Effect of preozonation and prechlorination on total organic carbon removal in surface water treatment in Iran

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Abstract

In drinking water treatment, prechlorination and preozonation are often applied in order to control micro-organisms and taste and odour causing materials, which may influence organics removal by pre-oxidation and adsorption.

Using commercial and natural water humid substances, the positive effect of prechlorination and preozonation as an aid to coagulation-flocculation of these compounds were confirmed by the removal of total organic carbon (TOC). These experiments were conducted at bench-scale through a series of jar tests using different pH, coagulant dosage and TOC concentration of approx. 4, 8 and 12 mg/l. In addition to TOC removal, the existence of an optimum preozonation dose and an optimum prechlorination dose were also confirmed. Experiments show that prechlorination and preozonation can improve coagulation and flocculation depended on TOC concentration of influent surface raw water. The results demonstrate a differential effect between prechlorination and preozonation on removal of TOC. Preozonation showed a positive effect on a system with low influent TOC and very low molecular weight (noncolloidal) humic substances.
Keywords: *prechlorination, preozonation, TOC, surface raw water, preoxidation.*

1 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 [11]).

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 US Environmental Protection Agency (USEPA), 14.2% of surface water treatment systems servicing a population of 50,001-100,000 are using ClO2 as a predisinfectant compared to 47.5% using chlorine, 15.5% using chloramines, and 5.4% using ozone (USEPA [8]).

Although ozone can destroy phenolic compounds structure effectively, it is not economical to reduce the TOC to an acceptable level using single ozonation process due to high ozonation cost [10].

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. [5]). Thus, the conventional water treatment process with coagulation/sedimentation and filtration is unable to remove a significant amount of natural organic matter (NOM) [14].

Because of the formation of DBP, more advanced technologies including oxidation, adsorption, and membrane filtration were introduced to remove NOM prior to disinfection process. Ozone has been used as a strong oxidant for years, and several researches (Amy et al. [1], Jacangelo et al. [7]) have shown that ozonation prior to chlorination can lower formation potential of THM and HAA [15].
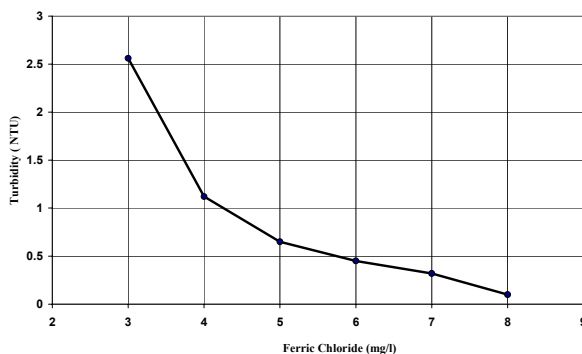

Figure 1:   Coagulant only jar test result for turbidity removal of humic acid synthetic water.

It has been reported that ozonation could convert NOM from humic substances to non-humic fractions and from higher- to lower-MW fractions (Amy et al. [1] Owen et al. [13]). In the preozonation process, ozone is added to source water prior to coagulation. The role of ozone acts as an oxidant

sometimes as a coagulant-aid. The dosage of preozonation to achieve the best coagulation ranges from 0.4 to 0.8 mg O3/mg carbon [4].

A study by Edwards and Benjamin examined the effect of preozonation on between coagulant and natural organic matter (NOM) and found that increasing the ozone dosage led to increase in metal residuals for both Iron and aluminium-based coagulants. As the zeta potential increased (became less negative) with increasing coagulant dosage, less metal residual was detected [6].

As the ozonation dosages increased, however, the flocs became more highly charged (more negative), and thus the critical coagulants (CCC) was increased for increasing ozone dosage. TOC removal was sometimes increased and sometimes decreased, depending on ozonation dosage and coagulant dosage. However, the amount of TOC removal by coagulation decreased with increasing ozone dosage because of transformation of NOM into more hydrophilic, less absorbable molecules. Overall TOC removal slightly increased with increasing ozone dosage at very high and low coagulant dosages but decreased at moderate coagulant dosages [6].
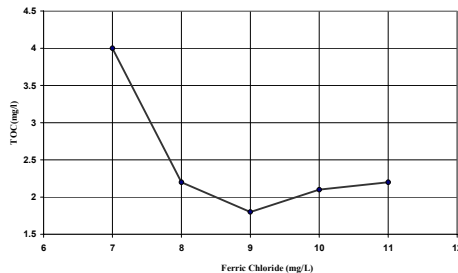

