/L), (c) high concentration of Mn^{2+} (9.98 ± 0.26 mg/L) with 5 mg/L OCl$^-$, and (d) low concentration of Mn^{2+} (0.1135 ± 0.003 mg/L) with 5 mg/L OCl$^-$.

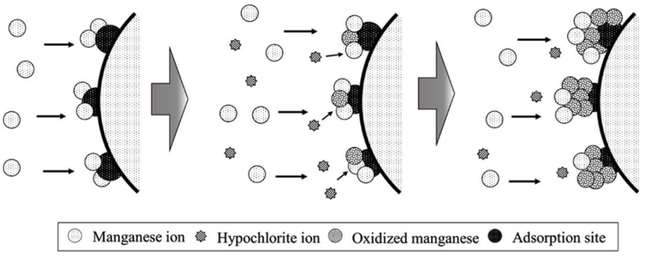

Fig. 5. Adsorption mechanism of manganese at the presence of hypochlorite ions.

$$Mn^{2+} + MnO_2 \cdot H_2O + H_2O \rightarrow MnO_2 \cdot MnO \cdot H_2O + 2H^+ \quad (1)$$

$$MnO_2 \cdot MnO \cdot H_2O + 2OCl^- \rightarrow 2MnO_2 \cdot H_2O + 2Cl^- \quad (2)$$

As represented in Eqs. (1) and (2) [24,29], the complexation between manganese ions and manganese dioxide (MnO_2, Mn(IV)) is first generated on the surface of adsorbent. The complexed manganese is then oxidized by hypochlorite, resulting in manganese dioxide:

$$\frac{-d[Mn(\text{II})]}{dt} = k\left[Mn(\text{II})\right] + k_1\left[Mn(\text{II})\right]\left[Mn(\text{IV})\right] \quad (3)$$

Then, the removal rate of manganese is enhanced by Mn(IV) according to kinetic shown in Eq. (3) [30], which works as an autocatalyst of such reaction [31,32]. Also, the oxidized manganese (Mn(IV)) acts as an additional adsorption site at the surface of adsorbent. Thus, faster removal reaction is derived according to repetitive reactions of manganese initiated by chlorine oxidation.

3.2. Evaluation of adsorption column performance

The effectiveness of the adsorption process was revisited in column tests with selected adsorbent under various operating conditions (i.e., EBCTs of 1 and 5 min, 0.1 mg/L Mn^{2+}, and 5 mg/L OCl^-). Fig. 6(a) presents experimental result of magnetite, and decreased manganese concentration was observed only with sodium hypochlorite dosing. When NaOCl was present, a removal rate of nearly 96% was observed at EBCT 1 min and more than 92% for EBCT 5 min. This level of removal efficiency was maintained for 12 h. In case of Ferox (Fig. 6(b)), the removal of manganese was observed for both of NaOCl presence and absence conditions, but increased removal efficiency was observed with NaOCl dosing. Lastly, in results of magnetite, higher rejection rate with EBCT 1 min compared with EBCT 5 min was observed, it could be explained as a result of change in manganese removal kinetics. Firstly, magnetite has relatively high surface area per unit volume than Ferox due to smaller particle size. More adsorption sites induce faster adsorption rate of manganese at the initial period. Then, as shown in Eq. (3), the generation of manganese dioxide promotes faster manganese removal rate. Furthermore, the autocatalytic reaction of manganese dioxide could accelerate manganese oxidation by contacting with the adsorbed manganese surface [31,32], inducing higher removal efficiency in the adsorption column.

