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Improvement of NOM Removal from Water Resources by Modifying the Coagulation Process

***F Vaezi** [1], **A Mohagheghian** [2], **J Nouri** [1], **M R Eshraghian** [3], **A Ghasri** [1]*

[1]*Dept. of Environmental Health Engineering, School of Public Health,*
Tehran University of Medical Sciences, Iran
[2]*Dept. of Environmental Health, Gilan University of Medical Sciences, Iran*
[3]*Dept. of Epidemiology and Biostatistics, School of Public Health, Tehran University of Medical Sciences, Iran*

ABSTRACT

As a result of the regulations on DBPs, interest in NOM removal is increasing and many water treatment plants in developed countries have started to measure the concentration of TOC in their finished waters. Promulgation of the rules will substantially increase these efforts in other countries too. Since the cost of TOC (and DBPs) determination was high, it was decided to study the traditional analysis of COD as a surrogate measure to detect the organic constituents in raw water and the extent to which optimized coagulation with ferric chloride can increase COD removal. The two water samples studied belonged to Karaj and Jajrood Rivers. For both samples the observed values of COD removal by coagulation at lower pH (about 1-1.5 pH values less than the regular pH) were about 85-95 percent without making water turbidity unacceptable. In order to determine the effects of organic content on coagulation, synthetic samples were also prepared with much higher COD values. Again, considerable increases in COD removal have been observed for most of these samples only by decreasing 0.5-2 pH value. The results indicated that a modified coagulation process without need to much increasing the amount of coagulant can be developed for these water samples.

Keywords: *Modified coagulation, Natural organic matter, Chemical oxygen demand, Turbidity, Tehran water sources*

INTRODUCTION

Most waters contain natural organic matters (NOMs) which should be removed because they include precursor compounds that form health-related disinfection-by-products (DBPs) when chlorine and other chemicals are used for disinfection and oxidation (Barrett et al., 2000). Besides, the majority of aesthetic problems (true color, taste and odor) are imparted by NOM. For these reasons, considerable attention is being directed at the removal of NOM by modifying coagulation in conventional water treatment plants (Clark, 1993). When the coagulation process is specially modified to ensure good removal of NOM, it is often known as enhanced coagulation. In fact, relatively few utilities found it cost effective to achieve increased NOM removal by this process. These plants have met new standards for DBP_S without need to utilize disinfectants other than chlorine (Crozes et al., 1995; White et al., 1997). Enhanced coagulation (also known as opti-

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***Corresponding author:** *E-mail: for_vaezi@yahoo.com*
Tel: +98 21 88954914, Fax: +98 21 88950188,

mized coagulation) is now considered as the best available technology for DBPs control in the Stage 1 Disinfectants/Disinfection By-Products Rule. Several studies have been conducted to assess the impact of pH pre-adjustment on total organic carbon (TOC) removal and plants operating costs (Crozes et al., 1995; Singer, 2004).

In most situations where NOM is present, it is more important for determining coagulant dosage than turbidity. NOM removal is higher at low pHs for all coagulants. To achieve the NOM removals designated by the D/DBP$_S$ rule, coagulation may be accomplished by increased coagulant dosages, lower coagulation pH values, or both (Bell-Ajy el al., 2000). At several utilities, pH is controlled by the addition of the coagulant. Some facilities, however, focus on independent control of pH through separate addition of acids. In these cases, it is possible to supplement the acidifying effect of coagulants with the addition of acid. This can better reduce the coagulants dose that would otherwise be required for pH adjustment, also reducing the quantity of sludge that would be associated with the added dose (Gregory and Duan, 2001; Budd et al., 2004). Good practices of NOM removal using less than 20 mg/L alum and ferric salts in the pH range of 4.5 to 6.5, have been reported from various case studies. Iron-based salts are capable of removing at least 12% dissolved organic carbon (DOC) more than their aluminum-based counterparts (AWWA, 1999; Lovins, 2003).