Figure 2:   Coagulant only jar test result for TOC removal of humic acid synthetic water.
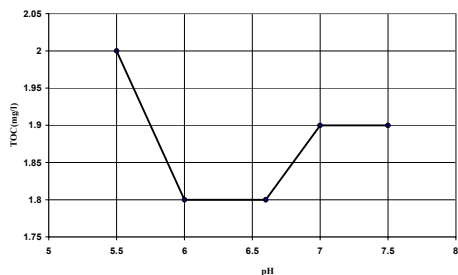

Figure 3:   Coagulant only jar test result for turbidity removal of humic acid synthetic water.

Edwards and Benjamin concluded that at constant pH, the dosage of metal salt coagulants required for optimal particulate removal in the presence of NOM increased with increasing ozone dosage. For organic polymer coagulants, however, the opposite proved true [6].

Becker found that oxalate (a common ozonation by-product) had an adverse effect on coagulation and filtration of turbidity and TOC when alum was used as the only coagulant [3].

Schneider and Tobiason concluded that when alum is used as a coagulant, preozonation leads to increases in settled water turbidity, TOC removal, and DOC at the conditions tested (0.5 to 0.8 mg/l ozone at bench scale). Also, they concluded that when cationic polymer is used as a coagulant, preozonation leads to increases removal of turbidity, TOC, and DOC. When PACl is used as a coagulant, preozonation leads either to increases or decreases in turbidity NOM removal [12].

The objectives of this research work are intended to: (1) prechlorination effect on TOC removal, (2) preozonation effect on TOC removal. (3) Comparing between prechlorination and preozonation effect on TOC removal. (4) Varying contact time effect of preozonation and prechlorination effect on TOC removal.

2   Materials and methods

2.1 Waters samples and materials

Clay, kaolin, humic acid in powder form used for simulation of raw water with desired turbidity and TOC. Commercial 60% chlorine used for prechlorination, which is used in the Tehranpars Water Treatment Plants. The humic acid was purchased in powder form of U. S. Acros Company. The ozonator model COG of Arda Company used for preozonation.

2.2 Analysis methods

Experiments were carried out at room temperature in a batch mode. Bench scale preozonation and prechlorination was performed. First, the raw water with turbidity of 20 NTU simulated with clay and kaolin. 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. Standard jar test procedures used to evaluate ferric Chloride requirements and the primary water quality parameters.

The model water rapidly mixed for 2 min. During this period, the pH of the water adjusted to the desired range by addition of 0.02 N sulphuric acid or 0.1 N sodium hydroxide. The beakers transferred to a six-place jar-test apparatus, and the water mixed at 35 rpm for 30 min. 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 Primary Drinking water Standards of USEPA (1997), Turbidity must be less than 0.5 NTU in 95% of samples per month. Thus, the ferric chloride optimum dosage for removal of turbidity in compliance with standard obtained for TOC of 4 mg/l. According to Primary Secondary Water Standards of USEPA (1997), TOC of filtered water should be less than 2 mg/l (or less than 2.0 SUVA) [9].
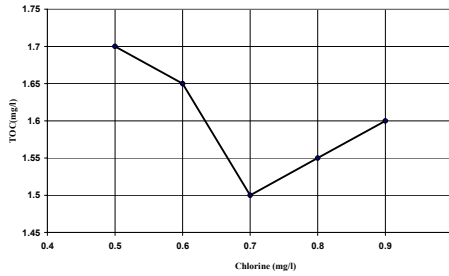
Figure 4:   Chlorine effect on TOC removal.

Thus, the ferric chloride optimum dosage for removal of TOC in compliance with standard obtained for TOC of 4 mg/l. Then optimum pH identified. In alternative 1 the optimum coagulant dosage and optimum pH determined 9 mg/l and 6.0, respectively. In alternative 2, TOC removal investigated with prechlorination. Thus, the chlorine optimum dosage for maximum removal of TOC determined. In alternative 3, TOC removal investigated with preozonation and ozone optimum dosage for maximum removal of TOC determined.

Finally, 3 alternatives compared with another. TOC analyzed using a TOC analyzer according to standard method [2].

