

RESIDUAL METAL CONCENTRATIONS IN ENHANCED COAGULATION WITH FERRIC CHLORIDE AND ALUM FOR TOC REMOVAL

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Abstract

Chemical coagulation with metallic salts has traditionally been used in water treatment for turbidity removal. However, coagulation is also capable of some degree of natural organic matter (NOM) removal, with NOM functioning as a precursor to disinfection by-products (DBPs) formation. Enhanced coagulation is thus introduced to most water utilities treating surface water. Jar-test experiments were conducted to compare the effectiveness of alum and ferric chloride in removing DBPs precursors from eight synthetic water samples, each representing a different element of the USEPA's 3×3 enhanced coagulation matrix, and the residual metal (aluminum/iron) concentration in the treated water was assessed. Coagulant type influenced the removal of total organic carbon (TOC) and which was enhanced with increasing coagulant dose. For all the treated samples coagulation with ferric chloride proved to be more effective than alum at similar doses and the mean values of treatment efficiencies were 51% and 32%, respectively. Ferric chloride was therefore considered the better chemical for enhancing the coagulation process. The results of residual metal concentration measurements in treated water showed that iron and aluminum concentrations had been increased as expected but the quality of water concerning the residual metal deteriorated much more in cases of under-dosing. Despite expecting high residual Al and Fe concentrations under enhanced coagulation, metal concentrations were frequently remained low and were not increased appreciably.

Keywords: Drinking water, enhanced coagulation, DBPs, residual metal

Introduction

Disinfection byproducts (DBP) are formed during water disinfection when chemical disinfectants such as chlorine react with the NOM. Many of DBPs are halogenated compounds such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are suspected to have adverse health effects (Reckhow *et al.*, 1990; Krasner *et al.*, 1989; Singer and Bilky, 2002). Concerns regarding the potential health effects of DBPs have resulted in a number of regulations developed by US Environmental Protection Agency (Anonymous 1999). This agency has set maximum contaminant levels for total THMs and five of the haloacetic acids (HAA) of 0.08 mg/L and 0.06 mg/L, respectively, under stage 1 of its

disinfectants and disinfection by-products (D/DBP) Rule. In addition, the rule mandates utilities using disinfectants to remove predetermined levels of total organic carbon (TOC) as a means of reducing DBP precursors. The USEPA has recognized either enhanced coagulation/softening as the best available technology (BAT) for controlling precursors of DBPs in stage 1 of D/DBP Rule (Black *et al.*, 1996; Anonymous, 1999, Volk *et al.*, 2000).

Enhanced coagulation is the practice of using coagulant dose in excess of what is normally required for turbidity removal, to achieve a specific reduction of TOC. Enhanced coagulation was selected as the stage 1 treatment of choice because it was effective for the removal of TOC and could be implemented at most water utilities treating surface waters using existing treatment processes. The rational concern behind the introduction of this treatment technique was that only a very small fraction of the DBPs and associated health risks have been identified, thus an increase in precursor removal would reduce overall known and unknown public health risks (Babcock and Singer 1979; Edzwald and Tobiason, 1999; Singer and Bilky, 2002). The enhanced coagulation requirements of TOC reduction are based on the TOC and alkalinity of the source water as shown in Table 1. The TOC removal criteria presented in Table 1 were selected so that a large majority (e.g., 90 percent) of plants required to operate with enhanced coagulation would be able to meet the TOC removal percentages (Anonymous, 1999).

In practicing enhanced coagulation, water systems are not expected to optimize or maximize the removal of DBPs precursors. So as not to be cost prohibitive, systems must meet target percent removals of TOC, where TOC serves as a surrogate for identified and no identified DBPs precursors. The percent removal requirements specified in Table 1 were developed with recognition of the tendency for TOC removal to become more difficult as alkalinity increases and TOC decreases. In higher alkalinity waters, pH depression to a level at which TOC removal is optimal (e.g., pH between 5.5 and 6.5) is more difficult and cannot be easily achieved through the addition of coagulant alone (Miltner *et al.*, 1994; Anonymous, 1999).

NOM removal is higher at low pH values for all coagulants. To achieve the NOM removals designated by the D/DBPs rule, coagulation may be accomplished by increased coagulant dosages, lower coagulation pH values, or both (BellAgy *et al.*, 2000). At several utilities, pH is controlled by the addition of the coagulant. Some utilities, however, focus on independent control of pH through separate addition of acids (Gregory and Duan, 2001; Budd *et al.*, 2004). Meeting the requirements of the Table 1 is termed as step 1 in the D/DBP Rule. Some plants required to implement enhanced coagulation which will not be achieved the removal levels indicated in Table 1, because their water quality characteristics are not unique. These plants require conducting jar or bench scale testing under step 2 procedures to establish an alternative TOC removal requirement. The D/DBP rule will force many water systems to move from conventional to enhanced coagulation and to expand their coagulation objectives to include TOC removal (Anonymous, 1999). The objectives of this investigation, focused at bench scale and for different synthetic waters, were to: 1) Compare the effectiveness of alum and FeCl₃ in removing DBPs precursors and 2) Evaluate the effect of enhanced coagulation implementation on residual metal (aluminum/ iron) concentration.

