Practical Paper

The on-site feasibility study of iron and manganese removal from groundwater by hollow-fiber microfiltration

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ABSTRACT

The aim of this research was to investigate the removal of iron and manganese from groundwater by aeration, chlorine oxidation and microfiltration (MF). Pilot-scale experiments were performed at the Chang-Hua Water Treatment Plant in Taiwan. The raw waters contained soluble iron (0.4 mg/L) and manganese (0.5 mg/L) which were oxidized by chlorine and then filtered by hollow-fiber PTFE-MF. The oxidized particles on membranes under appropriate backwash were also investigated. The particle size and quality of treated water were examined. The experimental results indicated that the concentration of the residual manganese remained greater than 0.1 mg/L in treated water during the initial operation period. However, it decreased to below 0.01 mg/L after 2 weeks processing time. The scanning electron microscopy (SEM) energy dispersive spectroscopy analysis of oxidized metal particles under each process illustrated that the particles accumulated on membrane enhanced removal of iron and manganese, through autocatalytic activity in the accumulated layer on membrane. Moreover, the membrane operation pressure over 120 kPa was suggested for the active backwash process, where no structural damage on membrane was confirmed by SEM analysis.

Key words | groundwater, hollow-fiber membrane filtration, iron, manganese, oxidation

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INTRODUCTION

Groundwater, existing in the pore spaces and fractures in rock and sediment beneath the Earth's surface, contributes about 20% of the world's fresh water supply. Groundwater is also an important resource that acts as natural storage, which can buffer against shortages of surface water. Taiwan has rich groundwater resources supplying 30% of its domestic water needs. However, due to the geological composition, groundwater often contains iron (Fe) and manganese (Mn) ions. In terms of industrial water and potable water quality, strict limits of Fe and Mn in the water are necessary; water with a high concentration of these elements may have a metallic taste, exhibit a red-brown color that stains clothes, and block water pipes. It may also color industrial products and impact their quality, e.g. dyeing, finishing, leather tanning, and paper

industries. In order to avoid such problems, water quality standards in Taiwan have set specific limits: Fe should be below than 0.3 mg/L and Mn should be below 0.05 mg/L.

There are several treatment methods for Mn-contaminated groundwater including biological, physical and chemical processes. Biological treatment is fundamentally a filtration process that takes advantage of the ability of certain bacteria to oxidize Mn and to assimilate Mn ions. The process also involves chemical oxidation in which oxidized Mn is deposited as a MnO_2 layer and acts as a catalyst for further oxidation of Mn^{2+} by dissolved oxygen (Tekerlekopoulou & Vayenas 2007, 2008; Burger *et al.* 2008). However, the formation of the MnO_2 layer and biofilm requires several weeks (Stembal *et al.* 2005).

In the traditional process, Fe and Mn in groundwater is initially oxidized using aeration and/or chemical oxidant such as chlorine, hypochlorite, chlorine dioxide ozone or potassium permanganate and then removed by filtration. The selection of different oxidants depends on the presence of other pollutants in the water, as they affect the water quality. Price is also an important consideration. After oxidation of Fe and Mn, the formation of Fe–Mn takes place, and is then filtered out through a greensand filter. When MnO_2 particles exist, the formation rate of Fe–Mn oxide is accelerated, contributing to the removal of Fe and Mn (Teng *et al.* 1998). Granular activated carbon is often used to enhance the adsorption of Mn^{2+} during filtration, although it has the drawback of needing frequent regeneration or replacement of the carbon (Xia *et al.* 2004; Mondal *et al.* 2008; Okoniewska *et al.* 2008).

In recent years, membrane processes have become popular in water treatment and wastewater treatment due to their advantages in water quality enhancement compared with traditional physical/chemical treatment, including space saving, and reduced chemical usage and resultant sludge (Munir 1998). The early development of membrane technology was to separate the soluble and colloidal components in water. These substances were evidenced by increased turbidity and numbers of microorganisms, causing harmful water quality, and affecting human safety and health. However, high capital and maintenance costs were considered as a major drawback, but in the past two decades, due to dramatic improvements of membrane science and technology, the manufacturing costs of membranes have declined year by year. Many water treatment plants in the USA have used membrane processes as a major water treatment (USEPA 2003).

Many water treatment plants are facing the problems of meeting new water treatment standards with the existing equipment. Membrane separation technology has been considered to be practical in removing metal oxide particles and improving the performance of existing equipment (Kimura *et al.* 2004). Therefore, PTFE hollow fibers, which have multi-purposes in water treatment procedures, are used directly as water treatment equipment to establish a new water treatment system (Jusoh *et al.* 2005); it is used as stepped-up equipment at the back-end of rapid filters to comply with the new water quality standards.