MATERIALS AND METHODS

Source water selection In the first phase of this work, two source waters were selected. These were Karaj and Jajrood Rivers-which are both influents to water treatment plants of Tehran, the capital of Iran. Both sources have water representative of classification specified in the D/DBPs Rule to be: < 140 mg/ L as $CaCO_3$. Sampling had been performed in the spring of 1999. Totally ten raw water samples were collected randomly as grab samples. To complete the evaluation, the second phase of work was performed by preparing eight synthetic water samples. For this purpose, natural soil from the river banks was used to provide the samples with desired concentrations of organic matter, by first screening and then blending the remained soil with tap water. About 90g of this soil was mixed with 12 liters of water by 20 min agitation at 80 rpm. After an interval of 60 min for sedimentation, the sediments were removed and the water which had been saturated with natural organic matter was used for coagulation experiments. The initial alkalinity values of these samples were in the range of 130 to 190 mg/L CaCO3.

Approach A bench-scale jar-testing program that mimicked full-scale operating conditions in Tehran water treatment plants was used. All tests were performed in 1-L jars at ambient conditions (~25^{o}C) with automated jar-test equipment. Treatment pH was monitored upon initiation of the coagulant, and further adjustments were made using lime or acid (when required). Rapid mixing was performed for 1 min at 100rpm. Slow mixing was performed for 20 min at about 40rpm for floc agglomeration and final quiescent settling was about 1 hour. Settled water samples were then collected from the port located in the center of each jar cell.

Determination of optimized coagulation conditions required evaluation of both optimal coagulant dosage and pH. The selected coagulant dosages for each source of water in this work were the minimum amount required for fulfilling coagulation (turbidity reduction) in the acidic pH. Then to determine optimized coagulation treatments (organic reduction) for the constant coagulant dosage selected, a series of bench-scale jar-tests were used to identify the optimal coagulation pH. This pH is specified as the highest pH at which there was maximum COD removal for that selected dosage.

Analytical tests It is important to recognize that the natural organic content (NOM) of a water sample is often determined by use of

TOC analyzer but for highly organic surface water sources, it is also possible to use COD (chemical oxygen demand) test as a cheap and still standard method (APHA, 1995). By this test it would be possible to readily detect organic concentrations above 5 mg/L and for lower concentrations (up to 1 mg/L) detection is still possible by further precision in preparation of more dilute titrants. Concentrations below 1 mg/L can not be detected and samples with less than 1 mg/L COD exhibit a result similar to the blank. Although this result (≤ 1 mg/L) could also be reported for these samples, but for this project such samples had been omitted by avoiding treating samples with initial COD values of less than about 6 mg/L.

Reagent-grade ferric chloride ($FeCl_3$ anhydrous, reported as Fe^{3+}) had been used as the coagulant. Residual metal concentrations were measured by atomic absorption spectrophotometry. Because the depression of coagulation pH can affect the turbidity level of the finished water, this parameter had been controlled as well and determination was performed by use of a nephelometric method.

RESULTS

Figures 1 and 2 summarize the jar-testing results for optimized coagulation conditions of water samples from Karaj River and influent to Water Treatment Plant No. 3 of Tehran by ferric chloride for each pH of treatment. These tests were conducted using constant coagulant dosage (12 mg/L and 20 mg/L $FeCl_3$, respectively) with varied pH of treatment. It should be explained that to determine the amount of base (or acid)-coagulant combinations needed to achieve a desired pH for each raw water sample, titration curves were first developed. The program involved adding base or acid in increments until specific increased or depressed pH goals were achieved. The COD of each jar-tested water was measured and then the percent of COD removal was plotted versus pH of treatment. Finally, Table 1 represents the results of coagulating the synthetic samples by ferric chloride solution.

