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Hybrid manganese/quartz sand filtration—nanofiltration processes for the removal of arsenic in water

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ABSTRACT

The arsenic contamination in water forced the water and health authorities to introduce stringent standards for arsenic levels in drinking water. Recently, arsenic attracted attention because some of the drinking water resources contain considerable concentrations of arsenic which cause acute and chronic symptoms in many countries. Of the available technologies for the treatment of arsenic in drinking water, membrane treatment is the technically superior method to obtain the low level finished water arsenic concentration. In this study, the+ removal of arsenic from water by a nanofiltration (NF) membrane was investigated with the pretreatment of manganese/quartz sand filtration. Experiments were carried out with synthetic water of ultrapure and tap water spiked by arsenic. Results showed that As(III) and As(V) could be removed effectively by manganese/quartz sand filtration with the influent arsenic concentration 250 μg/L, and the effluent arsenic concentration could be less than 50 μg/L, while the NF presents only 40–60% removal of As(III), although the removal of As(V) is satisfactory. Furthermore, the hybrid manganese/quartz sand filtration—NF processes were tested for the removal of both As(III) and As(V) to get an lower arsenic concentration of finished water.

Keywords: Drinking water; Arsenic removal; Manganese sand; Nanofiltration membrane

1. Introduction

Arsenic (As) is a toxic carcinogen widely distributed in nature [1,2]. Arsenic in natural waters existed in two forms: arsenate (As(V)) and arsenite (As(III)), the major form of arsenic in oxygen–rich water is As (V), and in oxygen-lack is As(III). When the pH in the neutral range, As(III) mainly exists in the form of H_3AsO_3 (pKa = 9.22), and As(V) is mainly exists in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$ (pKa = 2.19, pKb = 6.98, pKc = 11.5). Compared with As(V), As(III) is more toxic.

Due to the carcinogenic toxicity of arsenic, the limit value of arsenic concentration in drinking water of the Guidelines for Drinking Water Quality (1993) revised by the WHO was changed from 0.05 to 0.01 mg/L. Subsequently, the European Union, the United States, and other countries were respectively set the limit value of arsenic concentration of their Drinking Water Standards at 0.01 mg/L, and China's

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Drinking Water Health Standards (GB5749-2006) also regulated arsenic concentration indicators of 0.01 mg/L. Increasingly stringent drinking water standards have higher requirements for arsenic removal technologies.

In the study of arsenic removal for drinking water, due to the poor affinity of As(III) and metal oxide, sediment, and so on, the removal of arsenic is very difficult. Nanofiltration (NF) membrane separation as a new separation technology is increasingly being used in drinking water to remove arsenic [3–5], and studies have pointed out that the NF membrane with a high removal efficiency of As(V). Therefore, oxidizing As (III) to As(V) is an effective way to strengthen the removal of As. Mou Sen et al. utilized the oxidant of potassium permanganate to oxidize As(III) to As(V), which removed effectively by subsequent NF membrane filter. Wang Xiaowei et al. added a certain amount of sodium hypochlorite to the water to oxidize As(III) to As(V) and then filtered by the NF membrane, the results showed that the performance of arsenic removal was observably improved. In this article, manganese sand/quartz sand composite filtration column and NF membrane combined process was investigated as a new method of arsenic removal for drinking water, and the efficiency, security and applicability of this combined process were probed as well.

2. Materials and methods

2.1. The experiment setups

The composition of the test device shown in Figs. 1 and 2, and the main units includes the raw water tank, clear water tank, NF membrane module and manganese sand/quartz sand filtration column. Device 1, the arsenic raw water was pumped into the NF membrane module via raw water tank for crossflow filtration, the effluent and concentrates of membrane flow back to the raw water tank, to investigate the arsenic removal performance of NF membrane module. Device 2, the arsenic raw water was pumped into manganese sand/quartz sand composite column filtration, then the effluent into the NF membrane for crossflow filtration.

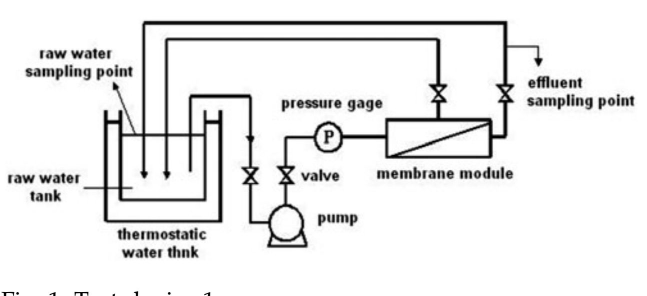

Fig. 1. Test device 1.

