Iranian J Publ Health, 2004, Vol. 33, No. 3, pp.47-53

Comparison of Nanofiltration and GAC Adsorption Processes for Chloroform Removal from Drinking Water

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Abstract

In this research, the Chloroform (CHCl3) removal effectiveness of two water treatment systems including membrane technology and granular activated carbon (GAC) adsorption were studied. Two bench-scales were designed and set up: 1) Nanofiltration (NF) spiral-wound modules and 2) GAC adsorption column. Chloroform was considered as trihalomethanes (THMs) basic indicator compound. The inlet and outlet CHCl3 concentrations were detected by gas chromatography (GC) with electron capture detector (ECD). The study was carried out for the two cases of spiked deionized water with CHCl3 and chlorinated Tehran tap water. Flow rate, CHCl3 and total dissolved solids (TDS) concentrations were considered in both treatment systems and the transmembrane pressures for membrane pilot, as the basic variables affecting removal efficiencies. Results showed that CHCl3 rejection coefficients for NF 300 Da, NF 600 Da and GAC Column, with various operation conditions had a range of 55.2% to 87.8%, 78% to 85% and 41.4% to 74.1%, respectively. It was found that removal efficiencies for NF 600 Da were lower than those of NF 300 Da and GAC column. The obtained data were analyzed by SPSS and non-parametric Kruskal-Wallis method. Results showed a positive correlation between the flow rate, CHCl3 concentration and chloroform rejection coefficients and the TDS concentration had no significant effect on chloroform removal efficiencies.

Keywords: *Drinking water, THMs, Chloroform, Nanofiltration, GAC adsorption*

Introduction

The two major reasons for drinking water disinfection are to protect the drinking water from pollution in the distribution systems and to control the population and the number of microorganisms, providing safe water for consumers (1). Chlorination, as the most widely used technique for drinking water disinfection is now considered as a basic factor for the formation of trihalomethanes (THMs). THMs formation in drinking water results from the reaction of chlorine with naturally or man-made occurring organic matters, principally humic and fulvic acids (2). Regarding the health related aspects of THMs, their presence in drinking water is of high concern, since these compounds have been linked to toxic or carcinogenic compounds. These organic compounds are categorized in group A of carcinogens and are announced to have the potential of increasing the rate of liver and kidney cancer and reproductive effects (3-5). For this reason, different countries have set specific limits for THMs concentrations in potable water. The permissible value for chloroform recommended by WHO is 30 µg/L (6). The current regulations in the USA demand stage 1 D/DBPR (Disinfectants / Disinfection By Products Rule) target of 80 µg/L for total THMs (TTHMs), and a more stringent level of 40 µg/L is proposed to be in effect as the stage 2 target (3,7). The European commission has proposed a new council directive with parametric values of 40 µg/L for chloroform and 15 µg/L for bromodi-

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chloromethane (4, 5). The Islamic Republic of Iran regulation of THMs for chloroform, bromoform, bromodichloromethane and dibromochloromethane is 200, 100, 60 and 100 µg/L, respectively [Institute of Standards and Industrial Research of Iran (ISIRI No.1053)]. Several treatment alternatives have been proposed for the removal of THMs and its precursors. The best option in water resources management is to protect water quality in dam reservoirs and rivers in order to minimize the concentration of THMs precursors. The second option is THMs precursors' removal with the aim of THMs formation minimization. But in the situations in which the up-mentioned options are not applicable (because of high level of water pollution and technical constraints in water treatment plant), THMs removal should be highly considered in order to protect the human health. Application of granular activated carbon (GAC) has been of special interest due to its ability to remove a wide range of compounds such as natural organic matters (NOMs), THMs, odor and color causing and other organic toxic compounds (4,8).The main objective of this research was to investigate the performance and efficiency of membrane technology for THMs removal from drinking water (deionized and Tehran tap water) and to compare the results with GAC adsorption under different operational conditions. The specific objectives were as follows:

Study the performance of nanofilters (NF) with MWCO=300 and 600 Da, under different operational conditions of flow rate, transmembrane pressure, chloroform & TDS concentrations. Study the performance of GAC adsorption column under various operational conditions of flow rate, chloroform and TDS concentrations.

