Preozonation and Prechlorination Effects on TOC Removal by Nanofiltration in Water Treatment

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ABSTRACT: In this study, NF membrane was used for surface water treatment. The rejection of organic material, measured as Total organic carbon (TOC), by Nanofiltration was examined. The effects of application of pre-ozonation and pre-chlorination on TOC removal are discussed and their performances are compared with the performances of Nanofiltraion system without pretreatment process. In NF, natural organic rejection is high and no pre-treatment are required. Coagulation targets large hydrophobic organics which foul NF membranes by precipitation and gel layer formation. The results showed that TOC removal in Preozonation-coagulation was higher than prechlorination-Coagulation. In addition pretreatment increases Nanofiltration efficiency.

Key words: Water treatment, Nanofiltration, Preozonation, Prechlorination, Total Organic Carbon removal

INTRODUCTION

In the early 1900s, the United States drinking water industry drastically reduced the number of fatal waterborne disease outbreaks when it began chlorinating drinking water. Some ninety years later, the United States Environmental Protection Agency imposed stringent regulations governing chlorination of drinking water supplies because this same chemical, which had saved so many lives, produced suspected carcinogens in the presence of naturally occurring organic matter (letterman, 1999). Two groups of these potential carcinogens are trihalomethanes (THMs) and haloacetic acids (HAAs). Both form when chlorine reacts with natural organic matter in raw water. According to the 1995 Community Water Systems Survey conducted by the USEPA, 14.2 percent of surface water treatment systems servicing a population of 50000-100,000 are using ClO2 as a predisinfectant compared to 47.5 percent using

chlorine, 15.5 percent using chloramines, and 5.4 percent using ozone (Hoehn *et al.,* 2001).Natural organic matter (NOM) is generated by physical, chemical and biological activities both in the watershed surrounding a water source and within the water source itself. NOM can be fractionated into hydrophobic and hydrophilic fractions (Marhaba *et al.,* 2003). The fractionation of NOM from water sources has recently gained crucial attention due to the need to determine NOM reactivity with disinfecting agents in water treatment facilities as this reaction could lead to the formation of potentially harmful disinfection by-products (DBPs). NOM is known to be a precursor to the formation of DBPs such as haloacetic acids (HAAs), trihalomethanes (THMs), and haloacetronitriles (HANs). HAAs have recently been regulated under the USEPA Disinfectant/Disinfection By-Products (D/DBP) Rule (United States Environmental Protection Agency or USEPA, 1989).

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Removal of organic matter during the production of drinking water brings several benefits. It is not only depriving heterotrophic bacteria of nutrients indispensable for their survival and multiplication in the water phase but also limits their colonisation of the drinking water distribution system. Moreover organic matter interacts with chlorine (commonly used as a disinfectant), which may lead to formation of carcinogenic and mutagenic disinfection by-products (Rook, 1974; Gray, 1994; Abd El-Shafy 2000).Although ozone can destroy phenolic compounds structure effectively, it is not economical to reduce the Total organic carbon TOC to an acceptable level using single ozonation process due to high ozonation cost (Ken *et al.,* 2000).Ozone had a beneficial effect on both turbidity and TOC removal in low TOC concentration of influent water. But, in high TOC concentration, chlorine had a beneficial effect (Torabian *et al.,* 2007).

Unfortunately, the anticipated maximum contaminant levels for haloacetic acids (HAAs) and trihalomethanes (THMs) of certain source water may not be using enhanced coagulation (Crozes *et al.,* 1995). Thus, the conventional water treatment process with coagulation/ sedimentation and filtration is unable to remove a significant amount of NOM (Orren *et al.,* 2000).Because of the formation of DBP, more advanced technologies including oxidation, adsorption, and membrane filtration were introduced to remove NOM prior to disinfection process (Jacangelo *et al.,* 1989; Amy *et al.,* 1991).Membrane filtration is an effective method to remove particles, micro organisms and organic matter from drinking waters. Compared with conventional treatment Methods, membrane processes (i) can provide better quality water, (ii) minimize disinfectant demand, (iii) are more compact, (iv) provide easier operational control and less maintenance, and (v) generate less sludge (Cleveland, 1999).

Ozone can break down large organic molecules. This implicates that the prevention of membrane fouling by combination of ozonation and membrane process is possible (Chen et al, 2005).It has been reported that ozonation could convert NOM from humic substances to non-humic fractions and from higher- to lower-MW fractions (Owen *et al.,* 1995).Membrane technology at the present time is extensively applied in many sectors of the manufacturing industry including gas separation and enrichment, water desalination and production of foods, beverages, pharmaceuticals and other biological products (Schweitzer 1988).The application of ozonation prior to membrane filtration reduces membrane fouling and enhances permeate flux (Schlichter *et al.,* 2003).

