THE EFFECT OF PH CONTROL ON TURBIDITY AND NOM REMOVAL IN CONVENTIONAL WATER TREATMENT

Ahamed Fadel Ashery¹, Kamal Radwan², and Mohamed I. Gar Al-Alm Rashed³.

¹Public Works Department, Faculty of Engineering – Mansoura University
²Public Works Department, Faculty of Engineering – Mansoura University,
   dr_kamal15@yahoo.com
³Public Works Department, Faculty of Engineering – Mansoura University,
   m_gar_alalm@yahoo.com

ABSTRACT

Natural organic matter, (NOM) is the term used to describe the complex matrix of organics originating from natural sources that are present in all water bodies. Effective removal of turbidity and soluble natural organic matter from water could be achieved by micro-floc formation process (coagulation) and macro-floc development (flocculation). These processes are used to destabilize suspended particles and to react with dissolved organic material in the raw water. Proper and optimum coagulation is essential for good filtration performance and for disinfection byproduct (DBP) control. This work provides guidelines and an explanation of the most suitable coagulant dose that should be used to improve turbidity and NOM removal from water and how pH should be controlled to achieve the maximum removal and to reduce the coagulant dose to the minimum in coagulation process. The best result for turbidity and NOM removal was found at pH ranges from 5 to 6, while at pH > 6 the removal of NOM was poor and may need high dosage of coagulant. Experimental results of the remaining DOC after treatment was assessed theoretically.

Keywords: Natural organic matter (NOM), Dissolved Organic Carbon (DOC), Turbidity, Alum coagulations.

1. INTRODUCTION

Natural organic matter (NOM) originating from natural sources that are present in all water bodies are caused by break down of vegetation that finds its way in water bodies. Usually NOM concentration increases when runoff occurs. NOM could be expressed as total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance at wavelength of 254 nm (UV254) absorption, and specific UV absorbance (SUVA) (Wang and Hsieh, 2000[1]; Egeberg et al., 2002[2]; Kim and Yu, 2005[3]). Dissolved organic carbon, (DOC), is a fraction of total organic carbon and has the operational definition of milligrams per liter of carbon remaining in the liquid after filtration through a 0.45-µm filter (Hendricks, 2006[4]; Kim and Yu,2005[3]; Rizzo et al.,2004[5]). The NOM is comprised of humic substance that are categorized as fulvic acids and humic acids (Bose and Reckhow, 2006[6]). Concentrations in surface water range from about 1 to 75 mg/L as dissolved organic carbon. Color is another indicator of humic matter with range 10 to 50 cobalt color units (Hendricks, 2006[4]). Another surrogate of organic matter is UV_{254} which is the easiest analysis technique. The problems of NOM
may be identified as its responsibility for color, certain organic compounds contribute to taste and odor in drinking water, organic matter acts as a substrate for bacteria in distribution systems, anion exchange resins may become fouled by NOM, organic compounds may interfere with oxidation and removal of iron and manganese, and finally disinfection by-products are formed as a result of chlorine demand by organic matter. (O’Melia et al., 1999; Wang and Hseih, 2000; Korbutowicz, 2004; Bond et al., 2010; Leeuween et al., 2005; Yan et al., 2008).

Natural organic matter is the term used to describe the complex matrix of organics originating from natural sources that are present in all water bodies. Hydrophilic in nature, the constituents that comprise NOM (e.g., low-molecular-weight acids, amino acids, proteins and polysaccharides, fulvic and humic acids) have a wide range of molecular weights (Matilainen et al., 2002). The humic acids have high molecular weights and can take on macromolecular (colloidal) properties whereas the other constituents of the NOM are considered to be dissolved (Crittenden et al., 2005; Matilainen et al., 2002). In the recent years, considerable effort has been made in water treatment technologies to develop methods with greater natural organic matter (NOM) removal efficiencies. Reduction in the level of NOM before disinfection minimizes the formation of the disinfection by-products and reduces the disinfectant residual that is required to control the bacteria regrowth in the distribution systems. This contributes to the improvement of water quality delivered to the consumers (Wang and Hseih, 2000; Thiruvenkatachari et al., 2002; Uyak and Toroz, 2006; Annadurai et al., 2003; Leeuween et al., 2004).