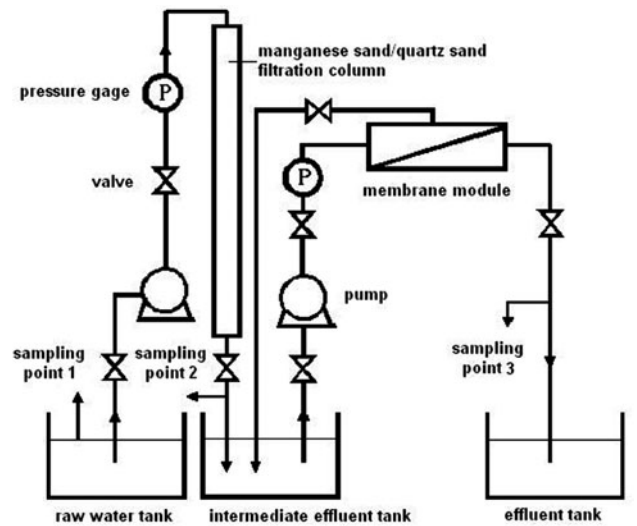

Fig. 2. Test device 2.

Manganese sand/quartz sand filtration column diameter of 7 cm, height of 100 cm. Filter material height of 70 cm, with the upper manganese sand filter material 25–45 cm in thickness, manganese sand particle size ranges from 0.5 to 0.8 mm; middle quartz sand 25–45 cm in thickness, quartz sand particle size range from 0.5 to 1.2 mm; the lower supporting layer thickness of 10 cm, the filtering speed of raw water is 8–12 m/h.

The NF membranes of NF90 used in this experiment were kindly supplied by Dow, and HL by GE. The effective membrane area is 60 cm^2, all NF membranes were pre-soaked in ultrapure water (Milli-Q) at least one day prior to use. A new membrane would be inspected before each test, using 2 L deionized water pressed membrane for 1 h before raw water test, the operating pressure of above NF membrane crossflow filtration devices were 0.5 MPa. The performance of NF membrane shown in Table 1.

2.2. Reagents and methods

$NaAsO_2$ and $Na_3As0_4{\cdot}7H_2O$ (AR) were used, respectively, to prepare As(III) and As(V) stock solution, which diluted with deionized water as arsenic raw water of the tests. Other reagents were of analytical grade. In addition, sample from a certain residential tap water also be used to prepare the used arsenic raw water with arsenic added. The water quality index shown in Table 2.

Table 1
Performance of NF membrane

Membrane type	NF90	HL
Material	Polyamide	Polyamide
APWF[a] (L m^{-2} h^{-1} MPa^{-1})	88	130
Average pore size (nm)	0.81	1.00
Applicable range of pH	2–11	2–11
Maximum operating temperature (℃)	45	50
Maximum operating pressure (MPa)	4.1	4.1

[a]APWF = average pure-water flux.

Table 2
Tap water quality index

Water quality index	Variation range
pH	6.8–7.05
Turbidity (NTU)	0.8–1.0
TOC (mg/L)	2.8–4.0
Water temperature (℃)	24
UV_{254} (cm^{-1})	0.07–0.09
Conductance (μS/cm)	600

2.3. Analytical approach

The total arsenic concentrations were measured by potassium borohydride—atomic fluorescence spectrophotometry (AFS-230E dual channel atomic fluorescence spectrometer). Total organic carbon (TOC) of the residential tap, conductivity, pH, UV_{254}, turbidity and water temperature were measured by the TOC-VCPH (Shimadzu, Japan), the conductance tester (Leici, Shanghai), the pH meter (Leici, Shanghai), the UV spectrophotometer (UV75B) and the turbidimeter (HACH2100N).

The initial water filtration flux (the flux when the deionized water just finished its pressure on membrane) was recorded as the value of J_0, the flux during the filtration process is denoted by the value of J, and comparing filter flux ratio (J/J_0) of water samples under different operating conditions. The solute rejection rate of NF membrane is

$$R = (1 - C_P/C_R) \times 100\% \quad (1)$$

The C_P and C_R in this formula was the solute concentration of permeated solution and raw water, respectively.

