

Comparison of nanofiltration efficiency with GAC adsorption and air stripping processes for CHCl_3 removal from Tehran drinking water

M. T. Samadi, S. Nasser, A. R. Mesdaghinea and M. R. Alizadehfard

ABSTRACT

The effectiveness of nanofiltration (NF) was compared with granular activated carbon (GAC) and air stripping (AS) using a packed column in water treatment for the removal of chloroform (CHCl_3), which is a basic indicator of trihalomethane (THM) compounds in many water resources. Pilot GAC and AS columns were designed and set up with nanofiltration polyamide and cellulose acetate blend spiral-wound modules with MWCO of 300 Da and 600 Da. The study was carried out for the two cases of deionized and chlorinated Tehran tap water. CHCl_3 concentrations for both inlet and outlet samples were detected by gas chromatography (GC) and using electron capture detector (ECD). Results showed that the maximum CHCl_3 removal efficiencies for NF 300 Da, NF 600 Da, GAC and AS packed columns under various operating conditions were 87.8%, 85%, 87.4% and 97.6% for deionized water and 86.1%, 72.3%, 85.1, and 91.2% for chlorinated Tehran tap water, respectively. Although NF, GAC and AS showed acceptable performance for CHCl_3 removal from drinking water, NF was significantly more effective ($p < 0.05$), providing simultaneously a higher flow rate and simpler operating conditions. This method may be considered for conventional water treatment plant finishing water.

Key words | air stripping, chloroform, GAC, nanofiltration, water treatment

M. T. Samadi (corresponding author)
Environmental Health Department,
School of Health and Center for Health Research,
Hamadan University of Medical Sciences,
PO Box 4171, Hamadan 65175,
Iran
E-mail: samadi@umsha.ac.ir

S. Nasser
A. R. Mesdaghinea
Center for Environmental Research,
Tehran University of Medical Sciences,
PO Box 6446, Tehran 14155,
Iran

M. R. Alizadehfard
Polymer Engineering Department,
Amirkabir University of Technology,
Tehran,
Iran

INTRODUCTION

Chlorine, the most commonly used disinfectant in water treatment plants, is now considered as a basic factor for the formation of trihalomethanes (THMs) (Gallard 2002). THM formation in drinking water results from the reaction of chlorine with naturally occurring or artificial organic matter, principally humic and fulvic acids (Siddiqui *et al.* 2000). Since THMs and mainly chloroform (CHCl_3) have been linked to toxic or carcinogenic compounds, their existence in drinking water is of great concern (Hammer 1996). These organic compounds, which are categorized in group A of the carcinogens, have a potential to increase the risk of liver and kidney cancer and the reproductive adverse effect of them is also considerable (Alicia & Alvarez 2000; Karakulski *et al.* 2001; Capar & Yetis 2002). The current US Environmental Protection Agency (USEPA) regulation for THMs in

drinking water is $80 \mu\text{g l}^{-1}$ (USEPA 1998). The Commission of the European Communities proposed a council directive with parametric values of $40 \mu\text{g l}^{-1}$ for chloroform and $15 \mu\text{g l}^{-1}$ for bromodichloromethane (Marawski & Kalenezuk 2000; Yoon & Lee 2003). The value for chloroform recommended by WHO is $30 \mu\text{g l}^{-1}$ (WHO 1998). In the Islamic Republic of Iran, the regulation for chloroform, bromoform, bromodichloromethane and dibromochloromethane MCL are 200, 100, 60 and $100 \mu\text{g l}^{-1}$, respectively (ISIRI 1997).

