STUDY OF THE EFFECT OF FERRIC CHLORIDE CONCENTRATIONS AND pH ON ORGANIC MATTAR REMOVAL PERCENTAGE IN AL-DEWANYIA WATER TREATMENT PLANT

Dr. Ali H. Ghawi

Department of Civil Engineering, Al-Qadisiyia University,
E-mail: ghawi2000@yahoo.com

ABSTRACT

Supplying drinking water in Al-Dewanyia city to meet Iraqi Drinking Water Guidelines is a challenge as source waters contain high concentrations of Natural Organic Matter (NOM) that often exceed 12 mg/L Dissolved Organic Carbon (DOC). The US EPA indicates that enhanced coagulation is the best available technology to control DOC in drinking water treatment plants. A water director of Al-Qadissiya has used enhanced coagulation at Al-Dewanyia Water Treatment Plants (WTP's) in Iraq since 2004 to improve water quality in the distribution system. NOM reduction has led to treated water with a lower chlorine demand allowing a greater residual penetration enabling improved bacteriological compliance. Since the cost of DOC (and Disinfection by-product 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 water samples studied belonged to Al-Dewanyia River. For samples the observed values of COD removal by coagulation at lower pH (about 1-1.5 pH values less than the regular pH (5.8 ~ 8.5)) were about 85-95 percent without making water turbidity unacceptable. In order to determine the effects of organic content on coagulation, The results indicated that a modified coagulation process without need to much increasing the amount of coagulant can be developed for these water samples.

Keyword: Water Quality, WTP, DOC, COD, NOM.

دراسة تاثير كلوريد الحديديك و الاس الهيدروجيني على نسبة الازالة للمواد العضوية في محطة معالجة مياة الشرب في الديوانية

د.علي هادي غاوي
مدرس
جامعة القادسية
كلية الهندسة

الخلاصة

ان عملية تجهيز الماء الصالح للشرب و المطابق للمواصفات العراقية في مدينة الديوانية يعتبر تحدي كبير وذلك لان

مصدر مياة الشرب يحتوي على مواد عضوية مثل المواد العضوية الذائبة عالية التركيز بحيث يتجاوز تركيزها 12 ملغ\ لتر. منضمة حماية البيئة العالمية أوصت باستخدام المواد المخثرة لإزالة المواد العضوية في الماء. تم استخدام مواد مخثرة محسنة في محطات تصفية مياة الشرب في مدن العراق ومنها مدينة الديوانية منذ عام 2004 لغرض تحسين نوعية الماء في شبكات توزيع المياه. ان تقليل تركيز المواد العضوية في المياه يؤدي الى تقليل كمية الكلور المضاف وبتالي سيتبقى كلور كافي لقتل البكتريا. ان عملية ايجاد المواد العضوية الذائبة مكلف لذلك تم أيجاد طريقة غير مكلفة و بسيطة بتحليل المتطلب الكيمياوي للاوكسجين لاكتشاف المواد العضوية الذائبة و استخدام كلوريد الحديد كمادة مخثرة لإزالة المواد العضوية. تم اخذ العينات من نهر الديوانية المغذي لمحطات تصفية المياة في مدينة الديوانية. وجد انة نسبة الإزالة للمواد العضوية تتراوح من 85–95% عند قيم الأس ألحامضي اقل 1– 1.5 مرة اقل من قيم الأس ألحامضي الاعتيادي والتي تتراوح بين 5.8 – 8.5 بحيث يضمن حصول عكورة ضمن المواصفات المطلوبة. أثبتت النتائج ان تحسين عملية التخثير في محطات المعالجة بدون زيادة كمية المادة المخثرة يمكن ان يعطي اداء أفضل لوحدات تصفية المياه.

INTRODUCTION

Al- Dewanyia Water Treatment Plant in Iraq (DWTP) was built in 1983. The untreated water is pumped from the Al-Dewanyia River to the DWTP by five large pumps and is then dispatched into flash mixer. The water then flows through a four calriflaculaters (flocculation, and sedimentation tank) and filtered through a sand bed (20 units) as shown in **Fig.** 1. After chlorination, the water is stored in two underground reservoirs (clear well). Five booster pumps, connected to the last reservoir, ensure the water supply in the Al- Dewanyia city network.

Providing cleaner water to the consumers also reduced maintenance demands as less routine flushing is required of the mains reticulation system. The higher turbidity levels previously resulted in sludge build up in the mains which reduced the quality of the water that reached the consumers and also affected the chlorine residual levels throughout the reticulation system. In Al-Dewanyia in Iraq, the DWTP, meeting seasonal water demands, provides water to the city, and some villages around, supplying around 96 000 m^3/day serving about 300 000 consumers. The water to the Al-Dewanyia city comes from the Al-Dewanyia River (**Fig. 2**) source and treatment in the Water treatment plant. As it is typical of the rivers of the Iraq, the flow is very irregular, having a high flow place in the months of December to April and a Low flow in the remain months.