Table 1: Variation in COD and turbidity of synthetic water samples at different pH

	Parameters \ pH	7.5*	4.5	5.5	6.5	7	7.5	9
Sample 1	COD, mg/L	36	35.2	27.2	21.5	17.6	20.8	26.8
	COD Removal (%)	-	2.2	24.4	40.2	51.1	42.2	25.5
	Turbidity, NTU	35	2.3	2.1	2.2	1.4	2.3	2
	Parameters \ pH	7.5*	4.5	5.5	6.5	7	7.5	9
Sample 2	COD, mg/L	21	11.1	6.4	6.2	1.6	8.8	7.2
	COD Removal (%)	-	46.4	69.5	70.4	92.38	58	65.7
	Turbidity, NTU	36	29.2	1.4	1.34	0.6	2.3	1.7

Table 1: Variation in COD and turbidity of synthetic water samples at different pH

Sample 3	Parameters \ pH	7.4*	4.5	5.5	6.5	7	7.5	9
	COD, mg/L	25	11.4	6.4	6.7	1.6	8.8	7.4
	COD Removal (%)	-	54.4	74.4	73.2	93.6	64.8	70.4
	Turbidity, NTU	27	2.9	1.5	1.2	0.3	2	1.7
Sample 4	Parameters \ pH	7.8*	4.7	6.6	9.5	10.5	-	-
	COD, mg/L	15.4	2.8	2.4	2.4	3.4	-	-
	COD Removal (%)	-	81.8	84.4	84.4	77.9	-	-
	Turbidity, NTU	4.5	1.2	0.95	0.7	2.2	-	-
Sample 5	Parameters \ pH	7.9*	6	7	8	10	-	-
	COD, mg/L	14.8	1.6	4.8	6.4	8	-	-
	COD Removal (%)	-	89.1	67.5	56.7	45.9	-	-
	Turbidity, NTU	4.5	0.6	1.4	1.8	2.3	-	-
Sample 6	Parameters \ pH	8*	4	5	6	7	8	10
	COD, mg/L	14.4	4.8	13.5	12	2.4	<2	3.2
	COD Removal (%)	-	66.6	16.9	16.6	83.3	88	77.7
	Turbidity, NTU	82.4	16.9	13.9	1.99	0.7	0.93	0.95
Sample 7	Parameters \ pH	8*	7.6	8.6	9	-	-	-
	COD, mg/L	16	12	12.8	12.5	-	-	-
	COD Removal (%)	-	25	20	21.8	-	-	-
	Turbidity, NTU	58.8	1.87	1.79	1.22	-	-	-
Sample 8	Parameters \ pH	7.8*	5.5	6.5	7.5	8.5	9.5	10.5
	COD, mg/L	12	1	1.6	4.4	7.5	7.3	11.2
	COD Removal (%)	-	93.3	86.6	63.3	37.5	39.1	6.6
	Turbidity, NTU	15	21	0.9	1.78	1.64	0.99	0.8