Materials and Methods

Two bench-scale GAC column and nanofiltration membrane were designed and constructed. The schematic flow diagrams for the GAC column & membrane system are shown in figure 1. The characteristics of GAC used in this study were:

Manufactured in China
Wood based carbon
Symmetrical cylindrical shape
Mesh size: (1.8 * 3.8)
Density: 0.65 g / m^3
Tolerable temperature: 320 ºC
Ash content at 550 ºC: 6 % of weight
Maximum dissolvable materials in acid: 7% of weight

GAC was washed with deionized water to remove all carbon fine particles, dried at 105 ˚C for 2 days and cooled in a desiccator. A plexcy glass column with internal diameter (ID) of 25 cm and height of 90 cm was filled with GAC. The sample water was pumped to the column in up-flow design with a Lowara Ind. Model peristaltic pump through Teflon tubing. The studies of membrane pilot were performed using the NF pilot plant equipped with two spiral-wound modules of NF membrane made of cellulose acetate blend (CAB) with a MWCO of 600 Da and polyamide (PA) with MWCO of 300 Da. Each membrane module had a total surface of 5 square feet. The characteristics of these modules are presentated in Table 1. Experiments were performed for 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 ºC. Samples of feed water and permeate were collected in order to measure solute concentration. All calculations were based on mean feed and permeate concentrations. THM (Chloroform) measurements in samples were performed by Shimatzu GC-17A gas chromatograph equipped with an electron capture detector (ECD). The column used had 0.32 mm diameter packed by DB-5. The initial column temperature of 100 ºC was raised to 200 ºC with a temperature ramp of 20 ºC /min and the carrier gas (high purity nitrogen) flow rate was adjusted to 40 ml/min. Ten milliliters of sample

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was extracted with 2 ml of *n*-pantane 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 (9, 10). Samples were preserved at + 4 ºC. To increase the reproductivity of the results, samples were measured and studied for three times.

Experimental steps for determination of removal efficiencies for GAC adsorbed column were as follows

- Adjustment of feed temperature at 17±0.5 ºC, flow rate at 1 L/min and preparation of chloroform samples with deionized water in concentration range of 50 to 300 µg/L of $CHCl_3$ in order to study the effect of THMs concentration on R% (R% is the chloroform removal percentage).

-Preparation of THMs samples with deionized water and with a concentration of 100 µg/L of chloroform, temperature of 17± 0.5 ºC and inlet flow rates of 0.5 to 3 L/min in order to study the effect of flow rate on R%.

-Preparation of THMs samples as above mentioned to study the effect of TDS concentration on R% of chloroform with different concentrations of 250, 500, 750 and 1000 mg/L.

-Conducting the up- mentioned steps with Tehran tap water and in upwards conditions.

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

-Measurement of the influent flux of deionized water at different temperatures and pressures.

-Determination of J_{ww} as the deionized water flux where:

J_{ww} = flow rate (Q) / membrane surface area (A) 1}

-Adjustment of feed temperature at 17 ± 0.5 ºC, flow rates at 3, 6 and 9 L/min and preparation of chloroform samples with deionized water with similar concentrations as for GAC column, to study the effect of THM concentration on R%.

-Preparation of THMs samples with deionized water with a concentration of 100 µg/L of chloroform, temperature of 17 ± 0.5 ºC and flow rates of 3, 6 and 9 L/min, to study the effect of flow rate on R%.