It has been observed that NOM reacts or bind with metal ion coagulants and many researchers feel that the coagulant dosage at most operating plants are determined by the NOM-metal ion interaction and not particle-metal ion interaction (Matilainen et al., 2002; Rizo et al., 2004; Leeuwen et al., 2004). No quantitative observations about coagulant dosage can be made because solution conditions that affect dosage and effectiveness of coagulants such as pH, hardness, and temperature also affect the speciation of humic substance.

For all raw water types, there are many parameters that affect coagulation performance including the amount and type of particulate material, the amount and composition of NOM, and chemical and physical properties of the water. The common parameters are: coagulant type, dose, and pH (Yan et al., 2008; Uyak and Toroz, 2006; Leeuween et al., 2004).

pH is the term used to express the intensity of the acid or alkaline condition of water. Higher alkalinity waters have higher pH. Metal coagulants are commonly acidic, coagulant addition consumes alkalinity. For low alkalinity waters coagulant addition may consume all of the available alkalinity depressing the pH values too low for effective treatment. High alkalinity waters may require high coagulant addition to depress the pH values favorable for coagulation (Edzwald and Van Benschoten, 1990).

The pH at which coagulation occurs is the most important parameter for proper coagulation performance as it affects the surface charge of colloids, the charge of NOM functional group, the charge of the dissolved phase solubility (Yan et al., 2008; Yang et al., 2009; Sharp et al., 2005). For aluminum based coagulants the best coagulation performance is generally seen at pH values that are as close as possible to the pH of minimum solubility of the coagulant. This controls dissolved Al residuals, as well as maximizing the presence of floc particles for adsorption of NOM (Hundt and O’Milia, 1988).

The undertaken work provides guidelines and an explanation of the most suitable coagulant dose that should be used to improve turbidity and NOM removal from water and how pH should be controlled to achieve the maximum removal and to reduce the coagulant dose to the minimum in coagulation process.
2. MATERIALS AND METHOD

The experimental work was executed at Sanitary Engineering Laboratory, Public Works Engineering Department at Faculty of Engineering – Mansoura University, Egypt.

Synthetic raw water was prepared to grantee the homogeneity of used raw water with a specific turbidity and NOM concentrations. Chemicals and equipments used in this work are outlined as follows:

2.1 Organic compound

For simulating of the NOM in natural water, commercial compound of humic and fulvic acids as supplied from Eden Co for Production of Fertilizers, were used. The compound is composed of 68% humic acid, 17% fulvic acid, 15% different materials. It is in the form granular material.

2.2 Turbidity material

Synthetic turbid waters were prepared by using kaolinite particles take the form of pseudo-hexagonal platelets with widths that vary from 10 to 0.1 µm and less, with a chemical structure $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as supplied from Al-Gomhoria Co for Chemicals (Egypt).

2.3 Coagulant

Aluminum sulfate stock solution 1000 mg/L was prepared to develop different alum dose for coagulation process, as supplied from Al-Gomhuria Co for Chemicals (Egypt) with a chemical structure $\text{Al}_2(\text{SO}_4)_3.18\text{H}_2\text{O}$.

2.4 pH adjustment

To develop different pH in acidic zone a stock solution of (27% by weight) hydrochloric acid (HCl) was used. In order to develop different pH in alkaline zone a stock solution of (40 mg/l) sodium hydroxide was used, (as supplied from Al-Gomhuria Co for Chemicals, Egypt).

2.5 Spectrophotometer

UV absorbance at wavelength 254 nm ($\text{UV}_{254}$) was measured by digital spectrophotometer (Unico 2100) with Single Beam, Grating System 1200 lines/mm and 10 mm quartz cell.

2.6 Turbiditymeter

To measure the turbidity (Hanna turbiditymeter HI93703) was used with 10 mm cell.

