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Article

Effects of Activated Carbon and Cationic Exchange Resin Pretreatments on Groundwater Defluoridation by Reverse Osmosis Process

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Abstract. The objective of this research was to study the effects of a pretreatment using activated carbon and cationic exchange resin on groundwater defluoridation by a reverse osmosis membrane. Actual groundwater containing a high fluoride concentration was collected and examined. Experiments were operated under controlled conditions: a transmembrane pressure of 0.6 MPa and temperature of 25 °C. The reverse osmosis system with activated carbon and cationic exchange resin pretreatments had higher fluoride removal than the one without the pretreatments, 97% compared to 95%, respectively. Additionally, the reverse osmosis system with the pretreatments also produced a higher permeate flux, 1.1 × 10^{-5} compared 9.6 × 10^{-6} $m^3/m^2 \cdot s$ without the pretreatment. When the reverse osmosis systems with and without pretreatments were fouled, they showed a decrease in fluoride rejection, as well as a permeate flux decline. After the fouled reverse osmosis membranes were chemically cleaned, the permeate flux recovery and the fluoride rejection of the osmosis system with the pretreatments improved. It could be concluded that the activated carbon and cationic exchange resin played an important role in improving the reverse osmosis system as they contributed to high fluoride rejection and high permeate flux.

Keywords: Fluoride, permeate flux, reverse osmosis, membrane fouling.

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1. Introduction

Many provinces in the northern area of Thailand experience the problem of high fluoride contamination in groundwater; such provinces include Chiang Mai and Lamphun [1]. This could be attributed to fluoride minerals such as CaF_2 from their mountains, hot spring areas, and igneous and metamorphic rocks [2-4]. At present, many village waterworks do not have adequate natural surface water to produce sufficient amounts of clean water for their villages. Fluoride contaminated groundwaters have been utilized in households for cooking and drinking [5]. Maximum fluoride concentration in drinking water standard was set as 0.7 mg/L by The Ministry of Public Health in Thailand [6]. Adverse health impacts, such as dental and skeletal fluorosis, occur if fluoride contaminated water is not treated properly [7-11]. Therefore, people who live in fluoride contaminated areas should understand the health risks. A child education program has been undertaken to help with reducing effects of the high fluoride concentration in groundwater [12]. Not only the child education program but also a fluoride removal process should be considered.

Some technologies have been currently proposed such as adsorption via dolomite sorbent [13]. However, its moderate fluoride removal efficiency could be achieved. As a result, other technologies have been introduced. Membrane technology has been widely applied in the water supply production process, wastewater treatment process, and recirculation process [14-15]. In particular, reverse osmosis membrane filtration has been applied to defluoridate groundwater because of its ability to disinfect and remove other contaminants as well [1,16]. Furthermore, it now comes at a lower cost. A reverse osmosis system can be installed in a small space and does not produce chemical sludge. Pretreatment units can be added to enhance a system's defluoridation performance. In addition to its water pretreatment duties, a pretreatment unit can prevent the membrane from deterioration and foulants, and also expand the useful life of the membrane [17-18].

This research studies whether activated carbon and cationic exchange resin pretreatments can enhance the fluoride rejection efficiency of a reverse osmosis membrane filter used for groundwater defluoridation.

2. Materials and Methods

2.1. Experimental Setup and Sampling Points

The reverse osmosis membrane filter used in this study has a 200 L/d filtration capacity. An activated carbon filter and cationic exchange resin filter were used as the pretreatments. Microfiltration membrane was made from polypropylene with nominal pore size of 5 microns. Activated carbon filter was in granular form with a 25 cm length of cartridge and its service life of 10,000 L. Cationic exchange resin filter was a 25 cm length of cartridge for calcium and magnesium removals.

This research compared two systems: a system with the pretreatments and a system without the pretreatments. The experimental setup is shown in Fig. 1.