* Initial Water Sample

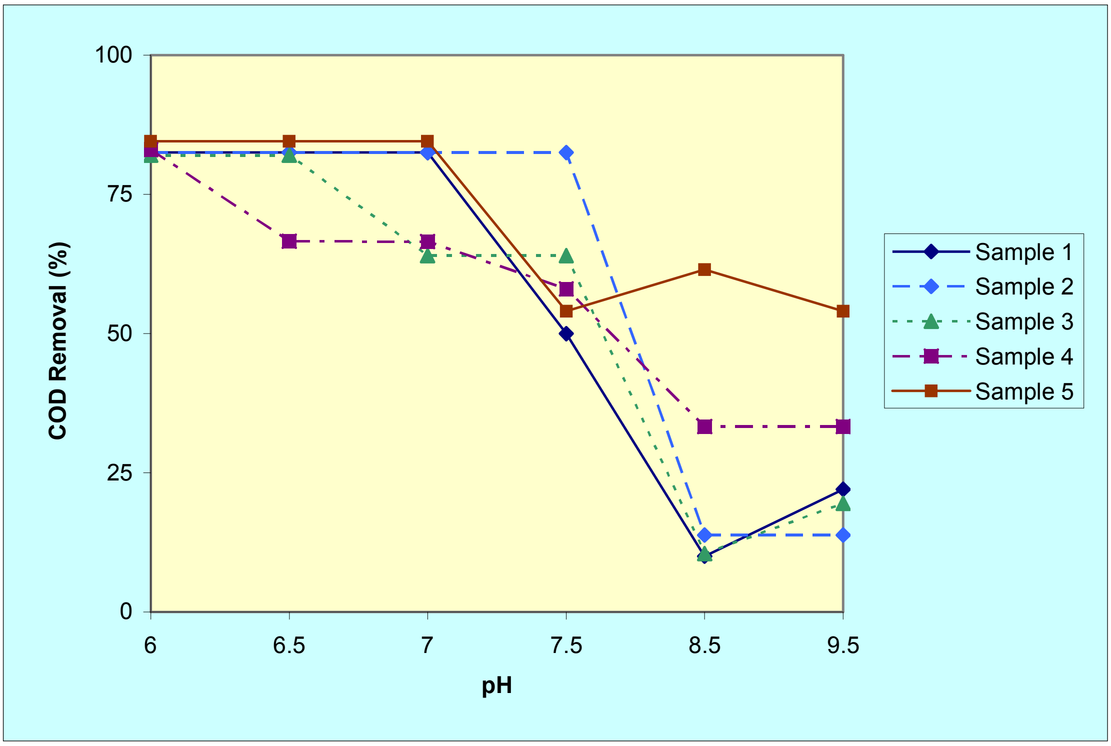

Fig. 1: Removal percentage of organic matter in various pH of water coagulation with 12 mg/l ferric chloride, Alk.<140mg/lCaCO3 (samples from Karaj River)

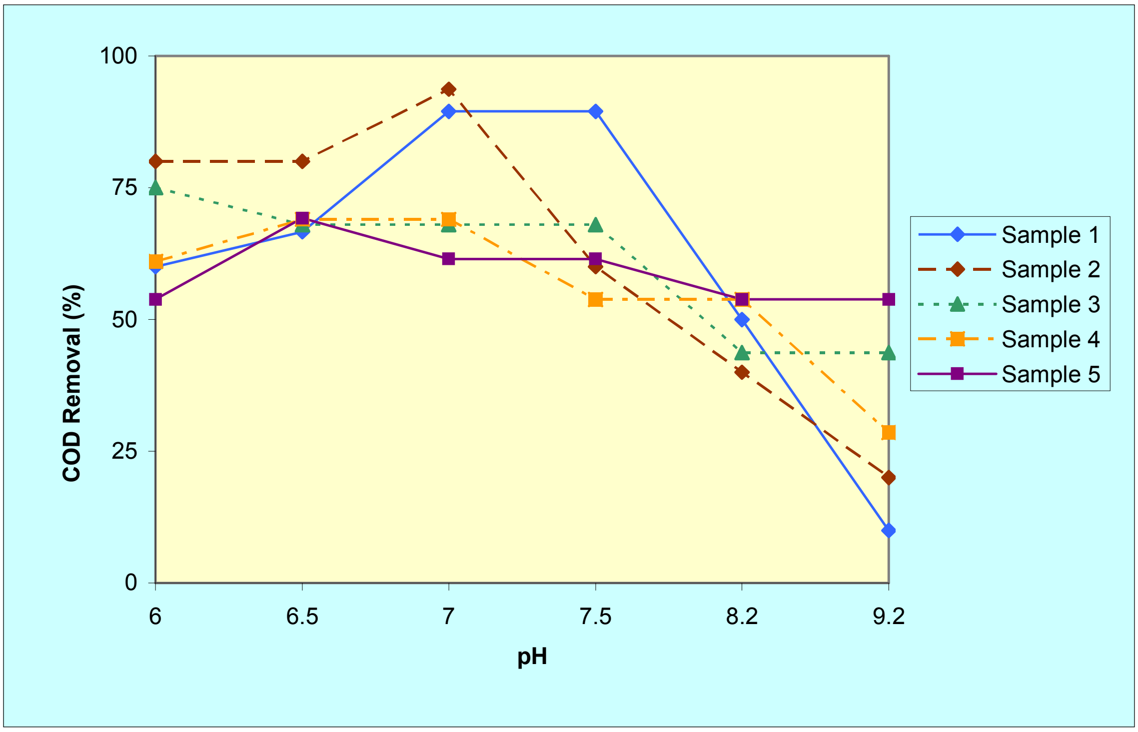

Fig. 2: Removal percentage of organic matter in various pH of water coagulation with 20 mg/l ferric chloride, Alk. <140mg/l CaCO3 (samples from Water Treatment Plant No. 3 of Tehran)