2.7 Jar test

A six paddle (Phipps& Bird PB-700) standard jar test with variable rotational speed and six 1000 mm jars was used. Every jar loaded with 500 ml sample.

2.8 TOC Analyzer

TOC was determined by subtracting the TIC (total inorganic carbon) from the TC (total carbon) as shown in Fig. 1 (Shi et al., 2009[21]). Using a Multi N/C-3100 analyzer at a burning temperature of 850°C (combustion-supporting gas: oxygen; catalyst: cerium oxide) in conjunction with NDIR (Non-dispersive infrared) detector (Analytik Jena AG Co., Germany), using NPOC mode. Potassium
hydrogen phthalate was used as external standards for TOC quantification with relative standard deviations (SD) of TOC 1%. DOC was determined by TOC analyzer after 0.45 µm Millipore filtration.

2.9 Analytical method

Jar tests were performed using six paddle standard jar test, and the coagulant added while stirring at 140 rpm. When testing samples with only kaolin turbidity the used alum dose ranges from 10 mg/L to 30 mg/L. When testing samples with organic material, the used alum dose ranges from 50 mg/L to 130 mg/L. Jar tests were performed with and without pH control. The pH was targeted from 3 to 8 using a fixed alum dose. The pH was adjusted by adding drops of acid or alkali prior to the addition of coagulant. After 1 minute flash mixing the rotational speed was reduced to 30 rpm for 20 minute. The samples were then allowed to settle for 30 minute. Then NOM concentrations was measured by the spectrophotometer at wavelength 254, and by TOC analyzer. The turbidity was measured by the turbidimeter for different samples. while the specific UV absorbance (SUVA) was calculated by the following equation (Crittenden et al 2005[13]):

\[
SUVA = \left( \frac{100 \text{ cm}^2}{1 \text{ m}^3} \right) \times \left( \frac{\text{UV}_{254}}{\text{DOC}} \right)
\]  

(1)

3. RESULTS AND DISCUSSION

3.1 Turbidity removal

3.1.1 Effect of pH control on high turbidity water
The effect of pH control was investigated by using a synthetic turbid water with initial turbidity of 130 NTU. Five repeated jar tests were performed to determine the optimum dose for this synthetic turbid water with pH 7. Another ten jar tests were performed with synthetic turbid water at pH 5 and pH 6 five for each and the average value was considered. The average value of the optimum dose was found to be 45 mg/L arriving an average minimum residual turbidity of 2.9 NTU for water with pH 7, 1.1 for water with pH 5, and 1.3 for water with pH 6 as indicated on Figs (2,3,4). The effect of varying the pH from 3 to 8 on the turbidity removal is shown on Fig. (5) indicating that the best turbidity removal efficiency was between pH 5 and pH 6. The difference between turbidity removal of neutral water and water at optimum pH is considerable.

3.1.2 Effect of pH control on low turbidity water

The effect of pH control was tested by using a synthetic turbid water with initial turbidity 30 NTU and using optimum alum dose issued from fifteen jar tests, five on neutral water with pH approximately 7, five on synthetic water with pH 5, and five on synthetic water with pH 6 as shown in Figs (6,7,8) which was 25 mg/L. The result as shown in Fig.9 indicate that the best removal efficiency was between pH 5 and pH 6. Fig.9 shows that the difference between efficiency removal at optimum pH and at neutral water was about 0.3 NTU which is not significant.
3.2 NOM removal

3.2.1 Calibration of organic compound concentrations by UV absorbance

The relationship between UV$_{254}$ absorbance and organic material concentrations is linear, as shown in Fig. 4, constituting a basis of conversion of UV$_{254}$ absorbance data to an equivalent of organic material concentrations (as humic acid and fulvic acid), with $R^2=0.998$ and after regression analysis.

$$Y=60.65(\text{UV}_{254}) - 1.84$$  

Where $Y$: Organic material concentrations in mg/L. The removal of organic material concentration projected on UV$_{254}$ absorbance was used to evaluate the removal efficiency in this study.