In the present study, a field test on a PTFE membrane treatment process for the groundwater containing Fe and Mn ions was performed. Using the same oxidation conditions, a period of filter testing was executed and evaluated, and the efficiency of membrane filtration and the traditional greensand process were compared.

MATERIALS AND METHODS

The water treatment plant that was investigated in this study is the Changhua Water Treatment Plant located in central Taiwan, where the groundwater is used as a potable water source and the treatment rate is about 30,000 m³/day. The raw water is drawn from 12 deep wells located in an area of 8 km². The depth of these wells ranged from 245 to 300 m beneath the surface. The analyzed concentrations of Fe and Mn ranged between 0.2 and 0.6 mg/L. The current metal removal procedures in this plant are: aeration, chlorination using sodium hypochlorite (NaOCl), and Mn sand filtration. In this study, two types of filtration – 0.1 μm PTFE micro-filter pilot devices and greensand filter – were used to filter the water sample after NaOCl oxidation and to evaluate performance on Fe and Mn removal.

Some details of operation conditions are described below: the cascade aeration time was 2 min; chlorination produced 0.3–0.7 mg/L residual chlorine, and the contact time was 10 min. The greensand filter was a reinforced concrete tank with internal dimensions of 3.25 m × 3.25 m in plan and an internal depth of 4 m. The filter medium was a 0.7 m deep single layer of silica sand surface-coated with Mn; the effective diameter of the filter medium was about 0.6 mm. The effective grain size d_{10} was 0.4 and d_{60} was 0.65, and the uniformity coefficient (d_{60}/d_{10}) was 1.63. The filtration rate for the greensand filter was 140 m/d. The operation for filter backwash depended on the head loss that reached to 1.5 m. The clean bed head loss was about 0.3 m.

The PTFE-based system was designed to utilize the oxidation process and membrane filtration in order to improve the quality of treated water and minimize the water problems caused by metals, such as color and odor. The characteristics of the PTFE membrane are shown in Table 1. The schematic diagram of the PTFE micro-filter pilot devices and sand filter is shown in Figure 1.

Table 1 │ Outline of the PTFE hollow-fiber membrane

Manufacturer (Item)	SUMITOMO Inc., JP. (Poreflon® Module OPMW-23005C48H2)
Membrane material	Poly-tetra-fluoro-ethylene (treated by hydrophilic polymer)
Membrane structure	Double layer (filtration and support layer)
Average pore size	0.1 μm (filtration layer), 2 μm (support layer)
Outer diameter	2.3 mm
Inner diameter	1.1 mm
Membrane surface area	48 m^2 (1,960 mm length, each element: 12 m^2, 4 elements in this module)
Housing material	PVC resin (Inlet side flange: Stainless)
Housing dimension	Inside diameter 216 mm × length 2,288 mm (Flange: outside diameter 330 mm)
Filtration mode	Submerged
Operation pressure	Max. 100 kPa
Backwash pressure	Max. 150 kPa
Physical cleaning condition	60 min intervals with 2 min air scrubbing and 30 s backwashing
Permeability of pure water	2,800 l/m^2/h
Cleaning in place for inorganic fouling	1–4% H$_2$SO$_4$, once every 3–6 months, and 12 h cleaning time; can reach more than 98% recovery rate

Fe–Mn removal achieved by microfiltration (MF) and the greensand process was compared and evaluated. Four sampling points were chosen and classified as raw water (point A), water after NaOCl oxidation (B), membrane module effluent (C) and greensand filter effluent (D) (see Figure 1).

The concentrations of Fe and Mn ions from raw water and filtrate were monitored by UV/VIS spectrophotometry (HACH DR4000U spectrophotometer). All filtered samples from MF membrane and greensand effluents were determined using the pyridylazonaphthol (PAN) method to analyze the Fe and Mn concentration. The PAN method is a highly sensitive and rapid procedure for detecting low levels of Mn and Fe. The principle is that an ascorbic acid reagent is used initially to reduce all oxidized forms of Mn to Mn^{2+}. An alkaline–cyanide reagent is added to mask any potential interference. PAN indicator is then added to combine with Mn^{2+} to form an orange-colored complex. The absorbance of the red-orange solution was measured by UV/VIS spectrophotometer at 560 nm (Chiswell & O'Halloran 1991).