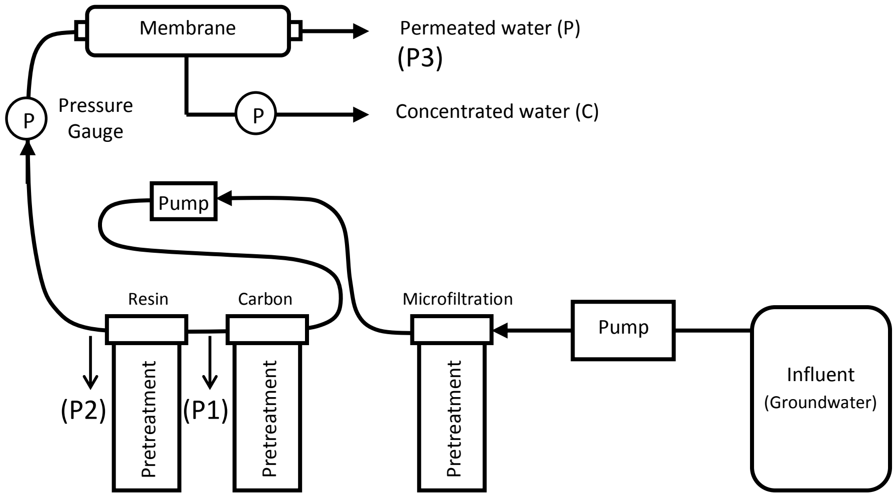

Fig. 1. Experimental setup.

The sampling points measured the microfiltration filtered water (P1), activated carbon filtered water (P2), cationic exchange resin filtered water (P3), permeate water (P), and concentrated water (C), respectively.

2.2. Synthetic Water and Actual Groundwater

To investigate the initial fluoride rejection efficiency of the reverse osmosis system, synthetic water was prepared from sodium fluoride at 10 mg/L, which is similar to the fluoride concentration in natural groundwater.

Actual groundwater from a sampling site at Baan-Buakkhang School in Sankamphaeng District, Chiang Mai Province, had a fluoride concentration of approximately 11 mg/L. Each system filtered 40 L of actual groundwater daily.

2.3. Experimental Methods

The two systems were operated at room temperature. Deionized water was filtered through the systems under transmembrane pressures of 0.2, 0.4, and 0.6 MPa, respectively, to determine the permeate flux and pure water permeability of each system.

To investigate the fluoride rejection efficiency, synthetic water was prepared from sodium fluoride (NaF). Synthetic water containing 10 mg/L of fluoride was fed to both systems under each transmembrane pressure (0.2, 0.4, and 0.6 MPa). Water samples from each of the sampling points of the systems were collected, and the fluoride concentrations were analyzed.

To treat the fluoride contaminated groundwater, 40 L of actual groundwater was filtered through the systems daily under a transmembrane pressure 0.6 MPa at room temperature. After that, the efficiencies of the two systems were evaluated by calculating their permeate flux and fluoride rejection values. A course of filtration was separated into 4 periods including (1) Initial period, (2) Steady state, (3) Membrane fouling, and (4) After cleaning, respectively. Initial period was observed during 0-160 L of the filter volume. Steady state was obtained at the filter volume of 161-600 L. Due to a poorly built groundwater well; turbidity of groundwater could be high especially in rainy season. As a result, kaolin was added to observe the effect of membrane fouling. The effect of membrane fouling on the membrane's performance was observed at the filter volume of 601-760 L by adding kaolin to increase the turbidity of groundwater until the turbidity reached 500 NTU. Finally, a recovery of the membrane performance (761-1,000 L) was examined after membrane cleaning with 0.1 N of sodium hydroxide and 0.1 N of citric acid, respectively [19].

2.4. Analytical Methods

The fluoride concentration was analyzed using a UV-visible spectrophotometer at 570 nm wavelength (Jenway 6400 spectrophotometer, Jenway, UK). Total hardness, the calcium concentration, and the magnesium concentration were determined by the titration method [20].