-Preparation of chloroform samples as above mentioned, to study the effect of TDS concentration on R% with different $CaCO_3$ concentrations of 250, 500, 750 and 1000 mg/L**.**

-Preparation of THMs samples with deionized water with a concentration of 100 µg/L, flow rates of 3, 6 and 9 L/min, temperature of 17 ± 0.5 ºC and pressure of 50, 89, 110 and 140 psi, in order to study the effect of pressure variations on R%. Transmembrane pressure is (ΔP) as follows:

$$\Delta P = P_2 - P_1 / 2 - P_3 \quad \{2\}$$

Where: P_1 = Flux pressure (Bar)

P_2 = Feed pressure (Bar)

P_3 = Atmospheric pressure (Bar)

The degree of chloroform rejection [RTHM (%)] was calculated from equation {3}:

$$R_{THM}\% = C_F - C_P / C_F * 100 \quad \{3\}$$

Where: C_F and C_P are inlet flow and permeate concentrations (µg/L), respectively (10)

-Conducting the study with Tehran tap water (in upwards conditions). Membranes chemical washing was conducted through rinsing with distilled water and washing with 1% HCl solution (for NF 300 Da) and 1% citric acid solution (for NF 600 Da), and final rinsing with distilled water. The distilled water flux after the second washing step (J_{WC2}) more hence determined.

Table 1: Characteristics of NF modules used in the study

Membrane	Material	Module Type	Size (m)	MWCO (Da)	T (ºC)	ΔP (psi)	Manufacturer
NF	Polyamide (PA)	Spiral-Wound	0.051*0.51 (2*20inch)	300	40	50-300	Perma-Pure
NF	Cellulose acetate(CAB)	Spiral-Wound	0.051*0.51 (2*20inch)	600	40	50-300	Perma-Pure

MWCO: Molecular Weight Cut Off

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Results

GAC adsorption column performance The correlation between chloroform removal percentage of deionized water with, variation of flow rate, chloroform concentrations and TDS concentrations is shown in Figure 2. The obtained data were analyzed by SPSS and non-parametric Kruskal-Wallis method. Results showed that there would a linear relationship between flow rate and chloroform concentration with chloroform R% but variations of TDS concentration had no significant effect on R% (R%=79.5 to 82.5). The best removal efficiency was obtained with flow rate of 0.5 L/min and chloroform concen- tration of 100µg/L (R%= 86.6). Changing the flow rate from 0.5 to 3 L/min results the decrease of R% to 69.1%. Also the amount of R% varied from 87.4% to 55.1% with increasing chloroform concentration from 50 to 300 µg/L (about 32% decreases).

Nanofiltration performance The variations of removal efficiency with chloroform concentrations, (flow rate of 3, 6 and 9 L/min) in nanofiltration system are shown in Figure 3. The highest R% with NF membranes 87.8%, was achieved with NF 300 Da (Q=9 L/min, 300 µg/L chloroform, 110 psi), but the best result with NF 600 Da in similar conditions was 74.6 %. Figure 4 presents the effect of TDS concentration (in range of 250 to 1000 mg/L $CaCO_3$) on chloroform R% in NF system. As shown in this figure, TDS concentration had no significant effect on R% for both membranes. The degree of chloroform rejection for these membranes approached 87%-79% and 74%-69% with 250 to 1000 mg/L $CaCO_3$ in feed water respectively (chloroform conc.300 µg/L, 17 ºC, Q=9 L/min). The experimental results indicated that the transmembrane pressure variation affects the rejection of chloroform in NF process. Results obtained for the deionized water contained 50-300 µg/L. The highest amounts of R% were 87.7% and 74.6% for NF 300 and 600 Da, respectively (transmembrane pressure=110 psi, flow rate=9 L/min, 17ºC, chloroform conc=300 µg/L). Increasing this pressure up to 140 psi, decreased slightly R%. In other words, R% was dependent on transmembrane pressure. Also results of this study indicated that the structure and MWCO of membranes had a significant effect on R%: for the case of NF 300 Da module, the chloroform rejection was between 63.7%-87.8% and 61.9%-74.6% for NF=600 Da (with ΔP= 110 psi, chloroform = 300 µg/L, 17 ºC). 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.