MATERIALS & METHODS

Humic acid in powder form used for simulation of raw water with desired TOC. The humic acid was purchased in powder form of U. S. Acros Company. The ozonator model C.O.G of Arda Company used for pre-ozonation. Nanofiltration membranes were purchased from FilmTec Company in USA. A NF90-4040 polyamide thin film composite (TFC) membrane with 7.2 m^2 Nominal Active Surface Area and 7.6 m^3/d permeate Flow Rate at 25ºC and 4.8 bar pressure was chosen due to their high TOC rejection. To prevent any coarse substances from entering the NF membranes, the water was treated over a cartridge filter as a pre-treatment. The influent discharge of system during the test was 13.7 L/min with 4 and 8 bar pressure. Because the effluent TOC was constant after 20 minutes, so the pilot was operated for 30 minutes every time finally the permeate analyzed as a TOC (mg/L), with Shimadzu model TOC- VCPH. Experiments were carried out at room temperature in a batch mode. Then, desired TOC concentration (4, 8, and 12 mg/L) simulated with adding of humic acid in powder form. Commercial 40% ferric Chloride (that is used in the Tehranpars Water Treatment Plants) used as a coagulant. Also Standard jar test procedures used to evaluate ferric Chloride requirements and the primary water quality parameters. The model water rapidly mixed for 2 min. The beakers transferred to a six-place jar-test apparatus, and the water mixed at 35 rpm for 30 min. Then the beakers removed from the jar-test apparatus, and contents allowed settling quiescently for 30 min. The 500-ml aliquots treated with different coagulant dosage at the same pH. According to U. S. EPA (1997) Secondary drinking water Standards, TOC of filtered water should be less than 2 mg/L (or less than 2.0 SUVA) (Kawamura, 2000). Thus, the ferric Chloride optimum dosage for removal of TOC in

compliance with standard obtained for TOC. In alternative 2, TOC removal investigated with pre-ozonation and ozone optimum dosage for maximum removal of TOC determined. In alternative 3, TOC removal investigated with prechlorination. Thus, the chlorine optimum dosage for maximum removal of TOC determined. Then, we have investigated TOC of synthetic water with desired TOC, after membrane filtration in 4 and 8 bar pressure. Permeate samples were collected in bottles stored in an ice-bath for the duration of the experiment and were analyzed immediately.

RESULTS & DISCUSSION

Data taken from the entire Jar test results in which ferric chloride used as a coagulant that is shown in Table1. The results demonstrated that, required coagulant dosage for TOC removal increases with TOC increment. Results of ferric chloride experiments for TOC removal are shown in Fig. 1. As illustrated in Fig 1, the optimum dosage for TOC removal is 9 mg/L.

According to Fig. 2, the Ferric chloride required for TOC removal increased with influent TOC increment. Figure 2 demonstrates relation between required optimum dosage of ferric Chloride and TOC removal which is linear. We repeat the test for 8 and 12 mg/L of TOC, the optimum ferric Chloride dosage for TOC removal were resulted 40 and 70 mg/L.

The addition of ozone before coagulation with ferric chloride in optimum dosages, increased removal of organic matter. As illustrated in Table 2 and Fig. 3, Pre-ozonation can improve removal of TOC during coagulation process with ferric chloride. When ferric chloride used as a coagulant in dosage of 9 mg/L, the optimum Ozone dose for TOC removal was 2 mg/L.

We repeat the test for 8 and 12 mg/L of TOC in their optimum ferric chloride dosages. The optimum ozone dosages for TOC removal were resulted 4.5 and 5.5 mg/L.

Table1. Coagulant only Jar test result for TOC removal of humic acid synthetic water

ferric Chloride (mg/L)	TOC (mg/L)			
	Try 1	Try 2	Try 3	Ave.
7	3.60	3.45	3.51	3.52
8	2.37	2.56	2.33	2.42
9 (optimum dosage)	1.70	1.90	1.80	1.80
10	2.25	2.31	2.22	2.26
11	2.26	2.21	2.25	2.24