2.5. Membrane performances

Transmembrane pressure (TMP) was calculated as follows:

$$\mathrm{TMP} = \frac{\mathrm{P_f+P_c}}{2} - \mathrm{P_p} \tag{1}$$

where P_f is the feed pressure (MPa), P_c is the concentrated pressure (MPa), and P_p is the permeate pressure (MPa) [21].

Permeate flux was determined as follows:

$$\text{Permeate flux} = \frac{\mathrm{V}}{\mathrm{A \times T}} \tag{2}$$

where V is the permeate volume (m^3), A is the specific surface area of the membrane (m^2), and T is the time (s).

Fluoride rejection (%) was computed as follows:

$$\text{Fluoride rejection} = \left[1 - \frac{C_p}{C_f}\right] \times 100 \tag{3}$$

where C_p is the fluoride concentration of the permeate water (mg/L) and C_f is the fluoride concentration of the feed water (mg/L).

3. Results and Discussion

3.1. Groundwater Characteristics

Groundwater characteristics are listed as follows (Tables 1 and 2). As mentioned above, the course of filtration was divided into 4 periods: an initial period, a steady-state period, a membrane fouling period, and an after cleaning period.

Table 1. Groundwater characteristics (pH, EC, alkalinity, turbidity).

Period	Parameter			
	pH	EC (µS/cm)	Alkalinity (mg/L as $CaCO_3$)	Turbidity (NTU)
Initial	8.0 ± 0.1	623 ± 2	54 ± 2	0.20 ± 0.1
Steady state	7.8 ± 0.1	525 ± 10	52 ± 4	0.20 ± 0.1
Membrane fouling (kaolin added)	7.9 ± 0.2	590 ± 23	52 ± 2	528 ± 42
After cleaning	7.8 ± 0.1	531 ± 35	52 ± 4	0.46 ± 0.1

Table 2. Groundwater characteristics (fluoride, calcium, magnesium).

Period	Parameter		
	Fluoride (mg/L)	Calcium (mg/L)	Magnesium (mg/L)
Initial	10.5 ± 0.4	5.6 ± 0.8	5.1 ± 1.2
Steady state	11.2 ± 0.5	4.4 ± 0.8	3.1 ± 0.4
Membrane fouling (kaolin added)	11.8 ± 0.8	4.4 ± 0.4	3.3 ± 0.4
After cleaning	10.6 ± 0.7	5.0 ± 0.2	3.1 ± 0.2

The fluoride concentration in the actual groundwater (as collected) ranged from 10.5 to 11.8 mg/L, which was expressively higher than the fluoride concentration in drinking water standard of 0.7 mg/L [6]. The values of the pH, electrical conductivity, alkalinity, calcium concentration, and magnesium concentration were approximately 7.9, 567 µS/cm, 53 mg/L as $CaCO_3$, 4.9 mg/L, and 3.6 mg/L, respectively. Turbidity was relatively low (0.2-0.5 NTU) during the initial period, steady state period, and after cleaning period. However, the turbidity significantly increased to 528 NTU after kaolin was added.

3.2. Reverse Osmosis Membrane Properties

The pure water permeability (k) of the reverse osmosis systems with and without pretreatments was obtained from a plot of the transmembrane pressures and pure water flux as shown in Fig. 2. The pure water permeabilities were 2.3 × 10^{-5} and 2.1 × 10^{-5} $m^3/m^2 \cdot s \cdot MPa$ for the reverse osmosis systems with and without pretreatments, respectively.