3. Results and discussion

3.1. Arsenic removal performance of different NF membrane

To investigate arsenic removal performance of NF membranes (of NF90, HL) with different pore sizes, adopted test device 1, deionized water was used to prepare raw water with arsenic concentration of 0.05, 0.25 and 0.50 mg/L, value of pH is 6.8, the experimental results shown in Figs. 3 and 4. Fig. 3 suggests that the membrane of NF90 which with smaller pore size has better capacity of removing arsenic through filtering, compared with the membrane of HL, whose removal rate of As(V) are only 67–75%, and the As(V) removal rate of NF90s were higher than 90%. None of the two kinds of NF membrane displayed desired removal performance of As(III), As(III) concentration of raw water ranges from 0.01 to 0.05 mg/L, change the As(III) removal rate of NF90 down from 66% to 54%, and the As(III) removal rate of HL can just reach 40%.

Currently, consider, screening effect and Donnan effect are the two main arsenic removal mechanisms of NF membrane. Due to the Donnan effect, the negatively charged As(V) in natural water bodies can get a good removal. Arsenic removal performance of NF membrane is influenced by pH of raw water, that is, because different pH will change the existing form of arsenic in water. When the value of pH less than 7, As(III) and As(V) mainly exists in the form of H_3AsO_3 and $H_2AsO_4^-$, and these would changed to be $H_2AsO_3^-$ and $HAsO_4^{2-}$ when the value of pH greater than 7, respectively. Membrane of NF90 with stronger screening effect than HL, and comprehensive utilization of the negative charge of the membrane

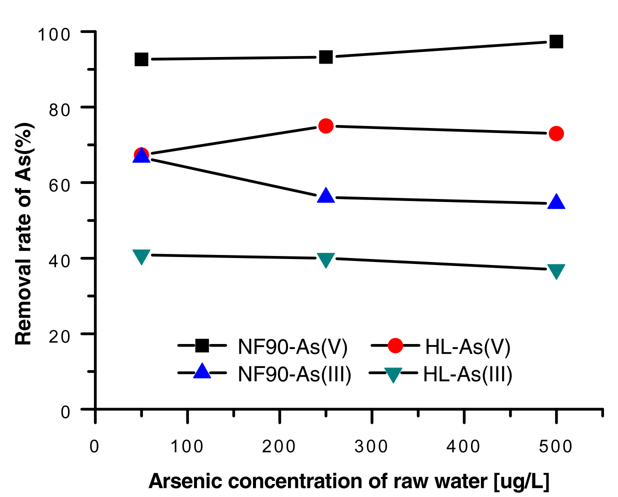

Fig. 3. Arsenic removal performance of NF membranes NF90 and HL.

itself, as a result, it got a higher removal efficiency of As.

Fig. 4 shows that, membrane flux of NF membrane NF90 and HL were gradually decline during the 390 min of running process, J/J_0 value of NF90 becomes 0.86 from the beginning of 0.99, and HL J/J_0 value changed from 0.96 to 0.88. The membrane flux downward trend of Nf90 and HL with arsenic raw water similar to the trend with deionized water; therefore, arsenic will not cause a sharp decline in NF membrane flux.

3.2. *Arsenic removal performance of different proportions of manganese sand/quartz sand filtration column combined with NF membrane*

To examine the water arsenic removal efficiency of different proportions of manganese sand/quartz sand filtration column, there are two given columns of different proportions: column 1 with manganese sand 45 cm in height and quartz sand 25 cm in height, column 2 with Mn sand 25 cm in height, quartz sand 45 cm in height. Raw water with As(III) concentration of 0.25 mg/L is prepared with deionized water, filtration column filter arsenic raw water 5 L/d, the continuous filtered raw water in 14 days is 70 L in total. When the filtration column 1 and filtration column 2 filter the first 70 L of arsenic raw water, NF membrane is installed, inspecting the arsenic removal efficiency of manganese sand/quartz sand filtration combined with NF membrane NF90 after 14 days. The experimental results are shown in Figs. 5 and 6.

As shown in Fig. 5, raw water (As(III) concentration is 0.25 mg/L) is filtered by the filtration column, concentrations of arsenic in the effluent are greatly reduced, filtration column 1 has better capacity of removing arsenic through filtering, compared with column 2. Effluents of column 1 and column 2 are 50 and 43 L, respectively, with the effluent arsenic concentration equal to or higher than 0.01 mg/L, and effluent concentration increased with the increasing of water flux. Manganese sand with a strong adsorption capacity for arsenic can oxidize As(III) to As(V). With the increasing of the water flux, the manganese sand adsorption points for arsenic gradually reduced, and the effluent arsenic concentration increased. Although the individual manganese sand filter can remove some arsenic, but the effluent arsenic concentration cannot meet the safety standards for drinking water.