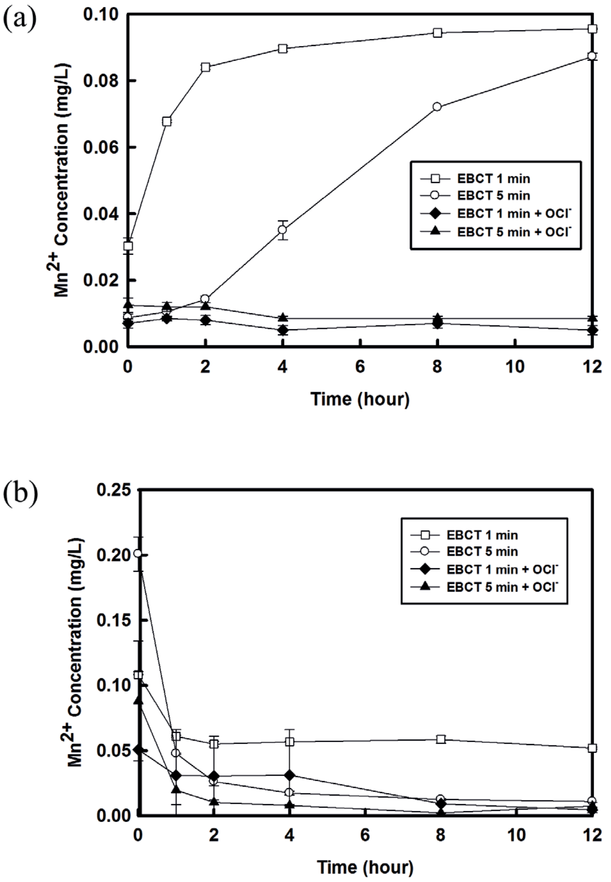

Fig. 6. Adsorption evaluation under sodium hypochlorite dosing (5 mg/L OCl^-) and varying EBCT for (a) magnetite (concentration of Mn^{2+}: 0.096 ± 0.5 mg/L) and (b) Ferox (concentration of Mn^{2+}: 0.1 ± 0.004 mg/L). Manganese concentration was measured from the effluent of the adsorption column.

The column test demonstrated that manganese could be effectively controlled with adsorption combined with oxidant dosing. High removal efficiency confirmed the potential of manganese adsorption, which could be installed as a pretreatment of membrane process before backwashing stage. Furthermore, stable efficiency despite of high flow rate (e.g., EBCT of 1 min) suggests the possibility of an economically feasible process design.

3.3. Fouling mitigation in UF membrane system

To verify the effectiveness of the proposed adsorption process for controlling membrane fouling caused by manganese, a series of UF fouling tests were carried out. These fouling experiments used feedwater containing relatively high concentration of manganese (1 mg/L) in order to clearly observe the tendency of manganese fouling. As shown in Fig. 7, under an EBCT of 1 min with NaOCl dosing, the amount of manganese in the effluent was around 0.01 mg/L, presenting over 99% removal efficiency after 4 h operation. Since magnetite exhibited slightly higher removal efficiency (99.6%) than Ferox (99.0%), magnetite was selected for adsorption for the pretreatment of backwashing stage.

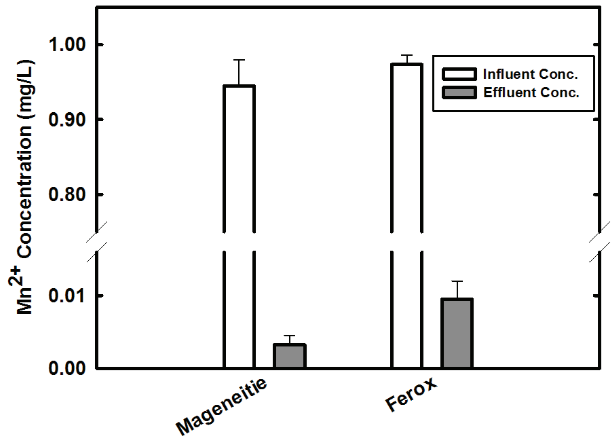

Fig. 7. Adsorption column test for high concentration Mn^{2+} (approximately 1 mg/L) to verify the mitigation of membrane fouling. Manganese concentration: magnetite = 0.945 ± 0.035 mg/L; Ferox = 0.974 ± 0.013 mg/ L.

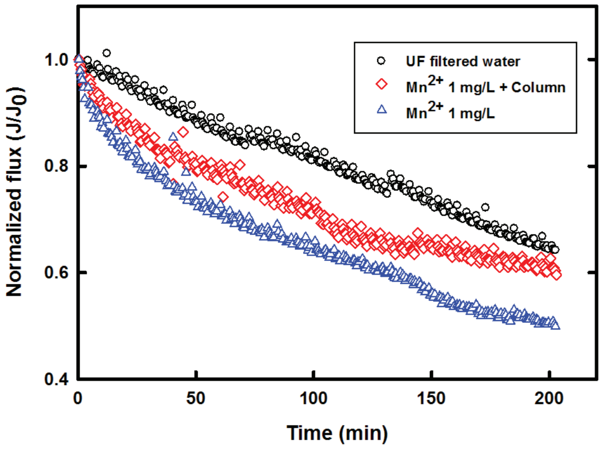

Fig. 8. Normalized flux decline in UF membrane fouling tests with and without adsorption during the backwashing step.