Particle numbers in the size range 2–15 μm were also measured after filtration by particle counters. The WGS267 (Met-One Inc., USA) is based on the principle of light blockage and measures particles from 2 to 15 μm. The KS28B (Rion Inc., Japan) is based on the light scattering theory and measures particles from 0.2 to 2 μm. The predominant chemical compositions of the sludge coated on PTFE were analyzed by X-ray diffraction (XRD) (Rigaku RU-H3R X-ray) and scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) (Nikon ESEM2700) at magnification 400×, 1,000×, and 3,000×. The pretested result showed that the fouling sludge was the inorganic material. According to the suggestion of the membrane manufacturer, H$_2$SO$_4$ was the appropriate cleaning agent for cleaning in place (CIP).
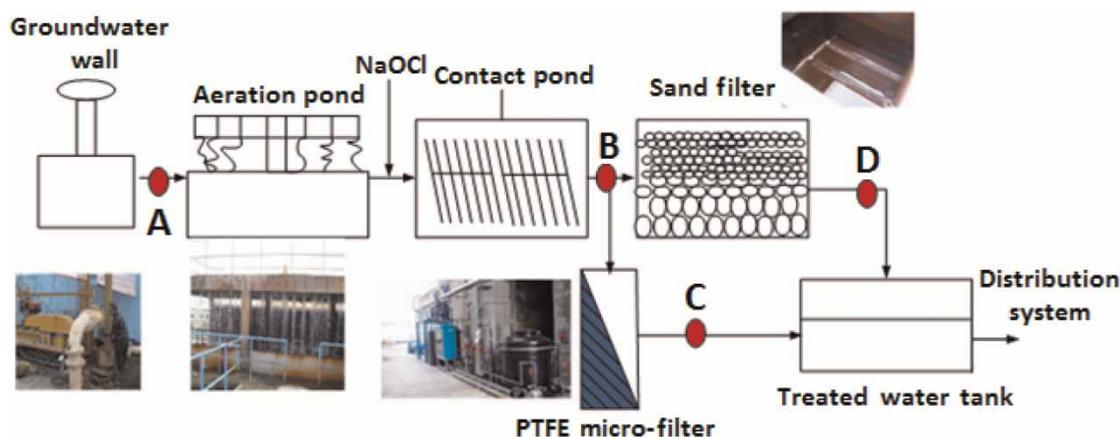
Figure 1 │ Sampling sites in Changhua Water Treatment Plant: (A) raw water, (B) after NaOCl oxidation, (C) after membrane filtration, (D) after greensand filtration.

RESULTS AND DISCUSSION

Manganese removal

Four water treatment samples, raw water (point A), before filtration (point B), after membrane filtration (point C), and after greensand filtration (point D), were monitored from 12 August to 28 October 2008 as shown in Figure 2. At points A and B, the Mn concentration was above acceptable level during the operating time, while the Mn concentration at point C gradually decreased from 0.1 to 0.01 mg/L after 2 weeks operating time. However, the Mn concentration after greensand filtration (point D) was about 0.02 mg/L, which is below the permitted level, 0.05 mg/L.

As shown in Figure 3, the removal efficiency of Mn gradually increased from 75 to 96% after membrane filtration, while it fluctuated around 95% after greensand filtration. Solid–liquid separation plays an important role
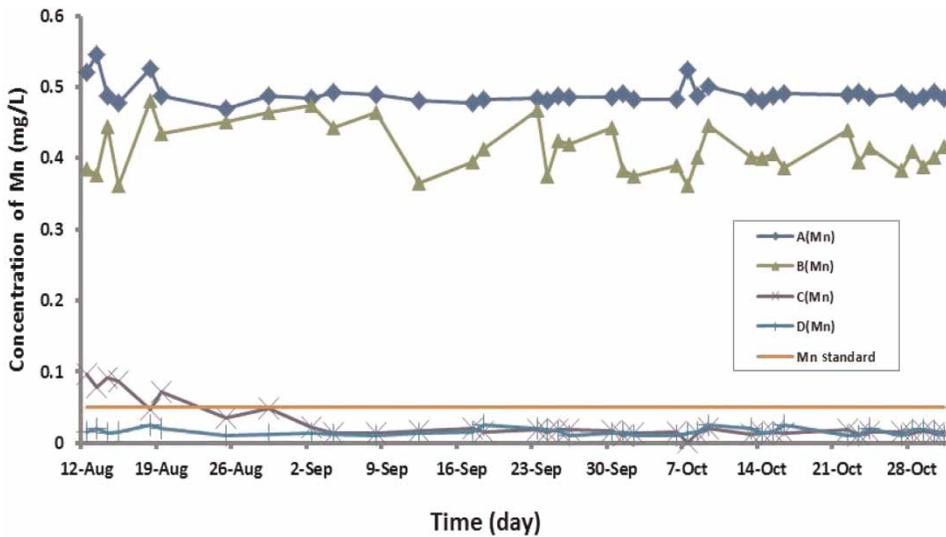