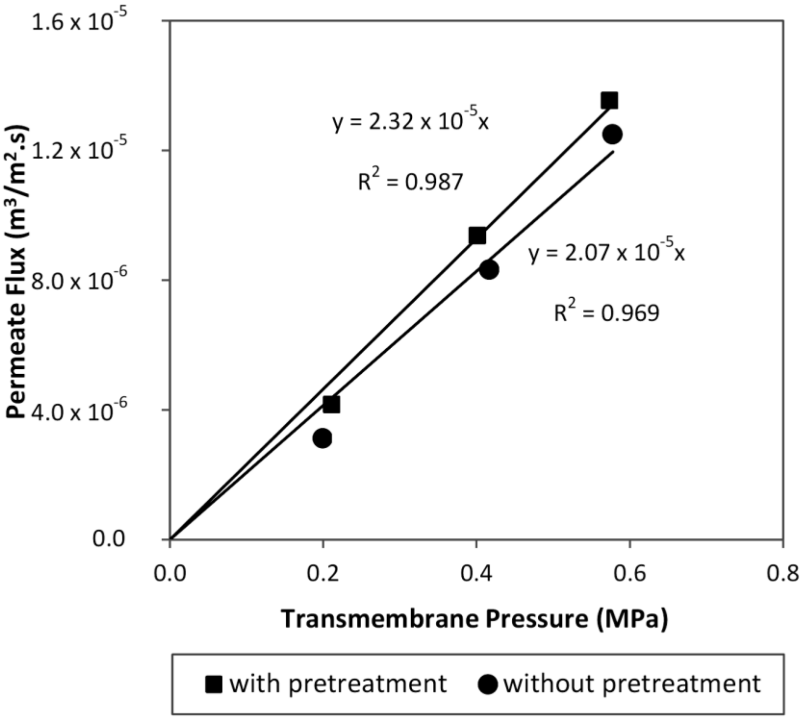

Fig. 2. Pure water permeability of the reverse osmosis membranes.

The fluoride rejection efficiency at various transmembrane pressures of the reverse osmosis systems with and without pretreatments was evaluated. The results are illustrated in Fig. 3. The fluoride rejection efficiencies of the pretreatments under the three different transmembrane pressures, 0.2, 0.4, and 0.6 MPa, were 96%, 99%, and 99%, respectively. In the system without the pretreatments, the fluoride rejection efficiencies under the same transmembrane pressures of 0.2, 0.4, and 0.6 MPa were 90%, 91%, and 92%, respectively.

For the reverse osmosis membrane properties, since some of the residual ions were removed in the deionized water, it can be implied that the activated carbon filter and cationic exchange resin filter pretreatment units could provide clearer water and resulted in higher pure water permeability [21-22]. Moreover, it was observed that the system with the activated carbon filter and cationic exchange resin filter pretreatments provided better fluoride rejection. The activated carbon and cationic exchange resin could have retained some ions contained in the feed solution, resulting in the low concentration polarization on the membrane surface [18, 23-24]. Consequently, higher fluoride rejection efficiency was obtained.

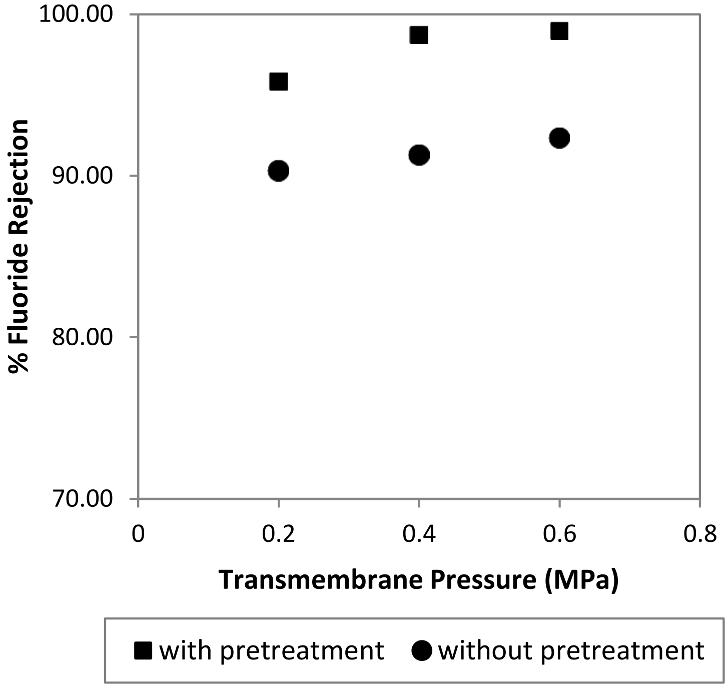

Fig. 3. Fluoride rejection efficiency.