Several treatment alternatives have been proposed for the removal of THMs and their precursors. Removal can be performed with adsorption on activated carbon, oxidation, stripping and biological treatment. USEPA has proposed utilizing these processes to eliminate or reduce potentially carcinogenic organic substances in public supplies (Ducom

& Cabassud 1999; Yang & Cheng 2000), but these processes have several drawbacks such as toxic by-product formation, transfer of pollutants to air or to the solid phase, and difficulties in adapting to variations in concentrations and feed flow with time (King *et al.* 2000; Marawski & Kalenezuk 2000). The best option in water resources management is to protect water quality in dam reservoirs and rivers in order to minimize the concentration of CHCl₃ precursors. The second alternative is THMs precursor removal through THMs formation minimization (Kosutic & Kunst 2002). But in situations in which the above-mentioned options are not applicable (because of a high level of water pollution and technical constraints in water treatment plant), CHCl₃ removal should be a top priority in order to protect human health. Application of both granular activated carbon (GAC) and air stripping (AS) columns has been given serious consideration because of their ability to remove a wide range of compounds such as natural organic matter (NOM), THMs, odour- and colour-causing compounds and other toxic organic compounds (Ducom & Cabassud 1999; Odom 1999; Lin *et al.* 1999; Mahmud & Kumar 2000; Wietlik *et al.* 2002).

The main objective of this research was to investigate the performance and efficiency of GAC and AS columns for THMs removal from drinking water (deionized and Tehran tap water) and to compare the results under different operational conditions. The specific objective was to study the performance of nanofilters (NF) with MWCO of 300 and 600 Da under different operational conditions of flow rate, transmembrane pressure, CHCl₃ concentrations and TDS (total dissolved solids) concentrations and compare this with results obtained from GAC and AS systems under similar conditions, as follows:

- Study of the performance of NF with MWCO of 300 and 600 Da, under different operational conditions of flow rate, transmembrane pressure, CHCl₃ and TDS concentrations.
- Study of the performance of a GAC column under different operational conditions of flow rate, CHCl₃ and TDS concentrations.
- Study of the performance of an AS column under various operational conditions of flow rate, CHCl₃ and TDS concentrations.

MATERIAL AND METHODS

Membrane pilot study

Pilot studies of the membrane were performed using the NF pilot plant equipped with two spiral-wound modules of NF membrane made of cellulose acetate blend (CAB) with MWCO of 600 Da and polyamide (PA) with MWCO of 300 Da. Each membrane module had a total surface area of 5 ft² (0.5 m²). The characteristics of the NF modules used in the study are shown in Table 1. Experiments were performed in 1 hour in a batch circulation mode and both permeate and retentate were conducted to the feed tank in order to keep a constant concentration. The temperature of the recirculating feed solution was maintained at 17 ± 0.5°C. Samples of feed water and permeate were collected in order to measure solute concentration. All calculations were based on mean feed and permeate concentrations.

For the NF pilot study, the operational steps were as follows:

- Adjustment of feed temperature to 17 ± 0.5°C, flow rates of 3, 6 and 9 l min⁻¹ and preparation of chloroform samples with deionized water in a CHCl₃ concentration range of 50–300 µg l⁻¹ in order to study the effect of concentration on R% (R% = chloroform removal percentage).
- Preparation of CHCl₃ samples with deionized water with a concentration of 100 µg l⁻¹ of chloroform, temperature of 17 ± 0.5°C and flow rates of 3, 6 and 9 l min⁻¹, to study the effect of flow rate on R%.

Table 1 | Characteristics of NF modules used in the study

Membrane	Material	Module type	Size (m)	MWCO (Da)	T (°C)	ΔP (psi)	Manufacturer
NF	Polyamide (PA)	Spiral-wound	0.051 × 0.51	300	40	50–300	Perma-Pure
NF	Cellulose acetate (CAB)	Spiral-wound	0.051 × 0.51	600	40	50–300	Perma-Pure

MWCO: Molecular Weight Cut Off.

- Preparation of CHCl₃ samples with deionized water at a concentration of 100 µg l⁻¹, flow rates of 3, 6 and 9 l min⁻¹, temperature of 17 ± 0.5°C and pressure of 50, 89, 110 and 140 psi (345, 614, 758 and 965 kPa), in order to study the effect of pressure on R%.
- Conduct the above-mentioned steps with Tehran tap water under the conditions listed above.