Figure 2 │ Concentration of Mn in time period at different sampling site (sampling date: 12 August–31 October).
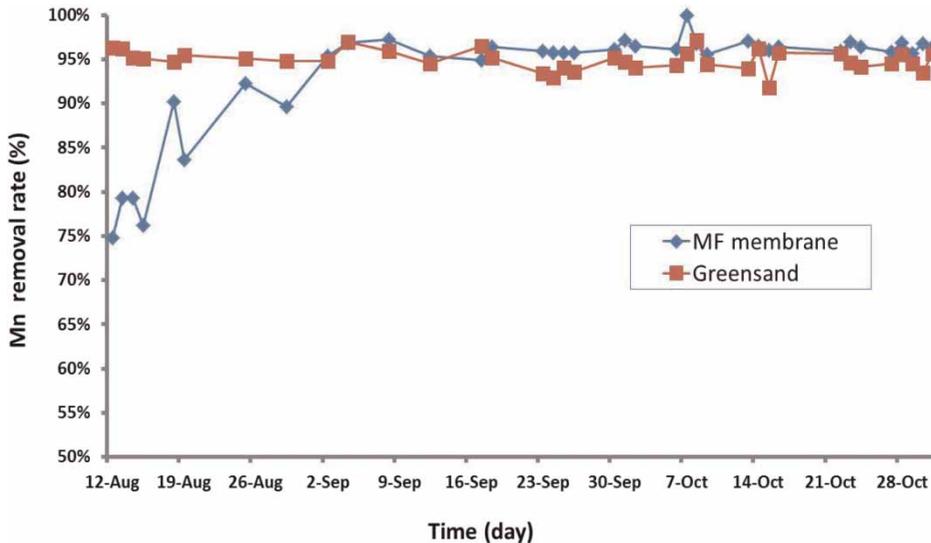

Figure 3 │ Removal rate of Mn in time period at C and D sampling site (sampling date: 12 August–31 October).

in membrane filtration. The oxide particles of Fe–Mn in feed water accumulate on the membrane surface where the Mn ions are removed by adsorption.

Based on the size analysis of particle counter (Figure 4), particles larger than 2 μm were referred to as micro-particles, and particles smaller than 2 μm were referred to as submicro-particles. In the initial stage of experiment, micro-particles were almost completely removed by membrane filtration. Nevertheless, the submicro-particles concentration increased to three times higher than that in raw water. No such phenomenon was observed after passing through greensand (point D). A possible mechanism for this result is as follows: In the first 2 weeks, when Mn sand was used as the filter medium in greensand filtration, the Mn

ions in raw water were removed through autocatalysis on the surface of the sand. However, the Mn concentration in the effluent of membrane filtration was still high during this time. After aeration and addition of NaOCl, Fe and Mn ions were oxidized forming Fe–Mn oxide particles, where some particles could pass through 0.1 μm MF. This supported why the concentration of submicro-particles in the membrane effluent were higher than that in the raw water. After a while, the Fe–Mn oxide particles continuously accumulated and formed a sludge cake on the membrane surface where the Mn ions were removed through autocatalysis. A similar phenomenon occurred in greensand filtration.

After 3 months of operation, micro-particles were removed more efficiently through MF than greensand, and
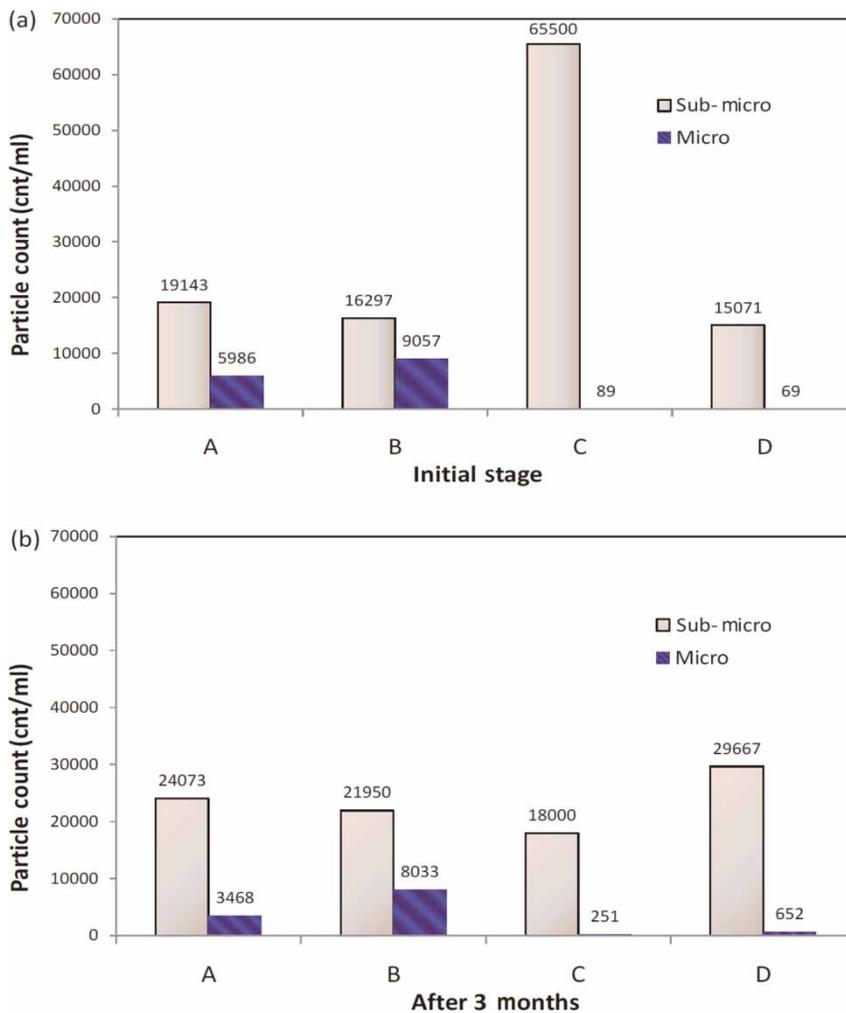