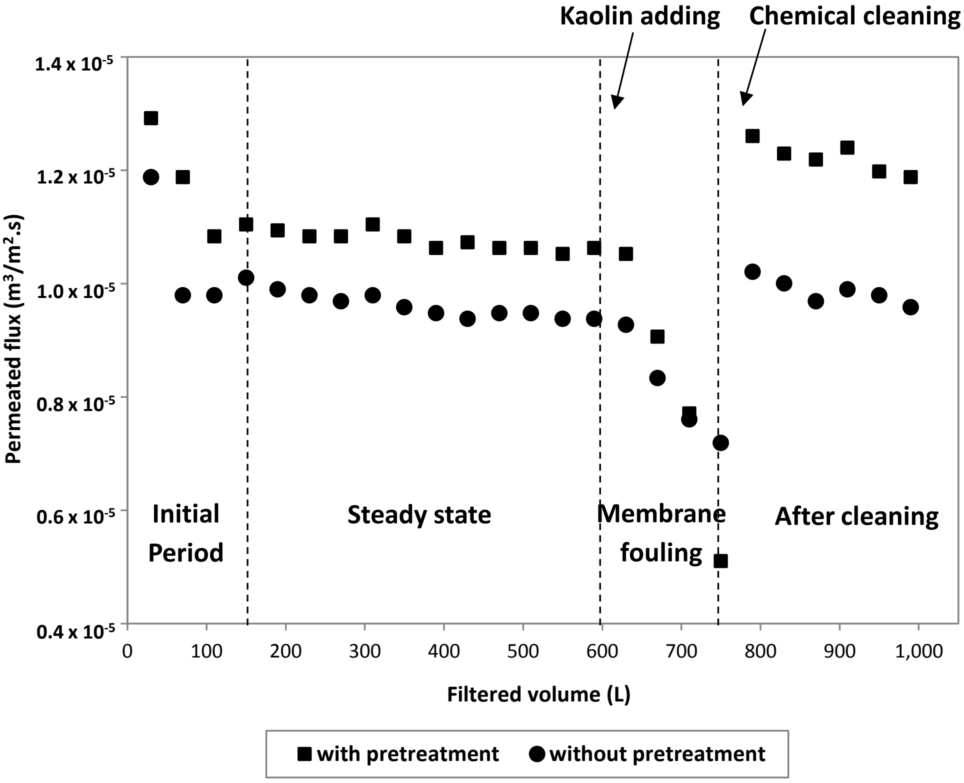

Fig. 4. Permeate flux during the course of filtration.

Effects of activated carbon and cationic exchange resin filters on total hardness reduction are shown as follows. Table 3 shows the filtered groundwater at a sampling point P2. The system with the pretreatments had lower total hardness than the other system. They averaged 10.2 mg/L and 24.6 mg/L, respectively.

Table 3. Total hardness in the filtered groundwater after filtration with and without pretreatments.

Period	Total hardness (mg/L)		
	Influent	Filtered groundwater after pretreatment (P2)	Filtered groundwater without pretreatments (P2)
Initial	34.2 ± 8.1	5.0 ± 1.4	25.0 ± 1.4
Steady state	25.8 ± 2.6	10.3 ± 0.6	26.3 ± 3.2
Membrane fouling (kaolin added)	25.0 ± 1.4	13.0 ± 1.4	24.5 ± 0.7
After cleaning	24.8 ± 0.5	12.5 ± 0.7	22.5 ± 2.1

Defluoridation during the course of filtration was investigated as follows. As seen in the results in Fig. 5, higher fluoride rejection efficiencies were observed in the system with pretreatments throughout all the operational periods. The two systems were not stable in the initial period (0-160 L of filtered groundwater). The efficiencies gradually became constant at around 97% and 96% for the system with pretreatments and without pretreatments, respectively, at 161-600 L of filtered groundwater. In the membrane fouling period (601-760 L of filtered groundwater), the efficiencies decreased from the previous period. However, the efficiencies were recovered to 97% and 95% for system with pretreatments and without pretreatments, respectively, after chemical cleaning (761-1000 L of filtered groundwater).