3   Results and discussion

3.1 Results

3.1.1 No preoxidation, prechlorinatiom and preozonation effects on TOC removal of 4 mg/l

Results of ferric chloride jar-test experiments for turbidity removal are shown in figure 1. As illustrated in figure 1, the optimum dosage for turbidity removal is 6 mg/l. Figure 2 demonstrates the optimum dosage for TOC removal. In general, removal of both turbidity and TOC in the Jar test results was good. The optimum dosage for turbidity removal is 9 mg/l.
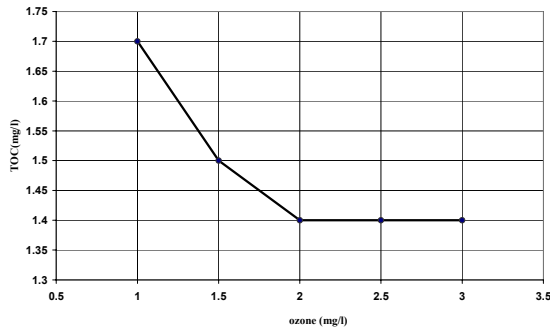

Figure 5:   Ozone effect on TOC removal.

Figure 3 demonstrates that the optimum range of pH for TOC removal is 6-6.5. The addition of chlorine before coagulation with ferric chloride increased removal of organic matter. Figure 4 shows results for Jar test experiments conducted at pH 6. Finally, the addition of ozone before coagulation with ferric chloride increased TOC removal. Figure 5 shows results for Jar test results.

As illustrated in figures 4 and 5, the optimum dosage of Prechlorinatiom and Preozonation are 0.6 and 2 mg/l, respectively.

3.1.2 No preoxidation, prechlorinatiom and preozonation effects on TOC removal of 8 and 12 mg/l

The results are as same as 3.1.1. Thus, the results listed at tables 1 and 2. Also, figure 7 illustrated the results.

3.2 Discussion

3.2.1 No preoxidation

Data taken from the entire jar test results in which ferric chloride used as a coagulant that is shown that required coagulant dosage for TOC removal increases with TOC increment. Figure 8 demonstrates relation between required optimum dosage of ferric Chloride and TOC removal.

Lowering pH to range of 6-6.5 causes to increase removal efficiency of TOC.

3.2.2 Prechlorination, coagulation

In general, when chlorine added to humic acid synthetic waters at pH 6.5, removal of turbidity and organic matter slightly increased. The results of analysed data are presented in figure 4.

Lowering pH during enhanced coagulation increases the disinfection efficiency of chlorine. The US Environmental Protection Agency (USEPA) contact timetables for chlorine reflect this change in disinfection efficiency relate to pH.

3.2.3 Preozonation, coagulation

The addition of ozone before coagulation with ferric chloride increased removal of turbidity and organic matter. These effects appeared after only 5 min of ozone contact time before coagulation addition. No definitive trend was observed with ozone contact time.

A comparison of ozonation and no ozonation shows that the addition of ozone had a beneficial effect on TOC removal.

A comparison of no ozone and applied ozone dosage of 2 mg/l dosage shows that the 2 mg/l dosage had a beneficial effect on turbidity removal and TOC removal. TOC removal was the reduction in negative surface charge following ozonation. The charge-neutralizing effect of preozonation may act in concert with the cationic polymer to decrease the ferric chloride to turbidity removal, thus providing "excess" ferric chloride to aid in the removal of TOC that would normally not be removed. The removal of the low–molecular-weight hydrophilic organic species is likely attributed to increased specific interactions between the organic materials and ferric chloride, followed by hydrophobic expulsion of

NOM-ferric chloride. The fact that the change in EPM seemed to occur on approximately the same time scale as the changes observed in the coagulation experiments supports this argument.

As illustrated in table 2, specific ozone dosage of 0.5 mg per mg TOC applied in the removal of TOC.