Figure 4 | The number of submicro- and micro-particles at points A, B, C and D; (a) at initial stage (sampling date: 15 August) (b) after 3 months (sampling date: 7 November).
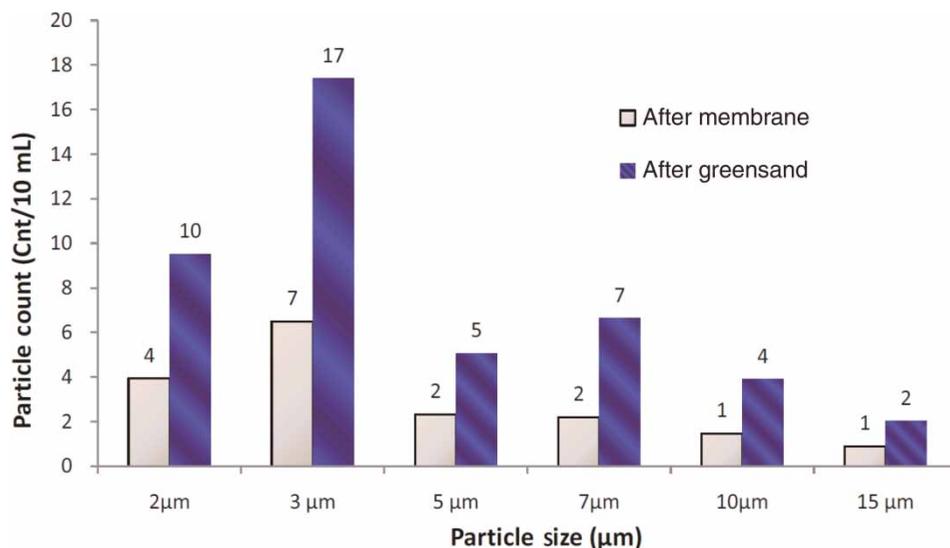
Figure 5 | Number of micro-particles in 10 ml of permeate after different filtration processes (sampling date: 8 November).

a similar removal effect of submicro-particles was also confirmed, which indicated that MF gave a slightly higher efficiency than greensand. Figure 5 shows the analysis of particle size distribution from 2 to 15 μm using MF and greensand. It is clear that the resultant particle count after the MF procedure were significantly lower than those through greensand.

Through the observation window of the equipment modules, it was observed that Fe–Mn oxide sludge accumulated on the hollow-fiber membrane, and increased over time. Complete sludge filling on the membrane was confirmed by removal from the system after 3 months. A similar phenomenon was confirmed on greensand. When Fe–Mn oxide particles formed on filters, autocatalysis occurred and was accompanied by precipitation, which entrapped the metal ions to produce better water quality. Thus, comparing the previous tests in this study, it was shown that both MF process and greensand filter could demonstrate high efficiency of Mn removal.

Iron removal

As illustrated in Figure 6, the Fe concentration in raw water generally ranged from 0.35 to 0.60 mg/L, which exceeds the water quality standards. After aeration and chlorine oxidation, the concentration drops to 0.1 mg/L on average

that is much lower that the water quality standard. Therefore, the impact of Fe removal is not the limiting factor for effective water treatment.