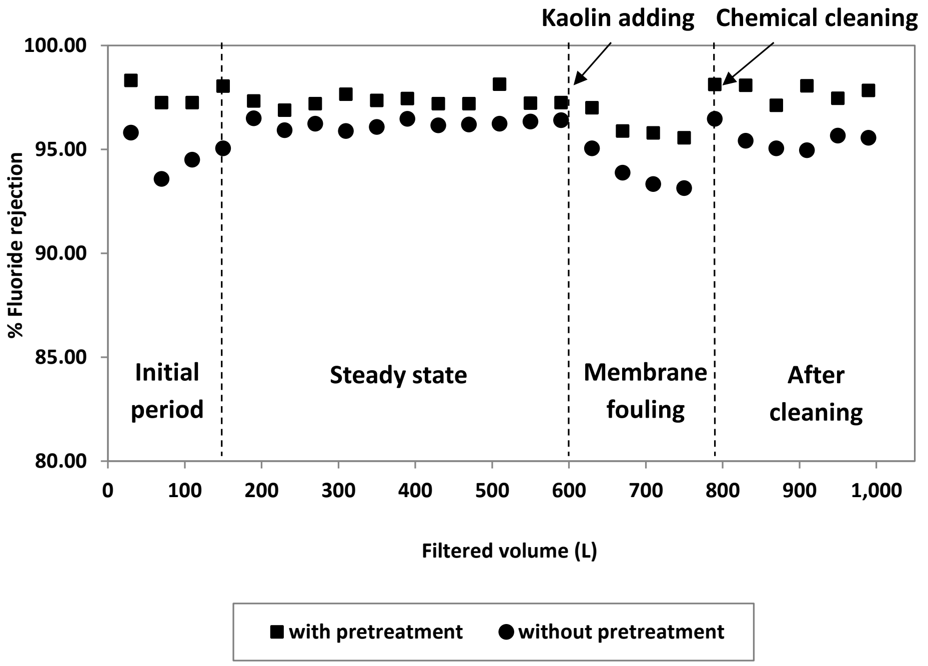

Fig. 5. Fluoride rejection during the course of filtration.

Additionally, fluoride concentration in the permeate water of the system with pretreatments and system without pretreatments are reported in Table 4.

Table 4. Fluoride concentration in the permeate water of the system with pretreatments and system without pretreatments.

Period	**Fluoride concentration (mg/L)**		
	Influent	**Permeate water with pretreatments**	**Permeate water without pretreatments**
Initial	10.5 ± 0.4	0.3 ± 0.1	0.6 ± 0.1
Steady state	10.9 ± 0.5	0.3 ± 0.1	0.4 ± 0.1
Membrane fouling (kaolin added)	11.7 ± 1.9	0.5 ± 0.2	0.7 ± 0.3
After cleaning	10.5 ± 0.6	0.2 ± 0.1	0.5 ± 0.1