Chlorinated Tehran tap water results In the next step, Tehran tap water was used as the feed for all of the up mentioned experiments. Comparisons between performances of GAC column and NF 300 and 600 in chloroform rejection from Tehran tap water are shown in Table3. The experimental results indicated that the presence of salts and other dissolved compounds did not interfere on THMs (chloroform) R% both in GAC and NF systems. Best results were obtained from Nanofiltration, making it an efficient process to remove THMs from drinking water. The rejection factors were very high (about 88% for NF300) regarding the quite small THMs molecule size.

Table 2: Comparison between performances of GAC column (Q=1 L/min, T=17ºC) and NF 300, 600 Da (Q=9 L/min, ΔP=110 psi, T=17 ºC) in rejection of $CHCl_3$ from Tehran tap water

Parameter	Inlet	GAC		NF 300 (Da)		NF 600 (Da)	
		Outlet	R%	Outlet	R%	Outlet	R%
pH	7.7	7.05	-	7.2	-	7.9	-
TDS (mg/L)	348	149.9	56.9	104.1	70.1	115.2	66.9
TSS (mg/L)	232	175.6	24.3	38.9	83.2	42.7	81.6
Residual chlorine (ppm)	0.2	0.0	100	0.0	100	0.0	100
Temperature (ºC)	17	17.8	-	20.8	-	21.3	-
Conductivity (µS/cm)	317	231.7	26.9	84.3	73.4	92.2	70.9
$CHCl_3$ conc. (µg/L)	56	13.2	76.4	7.8	86.1	15.5	72.3

R: Removal Efficiency

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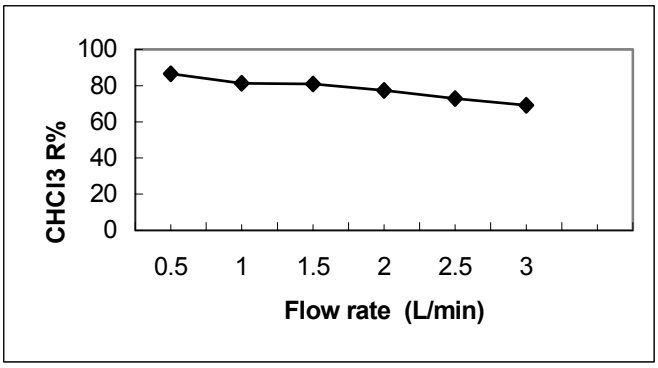
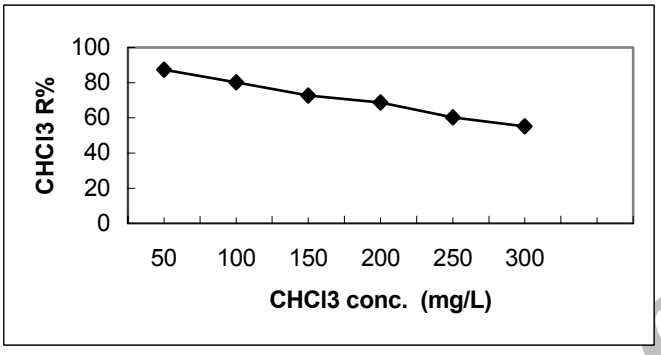


(a)