Table 2. Ozone effect on TOC removal

Ozone (mg/L)	TOC (mg/L)			
	Try 1	Try 2	Try 3	Ave.
1.0	2.12	1.95	2.43	2.16
1.5	1.78	1.89	2.46	2.04
2.0 (optimum dosage)	1.54	1.47	1.69	1.56
2.5	1.89	2.19	1.96	2.01
3.0	1.78	1.97	2.15	1.96
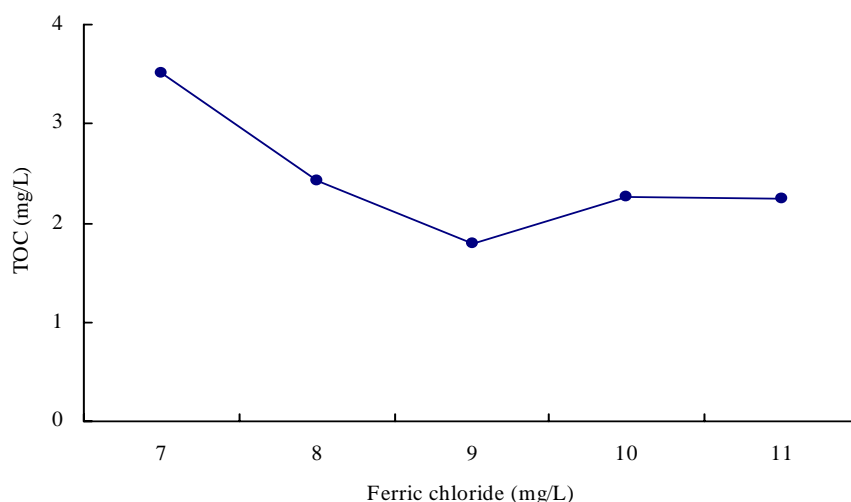
Fig. 1. Required optimum ferric Chloride dose for TOC removal
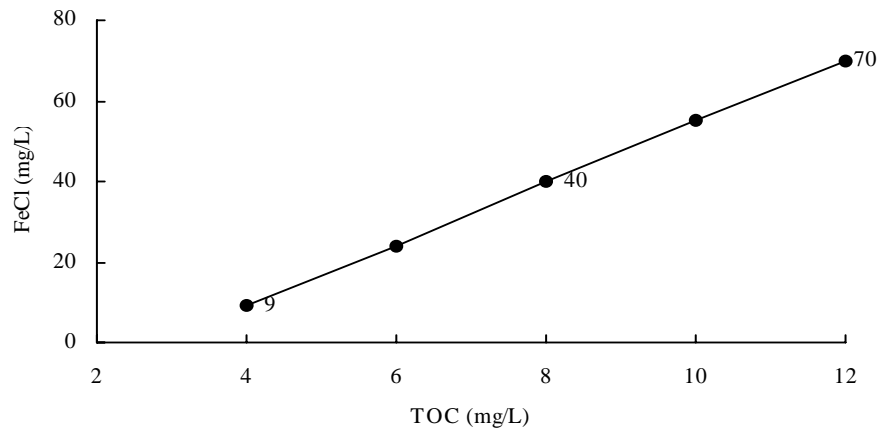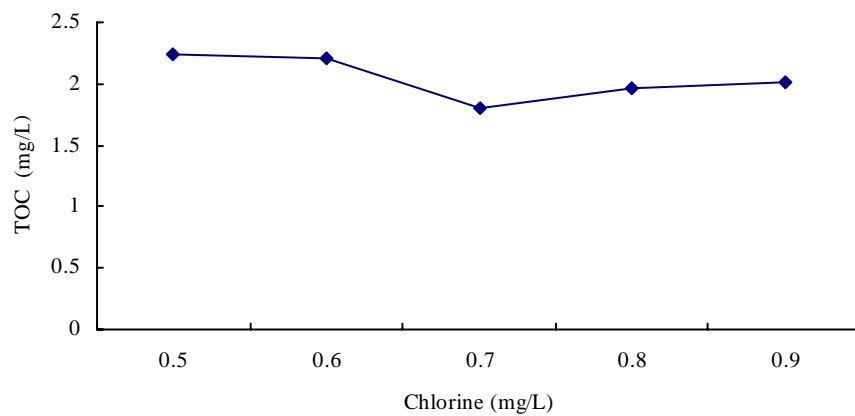
Fig. 2. Required optimum ferric Chloride dose for TOC removal
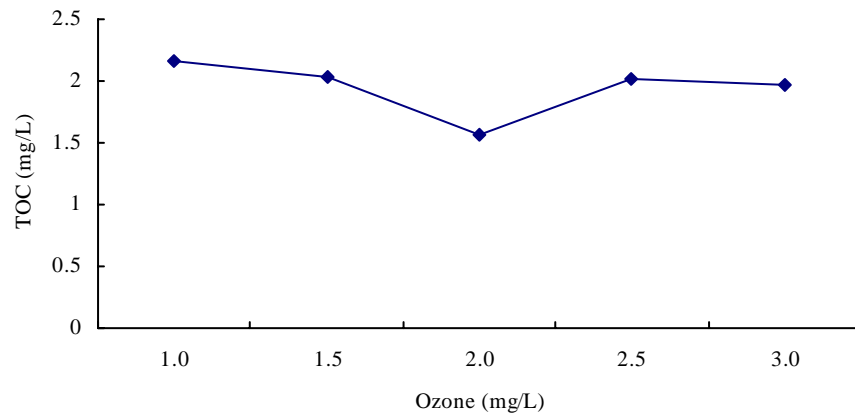
Fig. 3. Ozone effect on TOC removal