Materials and methods

For preparation of synthetic samples with different concentrations of TOC, tap water was first passed through a GAC column and predetermined amounts of commercial humic acid were added to its effluent. It is noted in literature that commercial humic substances have been found to be significantly different from the natural aquatic NOM, although the principal contents are similar (Malcolm and McCarty, 1986).

Reduction of water alkalinity to less than 60 mg/L as CaCO₃ was provided by boiling of treated water and for increasing to more than 120 mg/L as CaCO₃, soda ash addition was accomplished.

Turbidity adjustment of water samples was finally performed by addition of natural clay screened for 200 mesh.

Water samples were classified into eight groups according to their total alkalinity and TOC levels (Table 2). In other words, eight groups of synthetic water samples each representing a different element of 3×3 enhanced coagulation matrix was involved in this study. Jar tests were all accomplished by use of a standard six phase stirring apparatus at ambient temperature (Table 3). Addition of coagulant (alum or ferric chloride) was done during rapid mixing and doses applied were 5, 15, 30, 45, 60 and 80 mg/L. Doses above 80 mg/L were not chosen since they were not customary for use in actual plants and had not significant efficiencies.

After the end of the jar tests, sampling of the supernatants was conducted by an appropriate tip pipette from the depth of 10 cm below the water surface in the jar, so it was possible to sample the small quantities of settled water for analyses. Residual TOC, DOC, UV, pH, turbidity, alkalinity, and iron as well as aluminum concentrations were measured according to the procedures outlined in Standard Methods (Anonymous, 1998). Besides, the volume and weight of produced sludge were carefully determined.

Analyses of TOC and dissolved organic carbon were conducted at the Research Institute of Petroleum Industry in Tehran, while other parameters were determined at Department of the Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Iran.

Water samples were preserved with sulfuric acid at pH < 2. TOC and DOC were measured using a TOC analyzer (SM5310B, Combustion Infrared), (Anonymous, 1998). DOC measurements were made after filtering the samples through prerinsed 0.45µm membrane filters. A UV spectrophotometer with 1cm light pass was used to measure UV absorbance. As with DOC, samples were first filtered through prerinsed 0.45 m membrane filters. Filtered double deionized water was used to calibrate the instrument. Turbidity measurements were made using a turbidimeter.

Measurements of residual aluminum were made using Eriochrome Cyanine R method according to Standard Methods and residual iron concentrations were measured by atomic absorption spectrometer.

Results and discussion

Both alum and ferric chloride were used as primary coagulants and the data given in Fig. 1 are representative of the results obtained. Fig. 1 shows the effect of coagulant dose and pH on TOC removal from a water sample with initial TOC and alkalinity of 5.4 mg/L and 110 mg/L as CaCO₃, respectively. Other results were somewhat similar to this and only this representative sample is discussed here. The mean values of TOC removal were 32% and 51% by alum and ferric chloride, respectively. In the other words, the efficiency of this treatment by FeCl₃ was approximately 19% more ($P=0.003$). The maximum TOC removal rates obtained using alum and FeCl₃ were 88% and 93%, respectively. Furthermore, the alum and FeCl₃ doses needed to meet the TOC removal requirements are illustrated in Fig. 1.

According to Fig. 1 and overall results summarized in Table 4, the results of this research are similar to those found in other studies concerning NOM removal (Black *et al.*, 1996; Volk *et al.*, 2000; Singer and Bilky, 2002). Some investigators have reported that iron was superior to alum salts. For example, mean TOC removal using ferric sulfate was determined to be 65% and much more than results of water coagulation by alum which was reported to be 47% in experiments performed for treating Hillsborough River water

(Gianatasio *et al.*, 1995). On the other hand, results of another study which was performed on influent water to 46 treatment plants indicated that TOC removal was best achieved when alum was used with sulfuric acid (Lind, 1995). Simultaneously, Crozes *et al.*, (1995) and Volk *et al.*, (2000) reported that the efficiency of organic matter removal can be more increased using ferric chloride as compared with alum.