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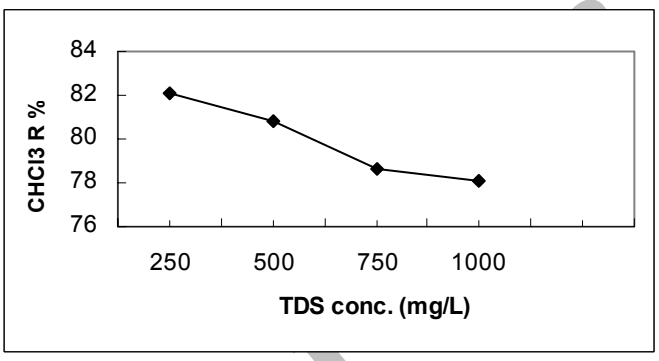
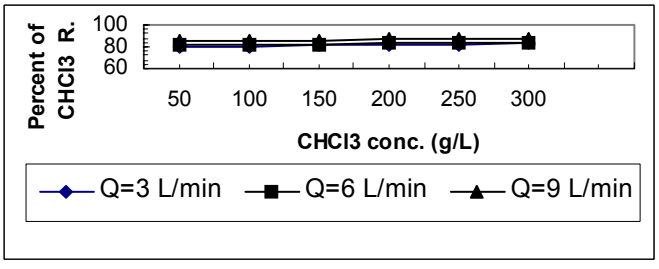
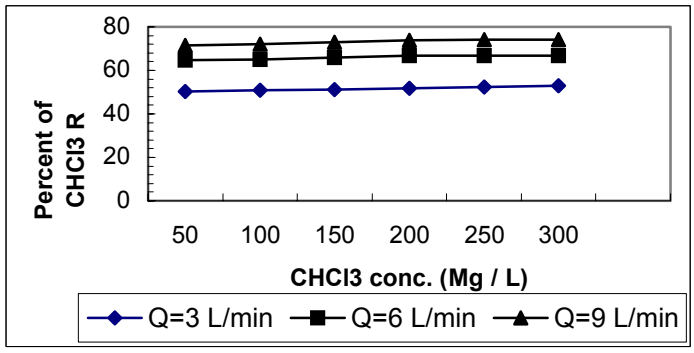


(c)

Fig. 2: Percent of chloroform removal from deionized water in GAC column versus flow rate, (a) chloroform concentration (b) and TDS concentration variation (c)

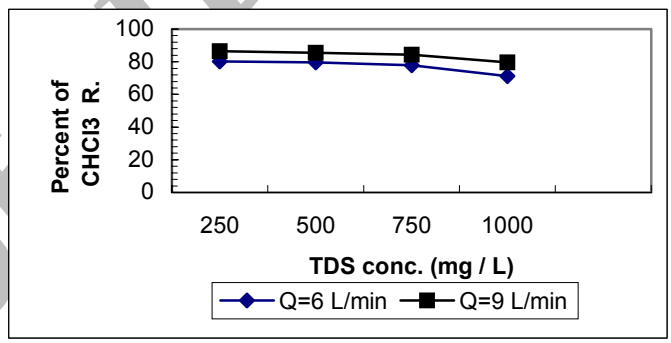


(a)

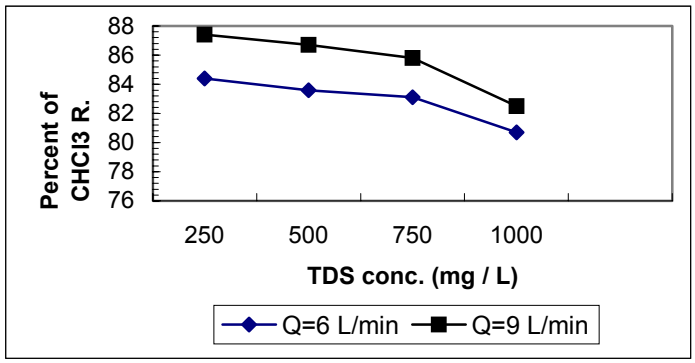


(b)

Fig. 3: Effect of CHCl3 conc. on the CHCl3 rejection of NF 300 Da (a), 600 Da (b) (ΔP = 110 psi, T= 17 ºC)



(a)



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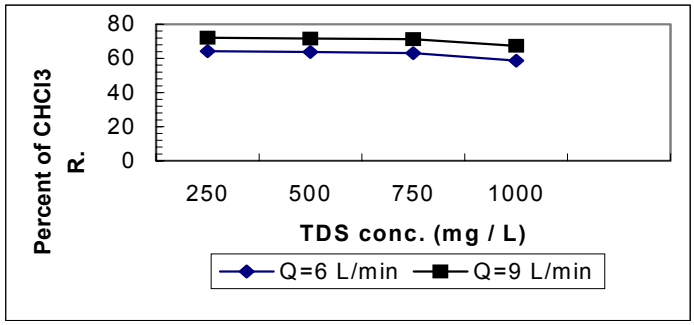