As can be seen in Table 4, the reverse osmosis system with pretreatments had higher fluoride rejection efficiencies than the system without pretreatments, as the efficiency of the pretreatment units prevented concentration polarization [23-24]. Influent fluoride concentration was measured prior to the reverse osmosis membrane filter. Nevertheless, the pretreatments did not help to remove fluoride. Fluoride concentrations at sampling points P1 and P2 were approximately 11.0 mg/L. In the initial and steady state periods, the fluoride concentration of the permeate water remained around 0.3 mg/L in the system with pretreatments, and 0.4-0.6 mg/L in the system without pretreatments. In the membrane fouling period, the fluoride concentration of the permeate water in the system with pretreatments was around 0.5 mg/L, which was higher than that of the previous period, but still lower than the standard (0.7 mg/L). Meanwhile, the fluoride concentration of the permeate water in the system without pretreatments increased to around 0.9 mg/L, which is above the standard [6]. After the cleaning period, the fluoride concentrations in the permeate water of the system with pretreatments and without pretreatments were around 0.2 and 0.5 mg/L, respectively, similar to the concentrations in initial and steady state periods. From a statistical analysis, the fluoride concentrations in permeate waters of the systems with and without pretreatments were significantly different (at $p<0.05$). Hence, the pretreatments were recommended to reduce the effect of membrane fouling on permeate water flux and quality.

While the activated carbon filter specializes in removing organic matter, color and odor from feed water by an adsorption process [25]. The cationic exchange resin filter can reduce cationic contamination, such as calcium and magnesium [26]. Put together, they increase the permeate flux and the fluoride rejection efficiency of reverse osmosis membranes.

4. Conclusion

The reverse osmosis system using pretreatments had higher fluoride removal than the system without pretreatments, 97% compared to 95%, respectively. The fluoride concentrations of the permeate water were 0.3 and 0.4 mg/L, respectively. Moreover, the reverse osmosis system using pretreatments produced higher permeate flux than the system without pretreatments, 1.1×10^{-5} compared to 9.6×10^{-6} $m^3/m^2{\cdot}s$, respectively.

When groundwater was added with Kaolin to study the fluoride rejection efficiency of the fouled membranes, it was found that the efficiency of the system with pretreatments decreased faster than that of the other system. After chemical cleaning, the permeate flux was recovered to 92% in the system with pretreatments, and 81% in the system without pretreatments. The fluoride concentrations in the permeate water of the two systems were recovered to concentrations that closely resembled the initial results. It was concluded that the pretreatment unit was necessary for the reverse osmosis system to maintain high fluoride rejection efficiency and have prolonged water production capacity.

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References

[1] T. Takeda and S. Takizawa, "Reducing the impact of fluoride intake in Thailand," *Asian Water*, vol. 23, pp. 22-26, 2007.

[2] S. J. Gaciri and T. C. Davies, "The occurrence and geochemistry of fluoride in some natural waters of Kenya," *J. Hydrol.*, vol. 143, pp. 395–412, 1993.

[3] D. Banks, C. Reimann, O. Røyset, H. Skarphagen, and O.M. Sæther, "Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters," *Appl. Geochem.*, vol. 10, pp. 1–16, 1995.

[4] D. R. R. Sarma and S. L. N. Rao, "Fluoride concentrations in ground waters of Visakhapatnam, India," *Bull. Environ. Contam. Toxicol.*, vol. 58, pp. 241-247, 1997.

[5] W. S. Deshmukh, S. J. Attar, and M. D. Waghmare, "Investigation on sorption of fluoride in water using rice husk as an adsorbent," *Nat. Env. Poll. Tech.*, vol. 8, no. 2, pp. 217-223, 2009.

[6] Ministry of Public Health of Thailand, "Drinking Water Standards," Bangkok, Thailand, 2002.

[7] C. B. Dissanayake, "The fluoride problem in the groundwater of Sri Lanka environmental management and health," *Int. J. Environ. Stud.*, vol. 19, pp. 195–203, 1991.

[8] W. M. Edmunds and P. Smedley, "Fluoride in natural waters. Essentials of medical geology: impacts of the natural environment on public health," in O. Selinus, B. Alloway, and J. A. Centeno, Eds. US: Academic Press, 2005, pp. 301–329.

[9] J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, and Y. Magara, "Fluoride in drinking water," World Health Organization, London, 2006.