The linear relationship with good correlation indicates that the UV$_{254}$ is a suitable parameter for studying the removal efficiency of NOM, using the synthetic water contains the organic material mentioned in 2.1.
3.2.2 The effect of pH on NOM removal efficiency

The effect of the solution pH on the removal of natural organic matter during coagulation and flocculation was studied on water with initial organic compound concentration of 30 mg/L at pH values of 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0. The alum dose used was the average optimum dose issued from fifteen jar tests, five on neutral water with pH approximately ≈7, five on synthetic water with pH 5, and five on synthetic water with pH 6 as shown in Figs (11,12,13,14,15,16) which was 100 mg/L. The relation between pH and NOM removal is investigated by five jar tests and measuring the UV$_{254}$ and DOC as shown in Figs (17,18) and SUVA computed from equation (1) as illustrated in table (1) and graphed in Fig (19). The results clarify that the best removal efficiency occurred when adjusting the pH down between 5 and 6 prior to alum coagulant addition which allows the formation of soluble NOM-aluminum complexes that link to each other, thereby forming large insoluble bridged complexes (micro-flocs) that also act as nuclei for macro-floc development (flocculation). However, qualitatively, as pH increases, humic substances will become more ionized because the carboxyl groups will loss protons, and the positive charge on metal coagulants will decrease. Consequently, higher coagulant dosages will be required at higher pH values.
Fig. 13. Effect of alum dose in DOC removal

pH = 5
organic compound = 30 mg/L
initial DOC = 11.53

Fig. 14. Effect of alum dose in UV$_{254}$ removal

pH = 6
organic compound = 30 mg/L
initial UV$_{254}$ = 0.535

Fig. 15. Effect of alum dose in DOC removal

pH = 6
organic compound = 30 mg/L
initial DOC = 11.53

Fig. 16. Effect of alum dose in UV$_{254}$ removal

pH = 6
organic compound = 30 mg/L
initial UV$_{254}$ = 0.535

Fig. 17. Relationship between UV$_{254}$ after coagulation flocculation process and pH

alum dose = 100 mg/L
initial UV$_{254}$ = 0.535

Fig. 18. Relationship between DOC after coagulation flocculation process and pH

alum dose = 100 mg/L
initial DOC = 11.53 mg/L
In order to pinpoint the optimum pH removal five jar tests were performed with different pH ranged from 4.5 to 5.75 with interval of 0.25. The results shown on Figs 8, 9, and 10 show that the optimum pH for the removal of NOM from water is about 5.5.

<table>
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<tr>
<th>pH</th>
<th>test 1</th>
<th>test 2</th>
<th>test 3</th>
<th>test 4</th>
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</table>

Table 1: SUVA computed from equation (1)

![Graph showing relationship between SUVA and pH](image1)

![Graph showing relationship between DOC and pH](image2)

![Graph showing relationship between UV254 and pH](image3)
Table 2: SUVA computed from equation (1)

<table>
<thead>
<tr>
<th>pH</th>
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<th>test 2</th>
<th>test 3</th>
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<td>1.55</td>
</tr>
</tbody>
</table>

### 3.2.3 Theoretical assessment of DOC remaining after treatment

In this work the empirical model developed by (Edwards, 1997[22]) will be applied to assess the DOC remaining after treatment. In the model development it was assumed that DOC is composed of adsorbable and nonadsorbable fraction. According to that, the effluent DOC after the coagulation process is the sum of the nonadsorbable DOC and the adsorbable DOC remaining at equilibrium after coagulation. The absorbable DOC remaining after coagulation was not adsorbed during the coagulation process because it was in equilibrium with the DOC adsorbed on the flocs.