(c)

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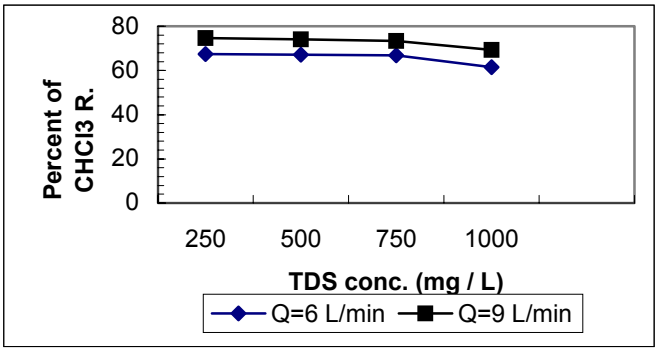
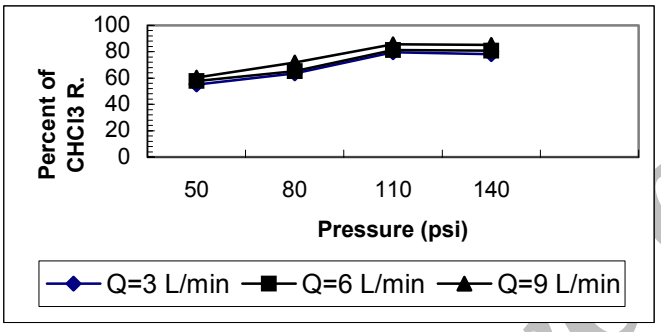
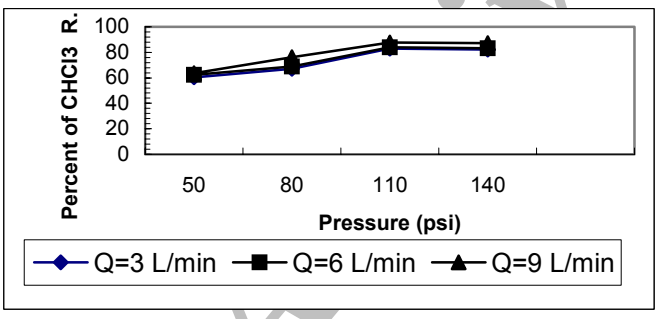


(d)

Fig. 4: Effect of TDS conc. on the CHCl3 removal coefficient of NF 300 Da with C = 300 µg/L (a), C= 50 µg/L (b) and NF 600 Da with C= 300 µg/L (c), C= 50 µg/L (d) (ΔP= 110 psi, T=17 ºC)



(a)



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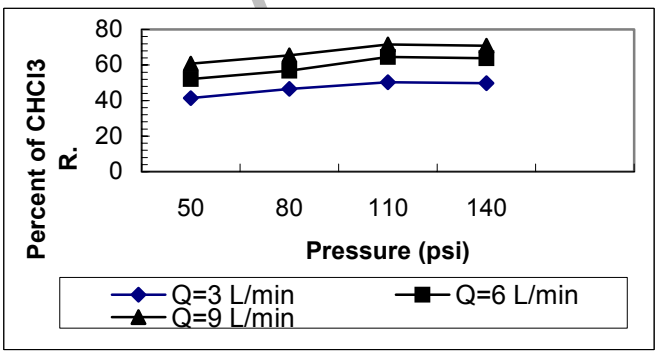

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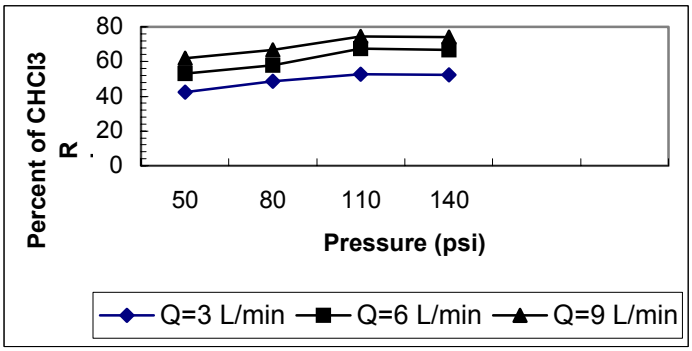