Fig. 4. Chlorine effect on TOC removal

Table 3. Chlorine effect on TOC removal

Chlorine	TOC (mg/L)			
(mg/L)	Try 1	Try 2	Try 3	Ave.
0.5	2.30	2.18	2.25	2.24
0.6	2.19	2.25	2.19	2.21
0.7	1.78	1.83	1.82	1.81
0.8	1.96	1.92	2.00	1.96
0.9	2.06	1.97	2.03	2.02

Table 4. Nanofiltration test results for TOC removal at 4 bar pressure

Influent TOC	Effluent TOC (mg/L)			
(mg/L)	Try 1	Try 2	Try 3	Ave.
4	0.15	0.1	0.23	0.16
8	0.12	0.24	0.21	0.19
12	0.23	0.20	0.19	0.20

Table 5. Nanofiltration test results for TOC removal at 8 bar pressure

Influent TOC (mg/L)	Effluent TOC (mg/L)			
	Try 1	Try 2	Try 3	Ave.
4	0.32	0.24	0.27	0.27
8	0.35	0.32	0.34	0.33
12	0.38	0.41	0.35	0.38

In addition the effect of pre-ozonation on coagulation is complicated and site specific. The key variables that seem to determine the effect of ozone are dosage, pH, alkalinity, and the nature of the organic material.As shown in Fig. 3, the addition of ozone had a beneficial effect on TOC removal. As illustrated in Fig. 3, the optimum dosage of Pre-ozonation is 2 mg/L, respectively.The addition of chlorine before coagulation with ferric chloride in optimum dosages, increased removal of organic matter slightly. As illustrated in Table 3, Pre-chlorination can improve removal of TOC during coagulation process with ferric chloride. When ferric chloride used as a coagulant in dosage of 9 mg/L, the optimum chlorine dose for TOC removal was 0.7 mg/L. A Comparison of ozone and chlorine shows that ozone had a beneficial effect on TOC removal in low TOC concentration of influent water. But, the effect of pre-chlorination and pre-ozonation on coagulant particle-NOM interactions are subtle and complex . As illustrated in Fig. 4, the optimum dosage of Prechlorination is 0.7 respectively. Finally, the addition of Chlorine before coagulation with ferric chloride increased TOC removal.

The effects of Nanofiltration on TOC removal are showed in Tables 4 and 5. In the first try permeate flow was 5.5 lit/min at 25ºC and in the second try the permeate flow rate was 7.1 l/min at 25ºC. According to table 4 and 5, when pressure increased, removal Of TOC slightly decreased. In addition, Nanofiltartion results show that produced permeate of the NF90-4040 complies with the EPA Drinking Water Regulations. In addition TOC removal in Nanofiltration is higher than Oxidation-coagulation combination. But the feed water of Nanofiltration must have special requirements such as influent maximum turbidity level and TOC level. So the preoxidation and coagulation are beneficial for reduction and Compliance of those parameters with regulations.

CONCLUSION

The results showed that TOC removal in preozonation-coagulation was higher than pre-chlorination-coagulation. Also pre-oxidation (preozonation and prechlorination) with coagulant had considerable results than coagulant lonely. Prechlorination and preozonation show that addition of ozone had a beneficial effect on TOC removal. , A Comparison of ozone and chlorine shows that ozone had a beneficial effect on TOC removal in low TOC concentration of influent water. Adversely, in high TOC concentration, chlorine had a beneficial effect on TOC removal. But, the effect of prechlorination and preozonation on coagulant-particle-NOM interactions are subtle and complex. Thus, use of prechlorination and preozonation as a coagulant aid will not likely be its primary application. A Nanofiltration had maximum level of TOC removal relative to above mentioned methods.

ACKNOWLEDGEMENTS

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