GAC and AS pilot studies

Two plexiglass columns with internal diameter (ID) 25 cm and height 90 cm were filled with GAC and plastic pieces and used as GAC and AS pilot plants. The sample water was pumped to the column in up-flow and down-flow design through a Lowara Ind. pump in the GAC and AS pilots, respectively. The sample water was pumped to the column in down-flow mode through a Lowara Ind. Model peristaltic pump with Teflon tubing. The air-to-water ratio was 20:1 and supplied by a Sibata compressor.

Experimental steps for determination of removal efficiencies for GAC and AS columns were as follows:

- Adjustment of feed temperature to 17 ± 0.5°C, flow rate at 1 l min⁻¹ and preparation of chloroform samples with deionized water in the concentration range 50–300 µg l⁻¹ CHCl₃ in order to study the effect of CHCl₃ concentration on R%
- Preparation of CHCl₃ samples with deionized water at a concentration of 100 µg l⁻¹ chloroform, temperature 17 ± 0.5°C and inlet flow rates of 0.5–3 l min⁻¹ in order to study the effect of flow rate on R%
- Conduct the above-mentioned steps with Tehran tap water under the conditions listed above.

CHCl₃ measurement

Chloroform measurements were performed using a Shimadzu GC-17A gas chromatograph equipped with an electron capture detector (ECD) and a column with 0.32 mm diameter packed by DB-5. The initial column temperature of 100°C was raised to 200°C with a temperature ramp of 20°C min⁻¹ and a carrier gas (high purity nitrogen) flow rate of 40 ml min⁻¹. Ten millilitres of sample was extracted with 2 ml of *n*-pentane by shaking for 1 min to obtain phase separation. The upper phase was collected

into 2 ml vials having air tight caps with Teflon septa (*Standard Methods* 1994; Kuivinen 1999; Cancho 2000). Samples were preserved at + 4°C. To increase the reproducibility of the results, samples were measured and studied in triplicate.

RESULTS AND DISCUSSION

The experimental results indicated that the transmembrane pressure variation affects the rejection of CHCl₃ in the NF process. Results were obtained for the deionized water which contained 50–300 µg l⁻¹ of CHCl₃. The highest levels of R% were 87.7% and 74.6% for NF with MW of 300 and 600 Da, respectively (transmembrane pressure = 110 psi (758 kPa), flow rate = 9 l min⁻¹, *T* = 17°C, CHCl₃ conc. = 300 µg l⁻¹). Increasing the pressure up to 140 psi (965 kPa), caused a slight decrease in R%. In other words, R% was dependent on transmembrane pressure.

The results of this study also indicated that the structure and MWCO of membranes had a significant effect on R%: in the case of the NF 300 Da module, the CHCl₃ rejection was between 63.7 and 87.8% and between 61.9 and 74.6% for the NF 600 Da (with ΔP = 110 psi (758 kPa), CHCl₃ = 300 µg l⁻¹, 17°C). Therefore the rejection performance of NF 300 Da was higher than that obtained for the NF 600 Da module as in the feeds previously used.

Moreover, the experimental results indicated that the presence of salts and other dissolved compounds did not interfere with chloroform R% in the GAC, AS and NF systems. The best results were obtained from nanofiltration, making it an efficient process for the removal of CHCl₃ from

