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EFFICIENCY OF DOMESTIC REVERSE OSMOSIS IN REMOVAL OF TRIHALOMETHANES FROM DRINKING WATER

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ABSTRACT

The reaction of disinfectants with natural organic matters existing in water lead to the formation of Disinfection By-Products. Potentially hazardous and carcinogenic characteristics of trihalomethanes (THMs) are recognized. Thus removal of THMs or its precursors are necessary for human health. The aim of this study was to study the efficiency of domestic reverse osmosis (RO) in removal of trihalomethanes from drinking water. A pilot scale of RO system with Polyamide membrane as Spiral-Wound, Tape wrapping module was used. Feed solution was made by using of pure chloroform. The samples containing chloroform were analyzed using a gas chromatograph equipped with a flame ionization detector. By increasing the flow, the removal rate of chloroform decreased and with declining removal of EC, the removal of chloroform declined too. In this research, at the worst condition, the efficiency of the pilot scale reverse osmosis reached to 80 % removal of chloroform.

Key words: Polyamide membrane, Reverse osmosis, Trihalomethanes, Precursor, Gas chromatograph

INTRODUCTION

The reaction of disinfectants with natural organic materials (NOM_S) existing in water lead to the formation of Disinfection By-Products (DBP_S). Chlorine is one of the most used disinfectants which reacts with NOMs and forms halogenated DBPs including trihalomethanes, haloacetic acids, haloacetonitriles, haloaldehydes, haloketones, chlorophenols and chloropicrin (Stevens *et al*., 2005; Zazouli *et al*., 2007a; Christman *et al*., 1983). Water samples with high dissolved organic matter (DOM) concentration have a higher chlorine demand compared to usual raw water and thus the formation of trihalomethanes take place (Lim *et al*., 2006). For the first time in 1974, THMs were detected in water by USEPA, Swiss and, Netherlands researchers (Samadi *et al*., 2006).

Many factors interfere in formation of THMs including pH, temperature, contact time, concentration and properties of chlorine and NOMs, residual chlorine, and bromide concentration (Singer 1993; Singer 1994; Zazouli *et al*., 2007b).

By increasing the pH and the contact time, formation of THMs increases too (Nikolaou *et al*., 2004; Krasner *et al*., 1989). When temperature increases, reactions take place much faster and consumption of chlorine increases, which lead to higher formation of DBPs(Williams 1997; Golfinopoulos *et al*., 1993; Golfinopoulos *et al*., 1994; LeBel *et al*., 1995). Many of THMs can be produced due to reaction of chlorine with NOMs, but the major ingredients of THMs that are present in water are : Bromodichloromethane ($CHBrCl_2$), Bromoform ($CHBr_3$), Chloroform ($CHCl_3$) and Dibromochloromethane ($CHBr_2Cl$

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((Golfinopoulos *et al*., 1996). In 1979 for regulation of disinfection by-products, , USEPA has set a Maximum Contaminant Level (MCL) for total THMs equal to 0.100 mg/L as an annual average (Samadi *et al*., 1996). According to Disinfectants/DBPs Stage 1 rule in 1994, USEPA lowered the MCL for total THMs from 0.100 to 0.080 mg/L (U.S. EPA, 1998a). In 199, according to Industrial Research and Iranian Standard Institute for physical and chemical quality of drinking water, a Maximum Contaminant Level of 200 µg/L is set for $CHCl_3$ (IRSII, 1997).