The reduction of TOC will decrease the demand and decay rate use result of the decrease in reactive material. Both of these reductions result in a lower ozone dosage required to achieve equivalent disinfection efficiency. Ozonation, when applied before enhanced coagulation, can sufficiently change the remove low molecular weight, non humic fraction.
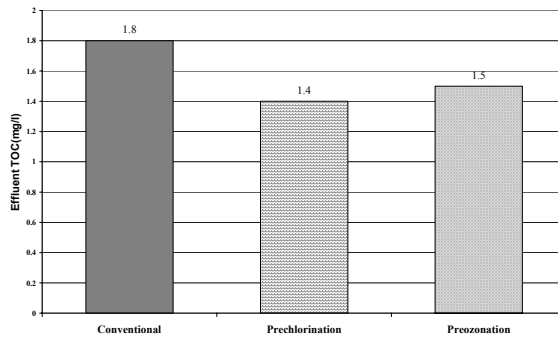
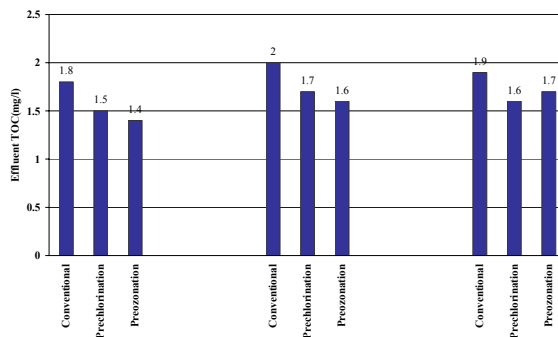Figure 6:   A comparison of conventional (no preoxidation), preozonation and prechlorination.

Figure 7:   A comparison of conventional (No Preoxidation), Preozonation and Prechlorination at TOC of 4, 8, and 12 mg/l (left to right).

3.2.4 Comparison of settled water TOC at no preoxidation, prechlorination and preozonation

The authors observed detrimental effects of non oxidation, prechlorination, and preozonation on TOC removal when ferric chloride used as a coagulant.

As illustrated in figure 6, a comparison of settled water TOC at no preoxidation, prechlorination, and preozonation shows that addition of ozone had a beneficial effect on both turbidity and TOC removal. A comparison of ozone and chlorine shows that ozone had a beneficial effect on both turbidity and TOC removal in low TOC concentration of influent water. Adversely, in high TOC concentration, chlorine had a beneficial effect on both turbidity and 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.

Table 1:   Jar test results for various TOC concentrations.

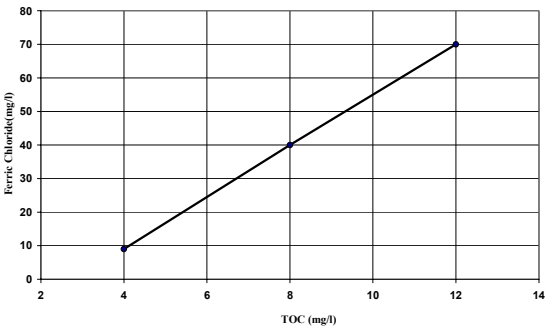| Optimum Dosage for turbidity removal	6	30	60
Optimum Dosage for TOC removal	9	40	70
Optimum pH	6.5	6.5	6.5

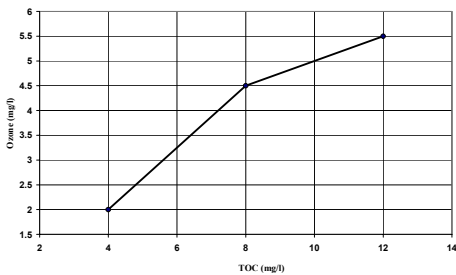Figure 8:   Required optimum ferric Chloride dose for TOC removal.

Figure 9:   Required optimum ozone dose for TOC removal.

Table 2:   Maximum TOC removal with No Preoxidation, Prechlorination, and Preozonation.

Alternative	TOC of 4 mg/l	TOC of 8 mg/l	TOC of 12 mg/l
No Preoxidation	1.8	2	1.9
Prechlorination	1.4	1.6	1.7
Preozonation	1.5	1.7	1.6

4   Conclusions

Based on the results of the described experiments and condition; the authors drew the following conclusions.

- When ferric chloride used as a coagulant, prechlorination and preozonation lead to decrease in settled water turbidity and TOC at the conditions tested.
- When ferric chloride used as a coagulant, required dosage increased with influent TOC increment.
- When ferric chloride used as a coagulant, preozonation leads to increase removal of turbidity and TOC. These increases are apparent after only a few minutes of contact time.
- Specific ozone dosage of about 0.5 mg per mg TOC (applied ozone dosage of approximately 2, 4.5, and 5.5 mg/l) aids in the removal of TOC.
- 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.
- Varying the preozone contact time from 5 to 30 min has little effect on settled water turbidity and TOC for the conditions tested.

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.

Acknowledgements

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