According to above discussion, it appears that colloidal destabilization as well as humates and fulvates formation both were better accomplished by FeCl_3 in dosages much less than the required amounts of alum (about one half). In addition, standard FeCl_3 solution (40-45%) is more acidic than 50% alum and so more alkalinity is consumed for formation of ferric hydroxides (Crozes *et al.*, 1995). Consequently, coagulation pH would be much less with FeCl_3 at similar coagulant doses. More favorable pH is undoubtedly the most important reason for better removal of TOC by iron salts. This indicates that the total coagulant demand can be decreased with FeCl_3 .

Another explanation for better efficiency of FeCl_3 could be that iron hydroxides differ from Al hydroxides in specific surface area and surface charge. According to literature, the specific surface area of Fe and Al hydroxides are in different ranges of 160-230 and 200-400 m^2/g ; however, due to higher active metal concentration in FeCl_3 and higher molecular weight of Fe, the total available surface is much more for FeCl_3 than for alum (Krasner, 1989 and Crozes *et al.*, 1995).

As an overall conclusion, it could be noted that FeCl_3 was one of the best chemicals for enhancing the coagulation process, since it could meet the TOC removal requirements without need to pH adjustment by acids mainly due to provision of higher acidity that results in higher removal of NOM. Moreover, and as our study clearly showed, the volume and weight of produced sludge were much less for ferric chloride than for alum. Thereby, treatment plants would be confronted to fewer problems with respect to final sludge disposal.

Two typical examples of the relationships between residual aluminum and iron concentrations and applied coagulant dose are shown in Fig. 2 and 3, respectively. As shown in Fig. 2, it may be noted that while residual Al concentration had increased from 0.025 mg/L in raw water to 3 mg/L by increased coagulant (alum) dose of about 15 mg/L, but by further dose increase to 60 mg/L alum, it has decreased to about 1.3 mg/L, and again this concentration had increased to about 2.5 mg/L by further addition of coagulant.

It is obvious that residual Al or Fe concentrations remained in drinking water after enhanced coagulation is a critical factor because these metals are suspected to be harmful to human and other living organisms and may lead to diseases such as Alzheimer's syndrome, osteoporosis, anemia, and anorexia for aluminum (Wen and Fung, 2002) and aesthetic problems (for iron). There was a general trend for residual metal concentrations that underdosing or overdosing of coagulants resulted in significant deterioration of water quality with respect to residual aluminum and iron concentrations, though the effect of under dosing is much more pronounced. It is an outstanding point that residual Al concentration is frequently remained low when coagulant doses required for meeting the TOC removal requirements are applied. In fact, the metal residuals are consistently lower than those obtained under the turbidity removal conditions. Even though more metal was utilized in the enhanced coagulation, more was precipitated. The study confirms the effect of alum dose on residual aluminum concentration as indicated in Fig. 2. Al concentrations were detected as minimum when alum doses required for 40% removal of TOC were added. This level of TOC removal is enough for meeting the requirements of the stage 1 D/DBPs rule. The use of excess coagulant to reach less Al concentration in drinking water is not recommended when excess production of sludge and/or shortened filter runs are experienced. On the other hand, use of fewer doses may not result in sufficient NOM removal and Fig. 3 indicates that NOM concentration sharply increased to its initial amount by reduction of coagulant dose. Similar

results and discussions would also be mentioned about residual iron concentration in drinking water.

Another problem is pH dependency. Based on the literature the solubility of different species of aluminum and iron are least at pHs 6 and 8, respectively. At pH values higher or lower than these pHs of minimum solubility, dissolved Al or Fe levels in settled water will increase. Besides, iron solubility is much less than Al solubility at normal pH of water (Anonymous, 2005). It should be noted that concentrations of iron reported by this study had been determined for unfiltered water samples and reducing pH to less than 2 for preservation objectives may cause re-dissolution of produced fine flocs. Finally, comparison of iron and Al solubility illustrates that iron salts produce non-dissolved forms in a broad pH range and hence they would be regarded as the best choice for coagulating water samples with high pHs. Accordingly, increasing coagulant dose should not always be considered as a trouble since better NOM removal can occur and so much better water quality would be expected.

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Table 1: Enhanced coagulation: required TOC percent removals (Anonymous, 1999)

Source water TOC (mg/L)	Source water alkalinity (mg/L CaCO ₃)		
	0-60	60-120	>120
2.0-4.0	35	25	15
4.0-8.0	45	35	25
>8.0	50	40	30

Table 2: Studied groups according to TOC and alkalinity

Source water TOC (mg/L)	Source water alkalinity (mg/L CaCO ₃)		
	0-60	60-120	>120
2.0-4.0	+	+	+
4.0-8.0	-	+	+
>8.0	+	+	+

+ : Tested, - : Not tested

Table 3: Jar-test mixing conditions

Parameter	Flash Mixing	Flocculation		Sedimentation
		Phase 1	Phase 2	
Speed (rpm)	100	40	20	-
Time (min)	1	7.5	7.5	30-60