Representative results of the membrane filtration tests were presented in Fig. 8. The water flux showed slight decrease when the feedwater was not contaminated by manganese, but severe membrane fouling was experienced with manganese existence. However, alleviated flux decline was observed with adsorption pretreatment before backwashing stage. While the water flux was dramatically decreased in the initial stage of other cases, the decline of flux was relieved with the elapsed time of operation. Specifically, after 200 min of membrane filtration, the results of flux decline for various treatment methods were as follows: 35% with filtered water, 40% with column-treated 1 mg/L Mn^{2+} at 5 mg/L OCl^-, and 50% with non-column-treated 1 mg/L Mn^{2+} at 5 mg/L OCl^-. The flux decline rate using the non-column-treated feedwater was relatively higher than that of other treatment methods due to manganese fouling.

As described in section 3.1, slow manganese oxidation resulted in particles which have not fully grown to be removed; therefore, manganese passes through the pores of UF membrane and accumulates inside of the pores by further oxidation during chemically enhanced backwashing [23]. Furthermore, the autocatalytic reaction of manganese accelerates fouling inside the membrane pores which affects the reversibility of the flux and backwashing efficiency [33]. In contrast, flux decline was mitigated when the feedwater was treated with adsorption column. The adsorption column treatment exhibited a 10% higher efficiency rate compared with other treatments without the use of the column consisting of magnetite adsorbents.

4. Conclusions

In this study, the adsorption process to mitigate membrane fouling caused by oxidized manganese during backwashing was examined systematically. In order to improve its applicability, a newly developed magnetite-coated adsorbent was adopted and compared with manganese-coated sand for the effective removal of manganese. The primary findings from this study can be summarized as follows:

- An oxidative adsorption process was newly developed with magnetite-coated adsorbent since manganese was not eliminated sufficiently by chlorine addition due to its relatively slow oxidation.
- Compared with typical manganese-coated sand (e.g., Ferox), higher manganese removal was generally achieved by magnetite-coated adsorption column, leading to more than 96% of removal efficiency with the addition of NaOCl.
- Fouling in UF membrane was significantly mitigated by treating feedwater with a newly developed adsorption column for manganese removal prior to the membrane processes.
- Further research should be performed to prove the synergetic effect of oxidation and adsorption more fundamentally under various feedwater characteristics, to optimize operating conditions for long-term operation, and to improve economic feasibility for real-scale applications.

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References

[1] A.Y.C. Lin, T.H. Yu, C.F. Lin, Pharmaceutical contamination in residential, industrial, and agricultural waste streams: risk to aqueous environments in Taiwan, Chemosphere, 74 (2008) 131–141.
[2] T.S.Y. Choong, T.G. Chuah, Y. Robiah, F.L. Gregory Koay, I. Azni, Arsenic toxicity, health hazards and removal techniques from water: an overview, Desalination, 217 (2007) 139–166.
[3] I. Chorus, I.R. Falconer, H.J. Salas, J. Bartram, Health risks caused by freshwater cyanobacteria in recreational waters, J. Toxicol. Environ. Health B Crit. Rev., 3 (2000) 323–347.
[4] K. Gopal, S.S. Tripathy, J.L. Bersillon, S.P. Dubey, Chlorination byproducts, their toxicodynamics and removal from drinking water, J. Hazard. Mater., 140 (2007) 1–6.
[5] L.I. Sly, M.C. Hodgkinson, V. Arunpairojana, Deposition of manganese in a drinking water distribution system, Appl. Environ. Microbiol., 56 (1990) 628–639.

[6] A. Takeda, Manganese action in brain function, Brain Res. Rev., 41 (2003) 79–87.

[7] B.A. Chowdhury, R.K. Chandra, Biological and health implications of toxic heavy metal and essential trace element interactions, Prog. Food Nutr. Sci., 11 (1987) 57–113.

[8] K. Ljung, M. Vahter, Time to re-evaluate the guideline value for manganese in drinking water?, Environ. Health Perspect., 115 (2007) 1533–1538.

[9] J.M. Davis, Inhalation health risks of manganese: an EPA perspective, Neurotoxicology, 20 (1999) 511–518.

[10] D. Ellis, C. Bouchard, G. Lantagne, Removal of iron and manganese from groundwater by oxidation and microfiltration, Desalination, 130 (2000) 255–264.

[11] A.A. Britton, G.C. Cotzias, Dependence of manganese turnover on intake, Am. J. Physiol., 211 (1966) 203–206.