DISCUSSION

The decision to implement optimization studies of conventional coagulation systems should be based not only on NOM removal alone but also on important considerations such as sludge production. Pointing to this necessity, treatment plants have to provide conditions that still sustain effective removal of NOM and turbidity without producing excess sludge. Thus, this study was aimed at establishing such conditions by decreasing the coagulation pH. Results of natural water treatment indicated that in all cases, decreasing the pH increased the COD removal and no restabilization or overdosing was observed over the pH range investigated. In fact, all samples with lower pHs were generally more amenable to COD removal and this treatment was possible without formation of an important increase in turbidity level (maximum increase to be 0.5 NTU and for all treated samples turbidity values were remained less than 2.5 NTU). As it could be seen from Figs. 1 and 2, about 40% reduction in organic matter content of both waters has happened only by one unit decrease in pH. Performing pair *t*-test for these 10 samples revealed that reduction of organic content of water samples was significant when pH of water treatment had been reduced only by one unit (*P*=0.001). By adjusting pH at 7.5, the mean reduction of organic matter was reduced to 4.6 mg/L [95% C.I., (3.37, 5.82)], meaning that the organics reduction occurred was statistically significant [65.4% (4.6/7.03)]. Similar analysis has been performed separately for each natural water sample and results indicated that mean reductions of organic matter were as much as 3.68 and 5.52 mg/L, respectively (with p-values of 0.001 and 0.004, respectively). These data indicate that 62.0% and 68.1% reductions in organic pollution of two source waters have occurred. The improved NOMs removal at lower pHs can be attributed to conversion of some dissolved forms of these pollutants to their nondissolved forms. In Tehran water treatment plants, the pH depression can easily be achieved by discontinuing the lime addition or reduction in lime consumption. The increase in iron concentration of treated water was not significant (the mean value=0.02 mg/L and maximum 0.08 mg/L as Fe). Likewise, the changes in turbidity level of water samples coagulated in lower pHs were not noteworthy; this meant that sources supplying water of Tehran might be better coagulated in pHs less than the original source, and without need to much increase in coagulant dose and subsequent sludge increase.

In order to identify the suitability of pH depression in the treatment of waters with high level of organic matter, eight synthetic samples with COD concentrations in the range of 15 to 36 mg/L were prepared, for which the results of jar-tests can be seen in Table 1. According to the results of this phase of the study it could be concluded that similar to coagulation of natural raw waters, it is possible to improve the reduction of organic matter of highly polluted water samples by changing the pH of treatment without suffering from the produced slight increase in turbidity. However, as the initial turbidity and alkalinity of these samples were much more than the original sources, the effect of pH change was more significant.

Because adding high dosage of coagulant to enhance coagulation at ambient pH may not always be operationally sound or cost effective, several researches by modifying coagulation process through changing pH have been performed in recent years. Crozes and coworkers (1995) showed that coagulation pH to be a determining factor for maximum NOM removal when ferric chloride was used as a primary coagulant. They proved that preadjustment of pH at a value of 6.0±0.2 increased NOM overall removal to as much as 65 percent and reduced the coagulant dose by as much as 60 percent. Another research showed that enhanced coagulation with increased coagulant dosages led to higher overall operating costs to achieve the NOM removals designated by the D/DBP Rule but adjustment of pH with acid reduced costs by lowering the coagulant dosage as well as sludge production (Jacangelo et at., 1995; Grozes, 1995). Finally, our results confirm those of previous researches that pH of coagulation is a key component to optimal NOM removal and our final conclusion is that much more organic matter than those at higher pH levels would be removed by treatment of Tehran water samples at less pH with ferric chloride.

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