Table 4: Average and maximum removal levels of TOC as a function of coagulant type Univariate tests

Coagulant	No. of Samples	Mean %	Mean difference	Pvalue	Maximum %
Alum	46	32.239	-19.097	0.003	88
FeCl ₃	48	51.335	19.097	0.003	92

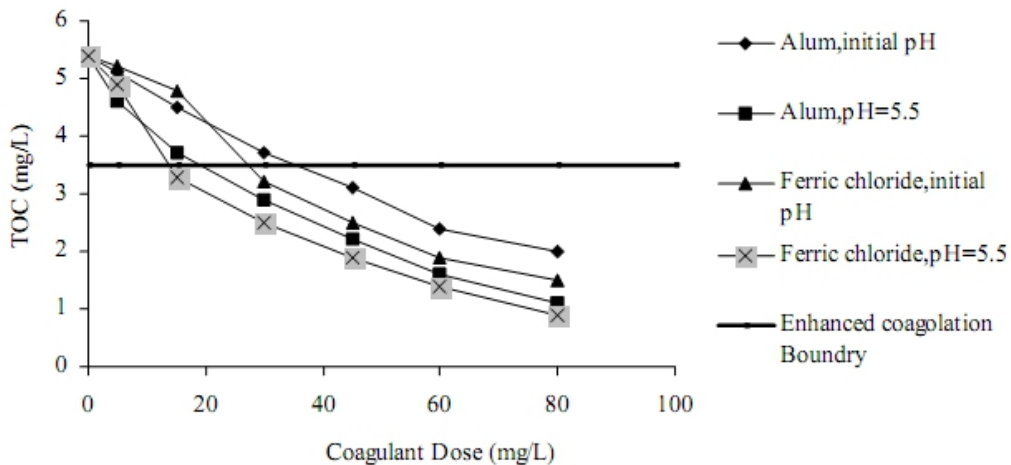


Fig. 1: Effect of coagulant dose on residual TOC [TOC₀=5.4 mg/L, Alk=110 mg/L CaCO₃]

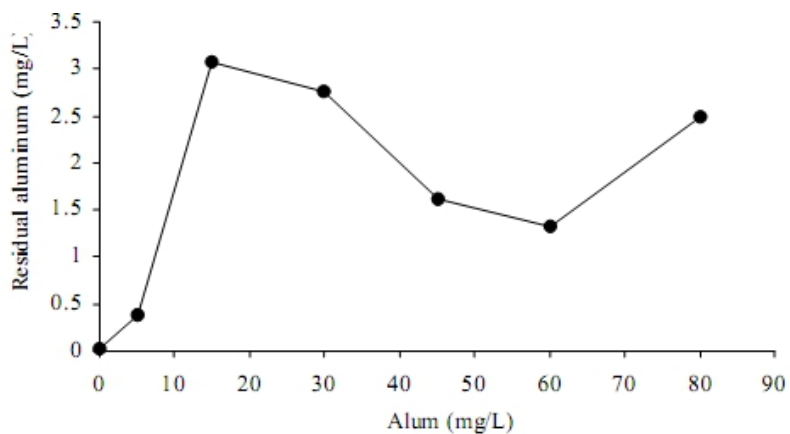


Fig. 2: Effect of Alum dose on residual aluminum concentration
[TOC₀=12.4 mg/L, Alk=115 mg/L CaCO₃]

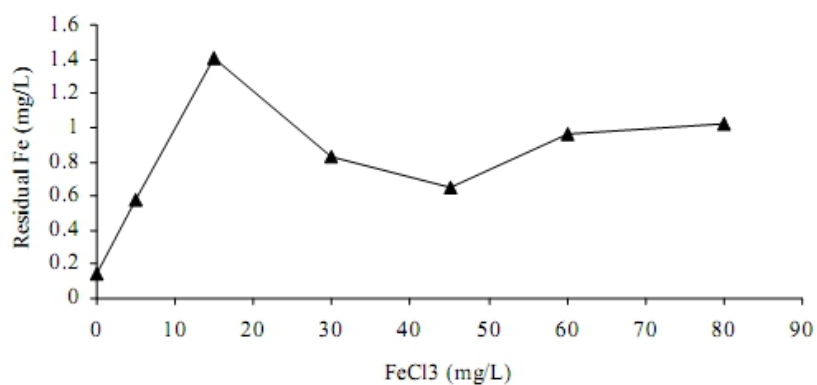


Fig. 3: Effect of FeCl₃ dose on residual iron concentration
[TOC₀=5.5 mg/L, Alk=144 mg/L CaCO₃]