Table 1: Standards/Guidelines related to THMs (mg/l) in various zone of the World (Sadiq and Rodriguez,(2004)(15)

Compound	WHO (1993)	USEPA (2001	Health Canada (2001)	AUS-NZ (2001)	UK (2000)	IR.IRAN
CHCl3	0.200	0.000*	-	-	-	-
CHCl2Br	0.060	0.060*	-	-	-	-
CHClBr2	0.100	0.000*	-	-	-	-
CHBr3	0.100	0.000*	-	-	-	-
TTHMs	(THM/WHO)≤1**	0.080	0.100	0.250	0.100	0.2***

*Maximum Contaminant Level Goals (MCGL)

**the sum of the ratios of the THM levels to the guideline values should not exceed 1.

***the sum of THMs described as CHCl3

Potentially hazardous and carcinogenic characteristics of THMs are recognized) Bull and Robinson .(1986 ,Therefore many studies have been done to remove the precursor of THMs or produced THMs from drinking water .One of the most important factors to control THMs formation is precursor removal including coagulation of THMs ,(granular activated carbon adsorption, membrane filtration process ,nanofilters with membranes having molecular weight cut-offs of 200-500 Daltons ,Powder activated carbon adsorption and preozonation) Mesdaghinia *et al*., 2005; Zazouli *et al*., 2008; Sandrucci *et al*., 1995; Premazzi *et al*., 1997). Another method is alternative disinfectants including use of monochloramine, Ozone, Chlorine dioxide, Permanganate, UV light, Ozone and chlorine dioxide are prevalent alternative disinfectants in the United States and in Europe (Cowman and Singer, 1994; Blatchley *et al*., 1996; Richardson *et a*l., 1996). Combinations of technologies can also prevent the formation of THMs (ozone-monochloramine, hydrogen peroxide-ozone, UV-ozone, UV-hydrogen peroxide) (Golfinopoulos *et al*., 1996). Third approach for controlling of DBPs is DBP removal after production that can be removed with several methods such as: air stripping, membrane technology, granular activated carbon (Premazzi *et al*., 1997).

Membrane technology is applicable in water treatment, advance wastewater treatment, and also in upgrading wastewater treatment plants (Naghizadeh *et al*., 2008).

Reverse osmosis (RO) similar to nanofiltration, microfiltration, and ultrafiltration is a pressure technology. For many purpose the use of RO for water treatment is very wide. This process for first time observed in 1748 by Jean Antoin Nollet. The materials used for most RO membrane are cellulose derivatives and polyamide derivatives. Many of them can remove 99% of dissolved material and have molecular weight cut-off in the range of 50 to100 Dalton (Crittennden *et al*., 2005). The membrane type and pore size are two important factor in rejection of contaminates.

The EPA has recommended that RO is a best available technology (BAT) for removal of many of inorganic contaminants such as, antimony, arsenic, barium fluoride, nitrate, nitrite, and selenium as well as radionuclides, such as beta particle, and photon emitters, alpha emitters, and radium-226 . Also RO can be effective in removal of large MW synthetic organics such as pesticides (Crittennden *et a*l., 2005). The aim of this study was to research the efficiency of domestic reverse osmosis (RO) in removal of trihalomethanes (THMs) from drinking water.

MATERIALS AND METHODS

In this research a pilot scale reverse osmosis set with spiral module was used. The RO material was Polyamide Spiral-Wound, Tape wrapping module made in Korea (model NO.RE2012-100) with Permeate Flow rate as gpd (L/day) equal 100

(397), Membrane Type : Thin-film Composite, Membrane Material : PA (Polyamide), Membrane Surface Charge : Negative, Element Configuration : Spiral-Wound, Tape wrapping, Salt rejection: 96% based on NaCl with 250ppm concentration and 60 psi, Dimension (inch) : Diameter; 2 and Length; 12. For feeding the synthetic solution, two diaphragm pumps, model WS o357674 with 125 psi maximum pressure and 1.6 L/min capacity were used, which applied intermittently. Quantity of feed water was controlled by a valve in end of membrane filter, by opening and closing of valve. When a single pump was used, the flow rate was 0.75 l/min, and when two pumps were used in penguin serial, the flow increased to 1.73 L/min. After set up of RO pilot, the effect of EC , chloroform concentration, and variation of flow were considered. THMs (chloroform) solutions were prepared in three different concentrations of 100, 300, and 500 µg/L. Preparation of these solutions conducted by diluting 99.94% pure chloroform and 1.481 densities into the water with three EC content (100, 500,1000 µs/Cm) , which include NaCl, $MgCl_2$, $MgSO_4$, and $CaSO_4$, to obtain the desired THMs and EC concentrations. After any run, the membrane was cleaned with recirculation of deionized water with 25-30 °C temperature for 15 min. containing a diluted acid, then rinsed it with deinozed water for 5 min. The influent and effluent concentrations of chloroform solution were measured with GC. EC was determined by WTW model EC meter. The pH was adjusted between 6 and 8. pH was measured by pH meter model Metrohm Herisau. Fig 1 shows the schematic diagram of RO membrane.