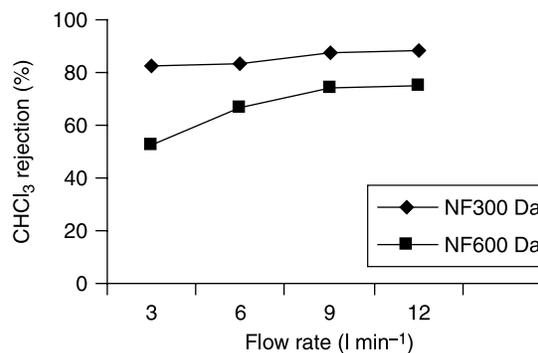
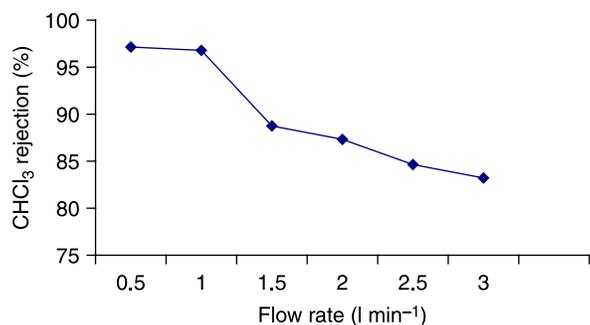
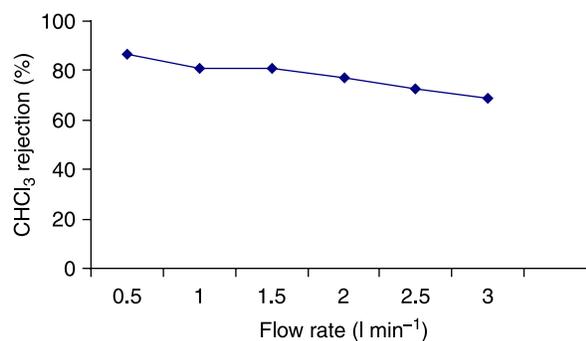


Figure 1 | Effect of flow rate variations on CHCl₃ removal efficiency in membrane system (transmembrane pressure = 140 psi (965 kPa), *T* = 17°C).

Table 2 | Comparison between performances of NF600 Da and NF300 Da on Tehran tap water ($Q = 9\text{ l min}^{-1}$, $\Delta P = 110\text{ psi}$ (758 kPa), $T = 17^\circ\text{C}$)

Parameter	Inlet	NF300Da		NF600Da	
		Outlet	R%	Outlet	R%
TDS (mg l^{-1})	348	78.8	70.1	117.3	66.3
TSS (mg l^{-1})	17.6	2.9	83.2	3.2	81.6
Residual chlorine (mg l^{-1})	0.2	0.0	100	0.0	100
Conductivity ($\mu\text{S cm}^{-1}$)	317	84.3	73.4	92.2	0.9
CHCl ₃ conc. ($\mu\text{g l}^{-1}$)	56	7.8	86.1	15.5	72.3

drinking water. The rejection factors were very high (about 88% for NF300) considering the quite small molecular size of CHCl₃. Effects of flow rate variations on CHCl₃ removal efficiency in the membrane system are shown in Figure 1 and a comparison between NF300 and NF600 performances is shown in Table 2. In the case of the GAC pilot the best removal efficiency was obtained with flow rate of 0.5 l min^{-1} and CHCl₃ concentration of $100\mu\text{g l}^{-1}$ ($R\% = 86.6$). Changing the flow rate from 0.5 to 3 l min^{-1} resulted in a decrease of $R\%$ to 69.1% . Effects of flow rate variations on CHCl₃ removal efficiency are illustrated in Figure 2. In addition, the level of $R\%$ varied from 87.4 to 55.1% with increasing CHCl₃ concentration from 50 to $300\mu\text{g l}^{-1}$ (about 32% decrease). The results showed that there is a linear relationship between flow rate and CHCl₃ $R\%$. The effects of flow rate variations on CHCl₃ removal efficiency in the GAC column are shown in Figure 3. The maximum efficiency for the AS pilot plant was 97.6% with flow rate = 1 l min^{-1} , air flow = 40 l min^{-1} , $50\mu\text{g l}^{-1}$ CHCl₃ and 17°C . A comparison of GAC and AS performances on Tehran tap water is given in Table 3. In the AS system, similar to the GAC column, a linear relationship between flow rate and chloroform concentration with

**Figure 2** | Effect of flow rate variations on air stripping column CHCl₃ removal efficiency (air flow rate = 40 l min^{-1} , $T = 17^\circ\text{C}$).**Figure 3** | Effect of flow rate variations on CHCl₃ removal efficiency in GAC column ($T = 17^\circ\text{C}$).

CHCl₃ $R\%$ was found but variations of TDS (total dissolved solids) concentration had no significant effect on $R\%$. Variation of TDS from 250 to $1,000\text{ mg l}^{-1}$ CaCO₃ changed the $R\%$ by only 1% . Comparison of CHCl₃ removal efficiency in different pilot configurations is displayed in Figure 4.