(d)

Fig. 5: Effect of transmembrane pressure on the CHCl3 rejection of NF 300 Da with C=50 µg/L (a), C=300 µg/L (b) and NF 600 Da C= 50 µg/L (c), C=300 µg/L (d)

Discussion

In this research, the obtained data from NF pilot and GAC column were analyzed by SPSS and non–parametric Kruskal-Wallis method. Results showed that there would a linear relationship between flow rate and chloroform concentration with chloroform. The ability of GAC column to removal of THMs precursors in Ankara drinking water was previously reported (4). They reported that GAC column had ability to effective removal of THMs precursors but they did not determine effect of TDS on efficiency of this system (4). The synthetic carbon spheres derived from phenol resin were used as a GAC for water purification from THMs (11). Accordingly, it might be possible to change the adsorptive properties of GAC by nitric acid treatment and creating a different complex on its surface that might be to increase adsorption abilities (11). Similar with GAC column, results of SPSS statistical analysis showed straight relationship between flow rate and chloroform concentration with chloroform R% in membrane system but variations of TDS concentration had no significant effect on R%. Variation of TDS from 250 to 1000 mg/L CaCO3 can change the R only 1%. Siddiqui and Amy reported disinfection by-product (DBPs) precursors from low turbidity surface waters can be significantly removed by application of NF (1). Also the effect of chloroform

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content in various types of water on performance of reverse osmosis (RO) composite membranes has been investigated (2). It was found membranes provided THMs rejection in the range of 80% to 99%. Also the experimental results of Tehran tap water indicated that the presence of salts and other dissolved compounds did not interfere on THMs (chloroform) removal efficiency both in GAC and membrane systems. Although both GAC adsorption and NF pilots showed acceptable performances for THMs removal from drinking water, NF 300 Da was simultaneously more efficient.

Acknowledgements

Authors would like to explain their gratitude to the Center for Medical Sciences Research of I.R.Iran for their financial support.

References

1. Siddiqui M, Amy G, Ryan J (2000). Membranes for the control of natural organic matter from surface waters. *Wat Res J,* 34(13): 3355-70.
2. Karakulski M, Gryta A, Morawski W (2001). Pilot plant studies on the removal of trihalomethanes by composite reverse osmosis membranes. *Desalination,* 140: 227-34.
3. Alicia C, Alvarez J (2000). DBP formation during chlorination. *AWWA J,* 92 (6): 76-90.
4. Capar G, Yetis U (2002). Removal of THM precursors by GAC. *Wat Res J,* 36(10): 1379-84.
5. Ducom G, Cabassud C (1999). Interest and limitations of nanofiltration for the removal of volatile organic compounds in drinking water production. *Desalination,* 124: 115-23.
6. Gallard H (2002). Chlorination of natural organic matter: kinetics of THM formation. *Wat Res J*, 36(1): 65-74.
7. Lin CH, Huang Y, Hao O (1999). Ultrafiltration processes for removing humic substances. *Wat Res J,* 33(5): 1252-64.
8. Gallard H (2002). Chlorination of natural organic matter: kinetics of THM formation. *Wat Res J*, 36(1): 65-74.
9. Kosutic K, Kunst B (2002). Removal of organics from aqueous solutions by commercial RO and NF membranes. *Desalination*, 142: 47-56.
10. Cancho B (2000). Determination, synthesis and survey of iodinated Trihalomethanes in water treatment processes. *Wat Res J,* 34(13): 3380-90.
11. Kuivinen J (1999). Determination of Trihalomethanes and some chlorinated solvents in drinking water. *Wat Res J,* 33(5): 1201-08.
12. Marawski A, Kalenezuk R (2000). Adsorption of trihalomethanes (THMs) onto carbon spheres. *Desalination,* 130:107-12.

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