[12] C.A. Johnson, M. Ulrich, L. Sigg, D.M. Imboden, A mathematical model of the manganese cycle in a seasonally anoxic lake, Limnol. Oceanogr., 36 (1991) 1415–1426.

[13] A. Wolthoorn, E.J.M. Temminghoff, L. Weng, W.H. van Riemsdijk, Colloid formation in groundwater: effect of phosphate, manganese, silicate and dissolved organic matter on the dynamic heterogeneous oxidation of ferrous iron, Appl. Geochem., 19 (2004) 611–622.

[14] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, Desalination, 216 (2007) 1–76.

[15] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, Science, 333 (2011) 712–717.

[16] S. Mondal, S.R. Wickramasinghe, Produced water treatment by nanofiltration and reverse osmosis membranes, J. Membr. Sci., 322 (2008) 162–170.

[17] V. Mavrov, H. Chmiel, J. Kluth, J. Meier, F. Heinrich, P. Ames, K. Backes, P. Usner, Comparative study of different MF and UF membranes for drinking water production, Desalination, 117 (1998) 189–196.

[18] L. Fiksdal, T. Leiknes, The effect of coagulation with MF/UF membrane filtration for the removal of virus in drinking water, J. Membr. Sci., 279 (2006) 364–371.

[19] J.M. Laîné, D. Vial, P. Moulart, Status after 10 years of operation – overview of UF technology today, Desalination, 131 (2000) 17–25.

[20] N. Lee, G. Amy, J.P. Croué, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res., 38 (2004) 4511–4523.

[21] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, Environ. Sci. Technol., 36 (2002) 3571–3576.

[22] K. Kimura, Y. Hane, Y. Watanabe, G. Amy, N. Ohkuma, Irreversible membrane fouling during ultrafiltration of surface water, Water Res., 38 (2004) 3431–3441.

[23] K.H. Choo, H. Lee, S.J. Choi, Iron and manganese removal and membrane fouling during UF in conjunction with prechlorination for drinking water treatment, J. Membr. Sci., 267 (2005) 18–26.

[24] D. Tiwari, M. Yu, M. Kim, S. Lee, O. Kwon, K. Choi, G. Lim, J. Yang, Potential application of manganese-coated sand in the removal of Mn(II) from aqueous solutions, Water Sci. Technol., 56 (2007) 153–160.

[25] P. Berbenni, A. Pollice, R. Canziani, L. Stabile, F. Nobili, Removal of iron and manganese from hydrocarbon-contaminated groundwaters, Bioresour. Technol., 74 (2000) 109–114.

[26] S.C. Homoncik, A.M. MacDonald, K.V. Heal, B.É. Ó Dochartaigh, B.T. Ngwenya, Manganese concentrations in Scottish groundwater, Sci. Total Environ., 408 (2010) 2467–2473.

[27] W. Balzer, On the distribution of iron and manganese at the sediment/water interface: thermodynamic versus kinetic control, Geochim. Cosmochim. Acta, 46 (1982) 1153–1161.

[28] C.-C. Kan, W.-H. Chen, M.-W. Wan, P. Phatai, J. Wittayakun, K.-F. Li, The preliminary study of iron and manganese removal from groundwater by NaOCl oxidation and MF filtration, Sustain. Environ. Res., 22 (2012) 25–30.

[29] J. Kim, S. Jeong, J. Kim, S. Park, Manganese removal in water treatment processes, J. Korean Soc. Water Wastewater, 19 (2005) 595–604.

[30] S. Güneş Durak, D.Y. Köseoğlu İmer, G. Türkoğlu Demirkol, T. Ormancı, B. Armağan, N. Tüfekci, Influence of ageing on the catalytic activity of MnO2 sludge for oxidation of Mn(II), Desal. Wat. Treat., 51 (2013) 5692–5700.

[31] J.F. Perez-Benito, Autocatalytic reaction pathway on manganese dioxide colloidal particles in the permanganate oxidation of glycine, J. Phys. Chem. C, 113 (2009) 15982–15991.

[32] J.F. Perez-Benito, C. Arias, E. Amat, A kinetic study of the reduction of colloidal manganese dioxide by oxalic acid, J. Colloid Interface Sci., 177 (1996) 288–297.

[33] Y. Kaiya, Y. Itoh, K. Fujita, S. Takizawa, Study on fouling materials in the membrane treatment process for potable water, Desalination, 106 (1996) 71–77.