As shown in Fig. 6, after filtration column filtered 70 L water within 14 days, the average concentration of effluent arsenic in combined process were less than 0.01 mg/L. After 70 L water filtrating, adsorption

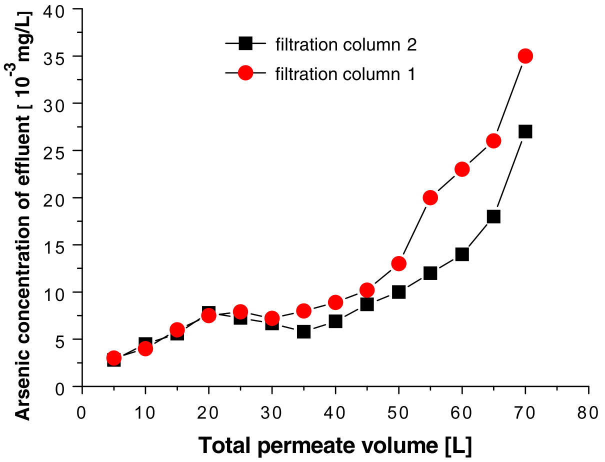

Fig. 5. Arsenic concentration curve of filtration column effluent.

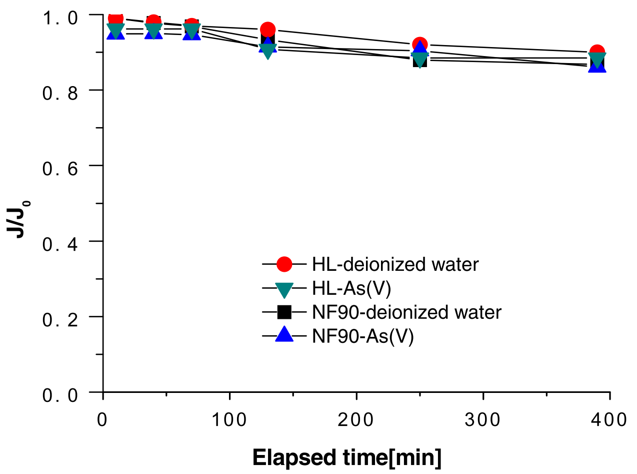

Fig. 4. Water flux of NF90 and HL during treatment of raw water and deionized water.

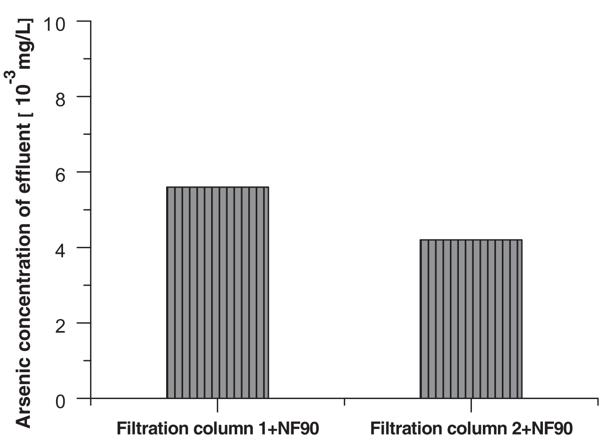

Fig. 6. Comparison of arsenic concentration of combined processes.

points of manganese sand/quartz sand filtration column for arsenic are gradually reduced, but the effluent arsenic concentration of combined process did not cause sudden increase, which contribute to reach the safety standard of drinking water.

3.3. *Arsenic removal performance of comparing different proportions of manganese sand/quartz sand filtration column combined with different NF membrane*

Take different proportion of manganese sand/quartz sand filter material filtration column 1 and 2, respectively, combine with the NF membrane to remove arsenic from water, and deionized water was used to prepare raw water of As(III) concentration of 0.25 mg/L and As(V) concentration of 0.25 mg/L, the experimental results shown in Fig. 7. The effluent arsenic concentration after the above combined processes were less than 0.01 mg/L, and the removal rate of arsenic reached 98% or more. Manganese sand with a strong adsorption capacity for arsenic, greatly reduced the load of the NF membrane; manganese sand can oxidize As(III) to As(V), leakage of arsenic from manganese sand/quartz sand filtration column is removed by the membrane intercept. NF membrane and manganese sand/quartz sand filtration column combined processes achieved a high removal rate of As(III) and As(V) in water, and removal efficiency is far greater than the individual manganese sand/quartz sand filtration system and a separate NF membrane process. So these combined processes are of security for removal of arsenic.