The potential of the GAC column to remove THMs precursors in Ankara drinking water has been previously reported (Capar & Yetis 2002). Those authors reported that the GAC column was able to effectively remove THMs precursors but they did not determine the effect of TDS on the efficiency of this system. Synthetic carbon spheres derived from phenol resin have been used as a GAC for water purification from THMs (Karakulski et al. 2001). According to those results, it might be possible to change the adsorptive properties of GAC by nitric acid treatment, creating a different complex on its surface and increasing the adsorption abilities. Another study has shown the successful removal of volatile organic compounds (VOCs) by AS (Mahmud & Kumar 2000), but those authors did not determine the effect of TDS concentration and flow rate

Table 3 | Comparison between performances of GAC column ($Q = 11\text{ l min}^{-1}$, $T = 17^\circ\text{C}$) and air stripping pilot ($Q = 11\text{ l min}^{-1}$, air flow = 40 l min^{-1}) on Tehran tap water

Parameter	Inlet	GAC		AS	
		Outlet	R%	Outlet	R%
TDS (mg l^{-1})	348	149.9	56.9	329	5.5
TSS (mg l^{-1})	17.6	13.3	24.4	17.3	1.7
Residual chlorine (mg l^{-1})	0.2	0.0	100	0.0	100
Conductivity ($\mu\text{S m}^{-1}$)	317	231.7	26.9	306	3.5
CHCl ₃ conc. ($\mu\text{g l}^{-1}$)	56	13.2	76.4	4.9	91.2

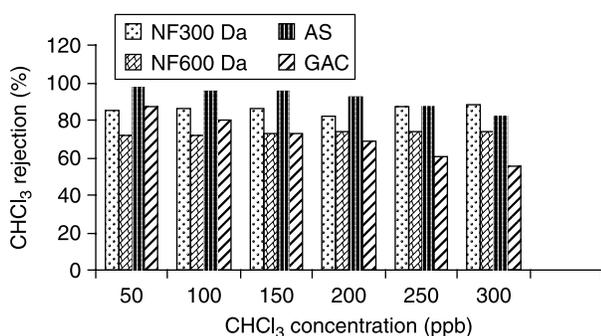


Figure 4 | Comparison of CHCl_3 removal efficiency in different pilots with deionized water and different CHCl_3 feed concentrations ($\mu\text{g l}^{-1}$), ($T = 17^\circ\text{C}$).

variations on VOC removal efficiency. Experimental results using Tehran tap water indicated that the presence of salts and other dissolved compounds did not interfere with THM (chloroform) removal efficiency in the GAC, AS and membrane systems. Although all three pilots showed acceptable performances for CHCl_3 removal from drinking water, the AS system was not only more efficient, but it may also be considered for the low flow rate and relatively high energy demand in large water treatment plants.

CONCLUSIONS

In this paper, the experimental results for removal efficiencies and performances of pilot-scale GAC and AS columns and an NF membrane for chloroform removal (as the main compound of THMs) from deionized and Tehran tap water were presented. The highest CHCl_3 rejection coefficient for the GAC column was 87.4% (with $Q = 11 \text{ min}^{-1}$, $C = 300 \mu\text{g l}^{-1}$) and the lowest was 55.1% ($Q = 11 \text{ min}^{-1}$, $C = 300 \mu\text{g l}^{-1}$). These values for NF 300 and 600 Da and the AS pilot were 79–87%, 69–74% and 82.3–97.6%, respectively. The maximum efficiency for the AS pilot was 97.6% with flow rate = 11 min^{-1} , air flow = 401 min^{-1} , $50 \mu\text{g l}^{-1}$ CHCl_3 and 17°C . In this pilot, R% varied from 82.3 to 97.6% with increasing CHCl_3 concentration from 50 to $300 \mu\text{g l}^{-1}$ and 83.2% to 97.2% with variation of feed flow rate from 0.5 to 31 min^{-1} .