[10] T. Takeda, A. Wongrueng, S. Takizawa, W. Choompolkul, S. Chaimongkol, and S. Wattanachira, "Estimation of fluoride intake sources and fluorosis among the population living in the Chiang Mai Basin," in *Proc. The XXVIIth Conference of the International Society for Fluoride Research*, Beijing, China, 2007, pp. 12-13.

[11] M. McGrady, R. Ellwood, P. Srisilapanan, N. Korwanich, A. Taylor, M. Goodwin, and I. Pretty, "Dental fluorosis in populations from Chiang Mai, Thailand with different fluoride exposures-Paper 2: The ability of fluorescence imaging to detect differences in fluorosis prevalence and severity for different fluoride intakes from water," *BMC oral health*, vol. 12, no. 1, p. 33, 2012.

[12] S. Takizawa, T. Takeda, A. Wongrueng, and S. Wattanachira, "Child-education program for the reduction of health risks due to fluoride in water sources in the Chiang Mai Basin, Thailand," *Water Sci. Technol.*, vol. 61, no. 9, pp. 2391-2397, 2010.

[13] A. Wongrueng, B. Sookwong, P. Rakruam, and S. Wattanachira, "Kinetic adsorption of fluoride from an aqueous solution onto a dolomite sorbent," *Engineering Journal*, vol. 20, no. 3, pp. 1-9, 2016.

[14] D. Depper, "R.O. for improved products in food and chemical industries and water treatment," *Desalination*, vol. 77, pp. 55-71, 1990.

[15] M. Mulder, *Basic Principles of Membrane Technology*. Kluwer Academic Publishers, 1996.

[16] M. Mohapatra, S. Anand, B. K. Mishra, D. E. Giles, and P. Singh, "Review of fluoride removal from drinking water," *J. Environ. Manage.*, vol. 91, pp. 67–77, 2009.

[17] S. Jeong, S. Kim, L. Kim, M. Shin, S. Vigneswaran, T. V. Nguyen, and I. S. Kim, "Foulant analysis of a reverse osmosis membrane used pretreated seawater," *J. Membrane Sci.*, vol. 428, pp. 434–444, 2013.

[18] S. Jamaly, N. N. Darwish, I. Ahmed, and S. W. Hasan, "A short review on reverse osmosis pretreatment technologies," *Desalination*, vol. 354, pp. 30-38, 2014.

[19] P. Samornkraisorakit. (2001). *Advanced Water Treatment. Training Course Yokohama Training Program in Japan*. [Online]. Available: http://www.mwa.co.th/download/prd01/water_technology/pdf

[20] APHA, AWWA and WEF, *Standard Method for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, Washington, D.C., U.S.A, 1998.

[21] S. Chaimongkol, "Effects of cations and temperature on defluoridation by ultra low pressure reverse osmosis membrane and nanomembrane," Master of Environmental Engineering thesis, Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, 2008.

[22] D. Bhattacharyya and M. E. Williams, *Membrane Handbook Vol. I*. New York: Van Nostrand Reinhold, 1992, pp. 265-353.

[23] L. Zeman and A. Zydney, *Microfiltration and Ultrafiltration, Principles and Application*. New York: Marcel Dekker, 1996, p. 350.

[24] A. Wongrueng, Y. Matsui, and S. Takizawa, "Effect of concentration polarization on fluoride removal by ULPRO membrane," in *Summary for the Extended Abstracts in Poster Session, The 44th Environmental Engineering Forum, Japan, 2007*, pp. 51-53.

[25] S. T. Nguyen and F. A. Roddick, "Pre-treatments for removing colour from secondary effluent: Effectiveness and influence on membrane fouling in subsequent microfiltration," *Sep. Purif. Technol.*, vol. 103, pp. 313-320, 2013.

[26] G. Darracq, J. Baron, and M. Joyeux, "Kinetic and isotherm studies on perchlorate sorption by ion-exchange resins in drinking water treatment," *JWPE*, vol. 3, pp. 123-131, 2014.