Fig. 8 shows the curve of the NF90 membrane flux in the combined process. The flux of NF90 downward trend similar to the trend of deionized water, manganese sand/quartz sand will not cause a sharp decline in NF membrane flux.

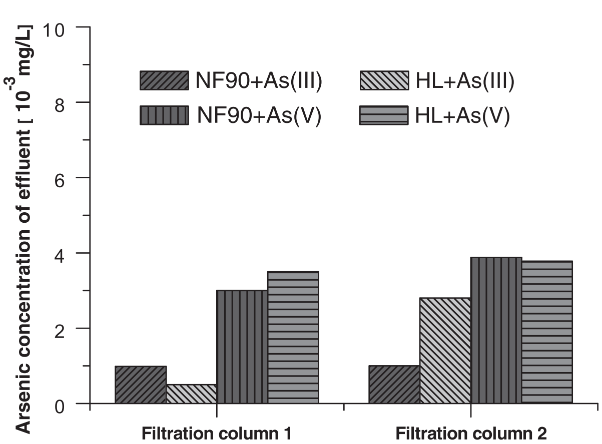

Fig. 7. Comparison of arsenic removal efficiency of different combined processes.

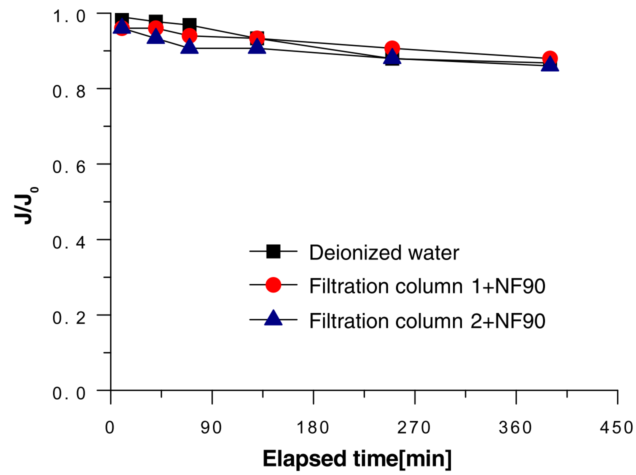

Fig. 8. Water flux of NF90 in combined processes.

3.4. *Comparison of arsenic removal efficiency of manganese sand/quartz sand composite filtration column and NF membrane combined processes between different arsenic concentration raw water*

Examine the arsenic removal efficiency of different proportion of manganese sand/quartz sand filter material filtration column 1 and 2 combine with the NF membrane in different arsenic concentration raw water, the raw water As(III) concentration of 0.10, 0.25 and 0.50 mg/L, the experimental results shown in Fig. 9. Raw water arsenic concentration of 0.10–0.50 mg/L, change the effluent arsenic concentration gradually increased, and effluent concentration of column 2 is higher than column 1. Filtration column combined with NF90 can get a good removal of water arsenic, and the effluent concentrations were less than 0.01 mg/L. Manganese sand/quartz sand filtration and NF membrane combined process can dispose high concentrations of arsenic raw water, raw water arsenic concentration fluctuations will not cause a sudden increase in the concentration of combined process effluent, so the combined process for arsenic removal in a high security.

3.5. *Performance of manganese sand/quartz sand filtration and NF membrane combined process in residential tap water arsenic removal*

Sample from a certain residential tap water, raw water is compounded with sampled tap water and As(III), whose concentration is up to 0.25 mg/L, the experimental results shown in Fig. 10. In tap Water conditions, the effluent arsenic concentrations of filtration column and combined process has no sudden fluctuations, and were less than 0.01 mg/L. Compared