Based on the analysis of Fe fractionation, the groundwater enters the water treatment plant, and oxidation took place after aeration and chlorination. The removal of Fe is about 70% with the concentration of 0.4 mg/L (sampling point A), where Fe ions could be easily oxidized and particles formed are larger than the membrane pore size (0.1 μm). After filtration (membrane or greensand), the concentration similarly dropped to less than 0.02 mg/L. This confirmed that the stability after MF is similar to that after the greensand process.

Analysis of sludge on PTFE membrane

After 3 months of operation, sludge was fully coated onto the PTFE hollow fibers (Figure 7). The backwashing procedure with treated water without any chemicals was employed. It was observed that the Fe–Mn sludge accumulated gradually on the outside membrane which could not be completely cleaned. The membrane pressure was increased from 110 to 120 kpa, thus a pressure drop of less than 10% was observed, which is an acceptable range for the control procedures. Figure 8 shows the original PTFE and the predominant chemical
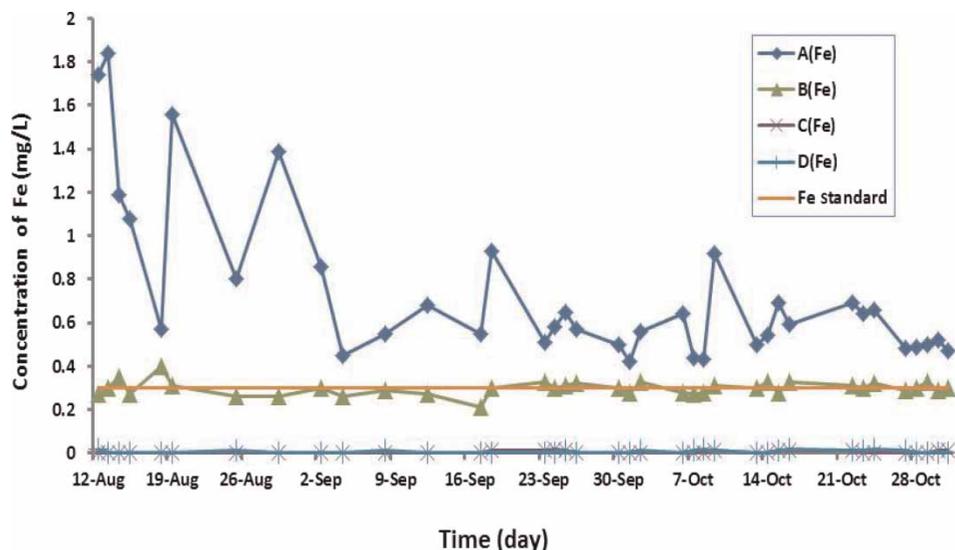
Figure 6 │ Concentration of Fe in time period at different sampling site (sampling date: 12 August–31 October).

Figure 7 │ The formation of Fe–Mn sludge on the PTFE membrane.

compositions of the sludge on PTFE before and after CIP as analyzed by SEM/EDS (for EDS data see Table 2). Chemical composition of the sludge included mainly Fe, Mn, Ca, and trace amounts of other oxides (Figure 8(a) and (b)). Moreover, the XRD analysis indicates the three-line patterns that confirm the existence of $-MnO_2$ and $-Fe_2O_3$ (Figure 9). Literature reviews have also confirmed the presence of Fe–Mn oxide in similar oxidative conditions (Jusoh *et al.* 2005; Zhang *et al.* 2007, 2009; Zhao *et al.* 2009).

Thus, the EDS and XRD analyses illustrate that the Fe and Mn ions in water were successfully oxidized by chemical reagents to form metal oxides. These oxide particles initially accumulated on the membrane surface, and finally induced about 10% pressure loss in the filtration process.

PTFE membrane analysis

Fouling and scaling problems are considered as major drawbacks for membrane filtration. It is essential to clean Fe–Mn sludge efficiently from the membrane. In this study, following safe operating procedures in the plant, the treated hollow fiber was washed by H_2SO_4 (5%) after 36 h of soaking. The field test showed that particles coated on the membrane were completely removed by chemical washing. In order to study the micro-structures of PTFE membrane before/after chemical cleaning, three groups of hollow fibers were selected for SEM analysis, including: (1) hollow fiber before chemical cleaning; (2) hollow fiber after chemical cleaning; (3) unused hollow fiber.