The nonadsorbable DOC is given by the equation

\[
DOC_{\text{nonadsorbable}} = [K_1(SUVA)_{\text{raw water}} + K_2] \times DOC_{\text{initial}}
\]

Where \( K_1 \) and \( K_2 \) are empirical fitting constants and for aluminum coagulants \( K_1 = -0.075 \) and \( K_2 = 0.56 \)

\[
SUVA_{\text{raw water}} = \frac{UV_{254} \times 100}{DOC} = \frac{0.535 \times 100}{11.53} = 4.64 \frac{L}{mg \cdot m}
\]

\[
DOC_{\text{nonadsorbable}} = [-0.075(1.64) + 0.56] \times 11.53 = 2.44 \frac{mg}{L}
\]

To compute the amount of DOC that is in equilibrium (\( DOC_{eq} \)) with the DOC adsorbed to the flocks Langmuir isotherm is used and in the final form of the model, the mass of DOC (mg) adsorbed per meq of coagulant to the amount adsorbed is equated to Langmuir isotherm as follows:

\[
\frac{[1 - K_2(SUVA)_{\text{raw water}} + K_2]}{M} DOC_{\text{initial}} - DOC_{eq} = \frac{x_1 pH^a + x_2 p^b H^a + x_3 p^b pH^a b DOC_{eq}}{1 + b DOC_{eq}}
\]

Where \( x_1, x_2, \) and \( x_3 \) are unitless empirical constants and for aluminum coagulants

\( x_1 = 284, x_2 = -74.2, x_3 = 4.91 \) (according to Edwards 1997)

\( b = \) Langmuir equilibrium constant \( L/mg \) DOC, and for aluminum coagulants \( b = 0.147 \)
M = the molar concentration of alum, M = 0.29 mM

Rearrange the last equation with substituted variable and develop an expression for \( \text{DOC}_{eq} \):

\[
\frac{A - \text{DOC}_{eq}}{M} = \frac{B}{1 + b} \text{DOC}_{eq}
\]

Solving the quadratic equation and use the positive expression:

\[
\text{DOC}_{eq} = \frac{- (M B + 1 - A b) + \sqrt{ (M B + 1 - A b)^2 + 4 A b}}{2 b}
\]

Substitute the constant values and solve for A and B:

\[
A = [1 - K_{SVUVA}]_{\text{raw water}} + K_2 \text{DOC}_{\text{initial}} = 9.086
\]

\[
b = [x_s pH^3 + x_{q2} pH^2 + x_{q4} pH]b
\]

Substitute the values of A and B into the equation to get \( \text{DOC}_{eq} \), then compute the predicted remaining DOC by the following equation:

\[
\text{DOC}_{\text{remaining}} = \text{DOC}_{\text{nonadssorbed}} + \text{DOC}_{eq}
\]

The results of predicted remaining DOC after treatment with variant pH are illustrated in tables (3). The results clarify that the mathematical model is considerably to be applicable on pH ranges from pH 5 to pH 7, while when the pH of raw water is below 3 or above 7 it is difficult to predict the remaining DOC after treatment by this model. The results of predicted remaining DOC for the pinpoint tests from pH 4.5 to pH 5.75 are illustrated in table (4) showing that the mathematical model is extremely applicable with minimum standard deviation between the predicted value and the average value from the test.

### Table 3: relation between predicted values and actual

<table>
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<th>pH</th>
<th>DOC(_{eq}) mg/L</th>
<th>DOC remaining mg/L</th>
<th>Average actual DOC remaining mg/L</th>
<th>Standard deviation</th>
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Table 4 relation between predicted values and actual values

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4. CONCLUSION

For low turbidity water there is no need to make any adjustment for the pH of raw water because the difference in removal of turbidity at optimum pH and at neutral water is not significant and doesn’t deserve the efforts of controlling the pH in water treatment plant. While for high turbidity water controlling the pH of raw water is more effective in turbidity removal and may be applied in water treatment plants according to the nature of raw water in these plants and according to considerable number of jar tests to these water because the optimum pH may becomes different on each type of water.

Effective removal of natural organic matter from low turbidity water can be achieved by aluminum based coagulants to make micro-floc formation (coagulation) followed by macro-floc formation (flocculation). The pH adjustment for raw water contains NOM is clear to be significant, and deserves the efforts of controlling the acidity of raw water specially in high capacity water treatment plants.

In this work the laboratory results of DOC removal were matching to the empirical model of Edwards (1997) in the range from pH 5 to pH 7 and this means that is applicable in the future to the raw water used in this work.

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