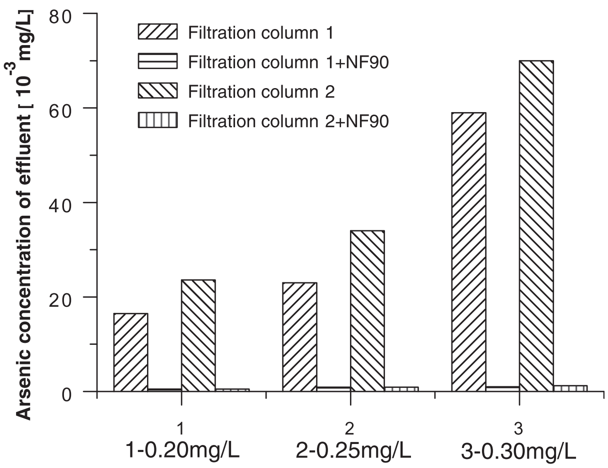

Fig. 9. Effects of arsenic concentration.

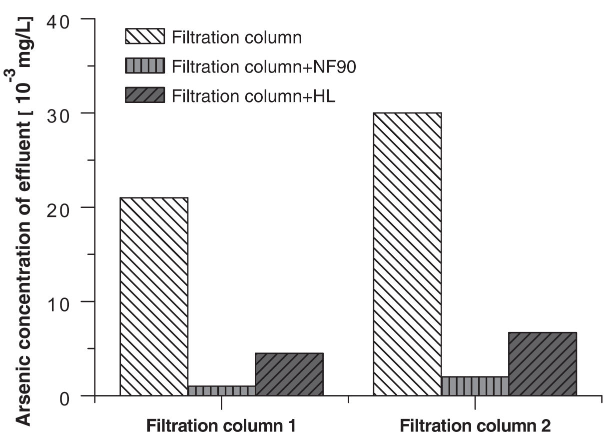

Fig. 10. Comparison of arsenic removal efficiency in tap water by different combined processes.

with the removal efficiency of arsenic raw water prepared by deionized water, the effluent arsenic concentration of arsenic raw water prepared by tap water is appreciably higher, due to the Inorganic ions exist in tap water, which reduce the arsenic removal efficiency of NF membrane.

Fig. 10 shows, the combined process of NF membrane NF90 and HL, respectively, effluent arsenic concentrations were less than 0.01 mg/L can reach the arsenic concentration in safety standards of drinking water. The combined processes have no strictly restrictions on the types of used NF membrane.

4. Conclusion

Due to the intrinsic difference of types of NF membranes and various existence forms of arsenic in water, there are discrepant arsenic removal performances between different NF membranes. The membrane of NF90 which with smaller pore size has better capacity of removing arsenic than the membrane of HL, their removal rate of As(V) are 90–98% and 67–75%, respectively. Both the two kinds of NF membrane are failed to show desired removal performance of As(III), the As(III) removal rate can just reach 40–60%. NF membrane and manganese sand/quartz sand filtration column combined processes achieved a high removal rate of As(III) and As(V) in water, and removal efficiency is far greater than the individual manganese sand/quartz sand filtration system and a separate NF membrane process. Manganese sand with a strong adsorption capacity for arsenic, can oxidize As(III) to As(V). Thus, the filtration column can greatly reduced the load of the NF membrane, and leakage of arsenic from it will be removed well by the membrane filtration simultaneously. Moreover, the applicable range of this combined process is wide for different arsenic concentration raw water, and also applicable to residential tap water arsenic removal. Therefore, the combined process is potentially very useful for drinking water arsenic removal.

Acknowledgments

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References

[1] D. Pokhrel, B.S. Bhandari, T. Viraraghavan, Arsenic contamination of groundwater in the Terai region of Nepal: An overview of health concerns and treatment options, Environ. Int. 35(1) (2009) 157–161.
[2] M.C. Shih, An overview of arsenic removal by pressure-driven membrane processes, Desalination 172(1) (2005) 85–97.
[3] K. Kosutic, L. Furac, L. Sipos, B. Kunst, Removal of arsenic and pesticides from drinking water by nanofiltration membranes, Sep. Purif. Technol. 42(2) (2005) 137–144.
[4] J.I. Oh, S.H. Lee, K. Yamamoto, Relationship between molar volume and rejection of arsenic species in groundwater by low-pressure nanofiltration process, J. Membrane Sci. 234(1–2) (2004) 167–175.
[5] J. Yoon, G. Amy, J. Chung, J. Sohn, Y. Yoon, Removal of toxic ions (chromate, arsenate, and perchlorate) using reverse osmosis, nanofiltration, and ultrafiltration membranes', Chemosphere 77(2) (2009) 228–235.