Figure 8(b) illustrates the hollow fiber before chemical-cleaning. The membrane surface was covered with many particles, including single particles, and sheet structures, which did not completely block the membrane pores; this is consistent with only 10% pressure loss after the experimental procedure. Figure 8(c) illustrates the hollow fiber after chemical cleaning; neither particles nor sheet structures were
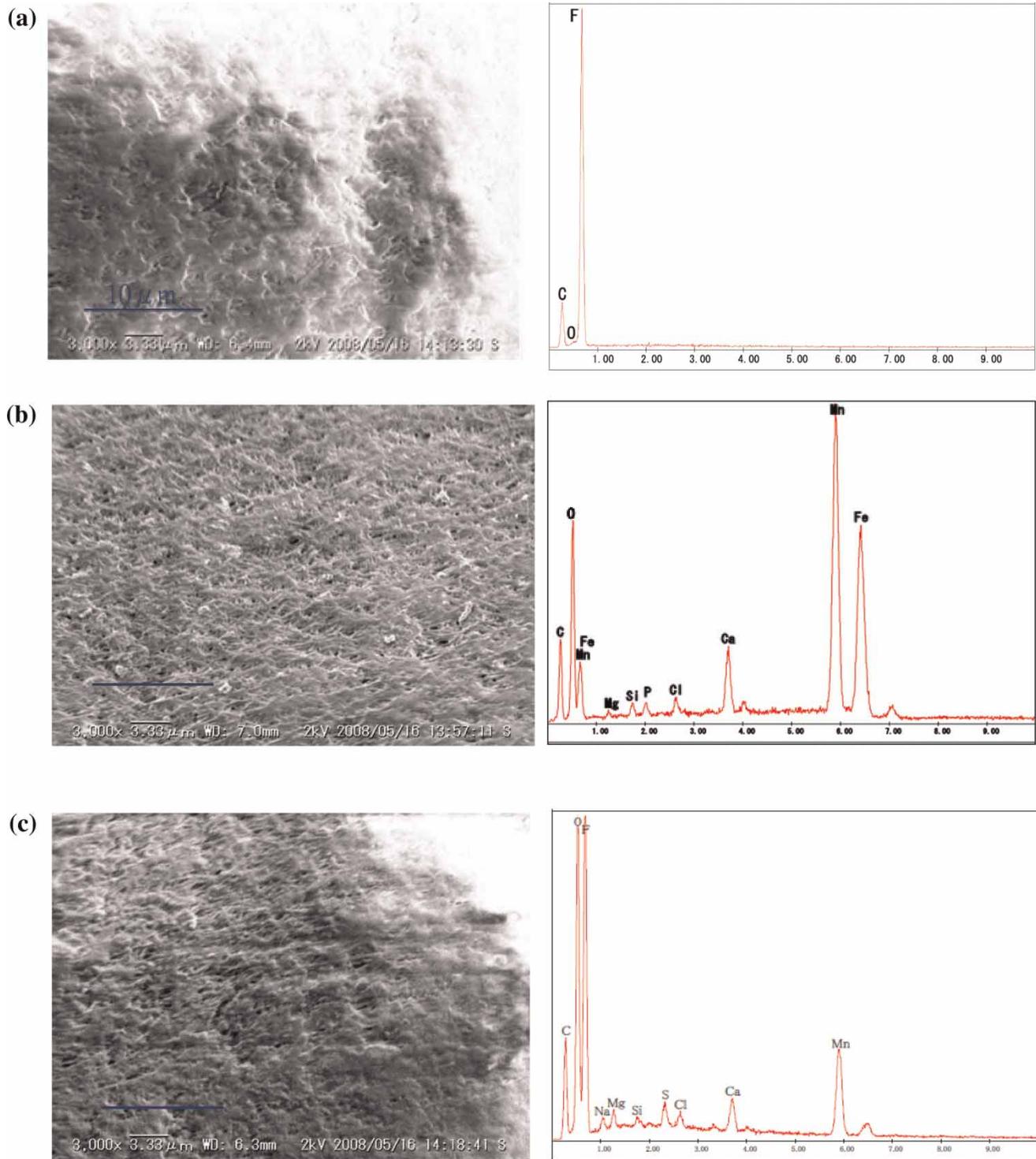
Figure 8 | Scanning electron micrographs and energy-dispersive X-ray spectroscopy of PTFE membrane (a) unused (b) before cleaning in place (c) after cleaning in place.