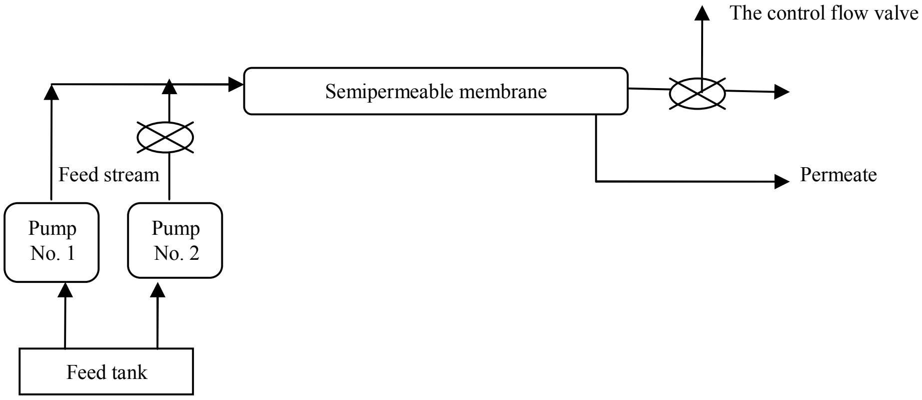

Fig. 1: Schematic diagram of separation process through reverse osmosis membrane

Any RO system has two flows that include permeate and concentrate flow (rejected). In this RO pilot the quantities of these flows were equal to 60% and 40 %, respectively. Molecular weight cut-off was approximately 100 Daltons. The RO membrane was cleaned using 4.5 L of diluted HCl solution. The cleaning solution was circulated through the membrane module for one hour. The units were then rinsed with deionized water for approximately 10 min. Then the filter was taken out from cartridge and dried in free air. For controlling the process, before any operation, the diluted water was injected and a sample was taken.

The samples containing chloroform were analyzed using a gas chromatograph (GC) model CP-3800 Australia VARIAN Company, equipped with a flame ionization detector (GC-FID) with COMBIPAL HS auto sampler. The analysis was made using headspace technique. After preparation of solutions used of 10 mL headspace vials were filled with 5 mL of sample by a 5 ml sterile pip.

After equilibrating the samples in an oven at 70 °C for 5 minu, 300 µL of the headspace was injected into the GC (CP- SIL 8 CB column model, 30 m x 0.32 mm, 0.25 µm film thickness, VARIAN, Australia). The column program was 35 °C (hold time of 8 minutes), 9 °C/minutes to 100 °C (hold time of 8 minutes). The inlet temperature was set at 100 °C, and temperature of FID was 280 °C. The carrier gas was helium with 11 PSI pressure with a rate of 35 mL/min, and nitrogen gas was supplied as makeup gas. The calibration standard curves were prepared by using of chloroform. The calibration standard curves were prepared in the range of 0-600 µg/L of chloroform in pure water.

RESULTS

Findings are summarized in Table 2 and Figs 2 and 3. Table 2 and Fig. 2 show the results of transmitted samples from RO with variation of THMs, EC concentration and flow. According to these results, significant relation (P-value<0.05) exist between removal of chloroform concentration and EC. Table 2 and Figs 2 and 3 show that with increasing the flow, the removal rate of chloroform decreased. By decreasing EC, the removal of chloroform decreased too. It can be concluded that the removal rate of chloroform is related to EC (P-value<0.05). By increasing the chloroform concentration from 100 µg/L to 500 µg/L, the removal rate decreased (P-value<0.05).