Although GAC adsorption, AS and NF processes showed acceptable performances for CHCl_3 removal from drinking water, NF was significantly more efficient ($p < 0.05$), providing simultaneously a higher flow rate and

simpler operating conditions and may be considered for conventional water treatment plants finishing water.

ACKNOWLEDGEMENTS

The authors are grateful to the Center for Medical Sciences Research of the Islamic Republic of Iran for its financial support.

REFERENCES

- Alicia, C. & Alvarez, J. 2000 DBP formation during chlorination. *J. Am. Water Works Assoc.* **92**(6), 76–90.
- Cancho, B. 2000 Determination, synthesis and survey of iodinated trihalomethanes in water treatment processes. *Water Res.* **34**(13), 3380–3390.
- Capar, G. & Yetis, U. 2002 Removal of THM precursors by GAC. *Water Res.* **36**(10), 1379–1384.
- Ducom, G. & Cabassud, C. 1999 Interest and limitations of nanofiltration for the removal of volatile organic compounds in drinking water production. *Desalination* **124**, 115–123.
- Gallard, H. 2002 Chlorination of natural organic matter: kinetics of THM formation. *Water Res.* **36**(1), 65–74.
- Hammer, M. 1996 *Water and Wastewater Technology*, 3rd edition. Prentice Hall, Upper Saddle River, New Jersey, pp. 240–246.
- ISIRI (Institute of Standards and Industrial Research of Iran) 1997 *Quality Standards of Drinking Water* No. 1053. ISIRI, Tehran, Iran.
- Karakulski, M., Gryta, A. & Morawski, W. 2001 Pilot plant studies on the removal of trihalomethanes by composite reverse osmosis membranes. *Desalination* **140**, 227–234.
- King, W., Doddas, L. & Allen, A. 2000 Relation between stillbirth and specific chlorination by-products in public water supplies. *Environ. Health Perspect.* **108**(9), 67–78.
- Kosutic, K. & Kunst, B. 2002 Removal of organics from aqueous solutions by commercial RO and NF membranes. *Desalination* **142**, 47–56.
- Kuivinen, J. 1999 Determination of trihalomethanes and some chlorinated solvents in drinking water. *Water Res.* **33**(5), 1201–1208.
- Lin, C. H., Huang, Y. & Hao, O. 1999 Ultrafiltration processes for removing humic substances. *Water Res.* **33**(5), 1252–1264.
- Mahmud, H. & Kumar, A. 2000 A study of mass transfer in the membrane air stripping process. *J. Membr. Sci.* **179**(12), 29–41.
- Marawski, A. W. & Kalenezuk, R. 2000 Adsorption of trihalomethanes (THMs) onto carbon spheres. *Desalination* **130**, 107–112.
- Odom, R. 1999 Benefit-cost analysis of the stage 1 D/DBP rule. *J. Am. Water Works Assoc.* **91**(4), 137–147.
- Siddiqui, M., Amy, G., Ryan, J. & Odem, W. 2000 Membranes for the control of natural organic matter from surface waters. *Water Res.* **34**(13), 3355–3370.

Standard Methods for the Examination of Water and Wastewater
1994 18th edition, American Public Health Association/
American Water Works Association/Water Environment
Federation, Washington, DC.

USEPA 1998 *Stage 1 Disinfectants and Disinfection By-products*
Rule. Office of Water (EPA), Washington, DC.

WHO 1998 Guidelines for drinking water quality (chloroform).
Health Crit. Sup. Info. **2**(1), 255–275.

Wietlik, J., Stanis, R. & Bodzek, M. 2002 Adsorption of natural
organic matter oxidized with ClO₂ on granular activated
carbon. *Water Res.* **36**(9), 2328–2336.

Yang, C. & Cheng, B. 2000 Association between chlorination of
drinking water and adverse pregnancy outcome in Taiwan.
Environ. Health Perspect. **108**(8), 45–58.

Yoon, J. & Lee, D. 2003 Low trihalomethane formation in Korean
drinking water. *Sci. Total Environ.* **302**(20), 157–166.

First received 15 January 2008; accepted in revised form 24 December 2008. Available online May 2009