Table 2 │ Composition of element of PTFE membrane energy-dispersive X-ray spectroscopy under different condition

Element (wt%)	C	O	F	Na	Mg	Si	P	S	Cl	Ca	Mn	Fe	Total
Unused	30.73	2.12	67.16	–	–	–	–	–	–	–	–	–	100.00
Before CIP	13.03	8.80	–	–	0.21	0.44	0.45	–	0.57	2.98	42.12	31.39	100.00
After CIP	12.52	33.02	29.30	0.26	0.35	0.24	–	2.57	1.88	3.65	16.21	–	100.00

CIP: Cleaning in place.
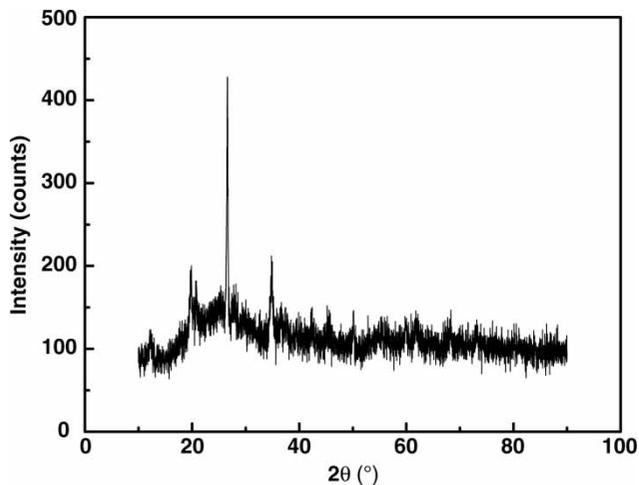
Figure 9 │ The X-ray diffraction pattern of Fe–Mn oxide from raw sludge on the membrane.

Table 3 │ Comparison of Fe–Mn removal from groundwater through PTFE module and greensand filtration

Item	PTFE module filtration	Greensand filtration
Power consumption (kW/ m³)	0.2–0.3	0.03–0.05
Water consumption (%)	2	6–8
Fe removal rate (%)	99	98
Mn removal rate (%)	97	93
Construction costs (US$/m³)	500	300
Operation costs (US$/m³)	0.05	0.03
Manpower of operation and maintenance (person/1,000 m³)	0.5	1
Microbial removal rate (%)	99.99	98.95
Land requirement (m²/m³)	3	15

visible on the outer membrane, which appeared the same as the unused hollow fiber (Figure 8(a)). Moreover, based on the comparisons between Figure 8(a)–(c), there was no structural damage to the membrane, which confirms that the cleaning procedure was effective, and the original operating flux conditions were re-established.

Economic analysis

Costs were compared based on module factory experiments and field devices at the Changhua Water Treatment Plant. Operating parameters for PTFE module procedures and the greensand process were recorded separately. Power consumption, water consumption, Fe–Mn removal efficiency, stability, construction costs, and operating costs were compared and analyzed (Table 3). The traditional greensand process illustrated good efficiency in Fe–Mn removal under low capital and operation cost, and low power consumption. However, their limitation on future expansion under more stringent water quality standards is significantly inferior to the PTFE module process, including larger land requirement (5 times more), higher amount of water used for backwashing (3–4 times more), more manpower needed for operation, and maintenance (double), and unanticipated variations in metal removal concentrations. Furthermore, to fulfill the increasing requirement of treatment capacity, the problems for current water treatment plants in Taiwan are already the lack of land and increasing amount of backwash water that is the major source of wastewater, and usually requires 2–10% of daily produced clean water. Based on Table 3, the water consumption for MF membrane filtration for backwash water is 3–4 times less than it for greensand filtration, which could save large quantities of water, and help to reach the goal of water reclamation in water treatment plants. Moreover, the advantage of modular design for this PTFE system permits a multistage process for the best quality or quantity purpose and performance, which could reduce usage of land area. In addition, because the

sludge on membranes provides entrapping, precipitation, adsorption and oxidation phenomena, the PTFE module illustrates a simple role of solid–liquid separation to provide steady removal efficiency, thus, it permits stable operation with lower water consumption, less manpower need, and land requirement.

CONCLUSIONS

In this study, the removal of Fe–Mn in groundwater by oxidation and filtration using the PTFE hollow-fiber and traditional greensand processes was investigated. The experimental results led to the following conclusions:

1. Fe was completely removed by PTFE hollow fiber, while Mn concentration was still higher than water quality standard (0.1 mg/L at the initial stage of operation). However, the concentration decreased to that of the greensand effluent (below 0.02 mg/L) within 2 weeks of operating time.

2. Stable PTFE hollow-fiber process gave Fe removal rate up to 99%, and Mn removal rate up to 97%, which was slightly better than greensand filtration. However, the PTFE hollow-fiber process illustrated better buffering capacity in facing future expansion under various operation conditions (e.g., land requirement, water consumption and needed manpower) compared with the greensand process.

3. The main composition of sludge was Fe–Mn oxide characterized by SEM-EDS. The formation of the sludge illustrates an important role in increasing removal efficiency of contaminants in water.

4. Based on economic analysis, the greensand process requires less construction and operation costs than the PTFE module process. However, under similar metal removal efficiency, membrane filtration shows better modification capacity in facing future expansion to fulfill more stringent water quality standards.

ACKNOWLEDGEMENTS

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