According to Table 2, maximum average removal of chloroform and EC was related to one pump condition at 100 µg/L and 100 µs/Cm average primary concentration of chloroform and EC, which were equal to 85.67 % and 90.46 %, respectively. Minimum average removal of chloroform and EC was related to two pumps condition 500 µg/L and 1000 µs/Cm average primary concentration of chloroform and EC, respectively which were equal to 81.98 % and 88.22 %, respectively.

Table 2: Removal efficiency of chloroform and EC

Chloroform concentration (µg/L)	Removal efficiency of $CHCl_3$ (two pumps)%	Removal efficiency of $CHCl_3$ (single pumps)%	Removal efficiency of EC (two pumps)%	Removal efficiency of EC (single pumps)%
100	83.78	85.67	88.85	90.46
300	82.48	84.74	89.57	90.05
500	81.98	83.91	88.22	89.34

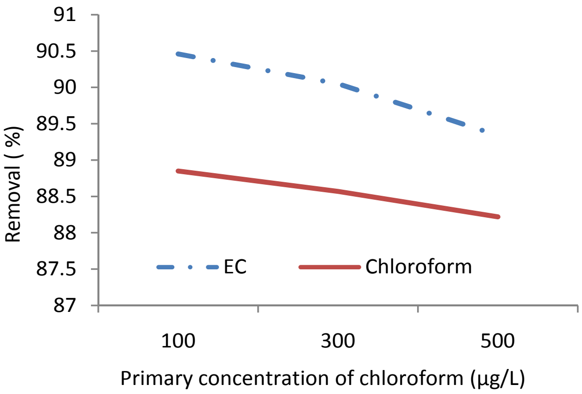

Fig. 2: Removal efficiency of chloroform and EC at single pump condition (0.75 L/min)

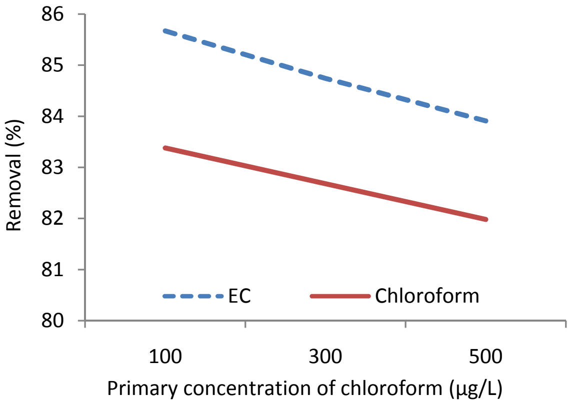

Fig. 3: Removal efficiency of chloroform and EC at two pumps condition (1.73 L/min)

Results show that with increase in EC from 100 µs/Cm to 1000 µs/Cm, removal efficiency of chloroform decrease from 100 to 300 µg/L. In this research it was found that at the worst condition in pilot scale of reverse osmosis, 80 % removal of chloroform is accessible.

DISCUSSION

According to the results, domestic reverse osmosis can be used as a process for removal of THMs at point of use (POU). Some of the conditions are discussed above, but availability of electricity or water with high pressure and agents are important.

Mayankutty *et al*., indicated that the trihalomethanes concentration of the finished water as well as the chlorinated well water from the three sea water desalination plants in the Eastern Province of Saudi Arabia, which supplied the city of Riyadh and several other areas, were significantly lower than the maximum contaminant levels set by WHO and various national organizations (Mayankutty *et al*., 2005). Pawlak *et al.,* in 2005 found that more than 98.5% reduction of arsenic by means of reverse osmosis systems in pilot study is achievable (Pawlak *et al*., 2006).

It is also noted that Chungsying Lu *et al*., in 2005 remarked that nanotubes can adsorb trihalomethanes from water as well as they found that $CHCl_3$, is the most preferentially adsorbed onto Carbon nanotubes, followed by $CHBrCl_2$, $CHBr_2Cl$ and then $CHBr_3$ (Chungsying *et al*., 2005) .

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