The surface water from Al-Dewanyia River very often contains suspended clay, sand and lime particles, various organic dissolved solids, heavy metal and other materials, which manifest themselves as turbidity, dissolved solids and other chemical parameters. This water has to be treated properly to make it suitable for drinking and domestic use. Raw surface and ground waters used for drinking purposes can vary markedly in their chemical organic content (natural organic matter and anthropogenic compounds, including pollutants) and micro-organisms present in raw water are key drivers for treatment processes that provide for safe and aesthetically acceptable drinking water. Conventional treatment at large scale water treatment plants (WTP) involves the use of inorganic coagulants to remove turbidity and colour, and more recently to maximize removal of organic compounds. The basis for the latter is to minimize the concentration of organics in treated water that leads to lower levels of disinfection by-products (post chlorination) and substrates for microbial growth in the water distribution system. Maximizing removal of organic matter using inorganic coagulants is impacted by the character and concentration of the organics, the turbidity and alkalinity of the raw water. Removal of organics is also influenced by the type of coagulant used, its dose rate and the pH at which coagulation occurs. To date, few attempts have been made to study the relationships between raw water quality parameters and the use of coagulants and pH control reagents for removal of organics, colour and turbidity. Study of water treatment processes have been described by Bazer-**Bachi et al. [1], Ellis et al. [2], Girou et al. [3], Ratnaweera and Blom [4] and van Leeuwen et al. [5].** These studies are mostly based on empirical relationships between raw and treated water quality and treatment conditions required to achieve a target water quality. The emphasis for removal of organics is recent and models developed for and relating to this include **Edwards [6], Urfer et al. [7], Baxter et al. [8], Ghaly,. [9] and Guida et al. [10].**

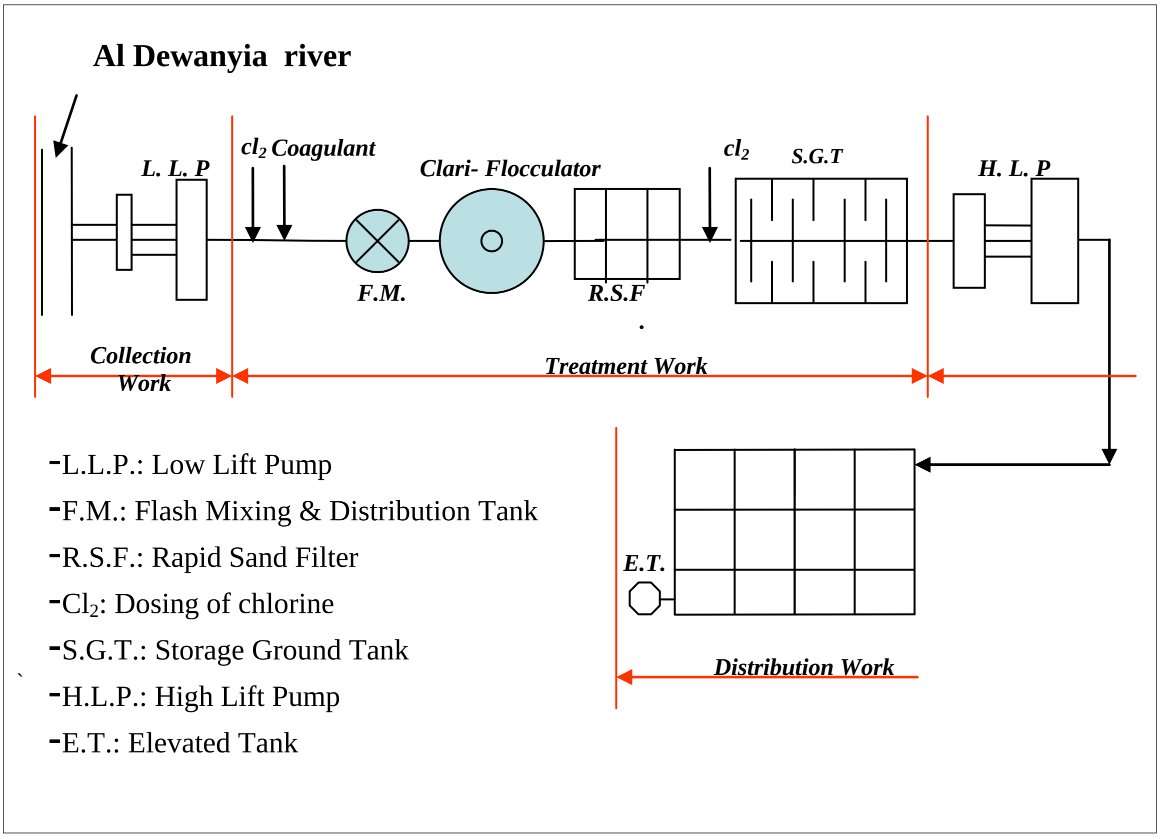

Fig. 1. Al-Dewanyia WTP layout

Al-Dewanyia River, with high density of residence located on both sides the use its water for drinking. **Fig. 3** and **Table 1** show seasonal characteristics of water quality in Al-Dewanyia River in 2010. Target compounds in Al-Dewanyia River are algae, taste & odor matter, Natural Organic Matter (NOM), disinfection by-products (DBPs) and micro pollutants. **Table 2** shows the comparison of water quality criteria between Iraq and US.EPA. Especially, domestic water quality is minimal requirement to meet present regulation, but drinking water treatment process is practically managed to meet the target water quality value which considered the reinforced water quality criteria and target compound concentration in Al-Dewanyia River. This paper reviews improvement strategies adopted at Iraq water operated conventional water treatment plants to meet Iraqi national water quality requirements. Also in this paper, Jar Test is described that relate raw water quality parameters to dose rates of the coagulants, ferric chloride, and pH control reagents. Also described is a study that relate the concentration and character of organics in raw water to targeted percentage removal of organics.

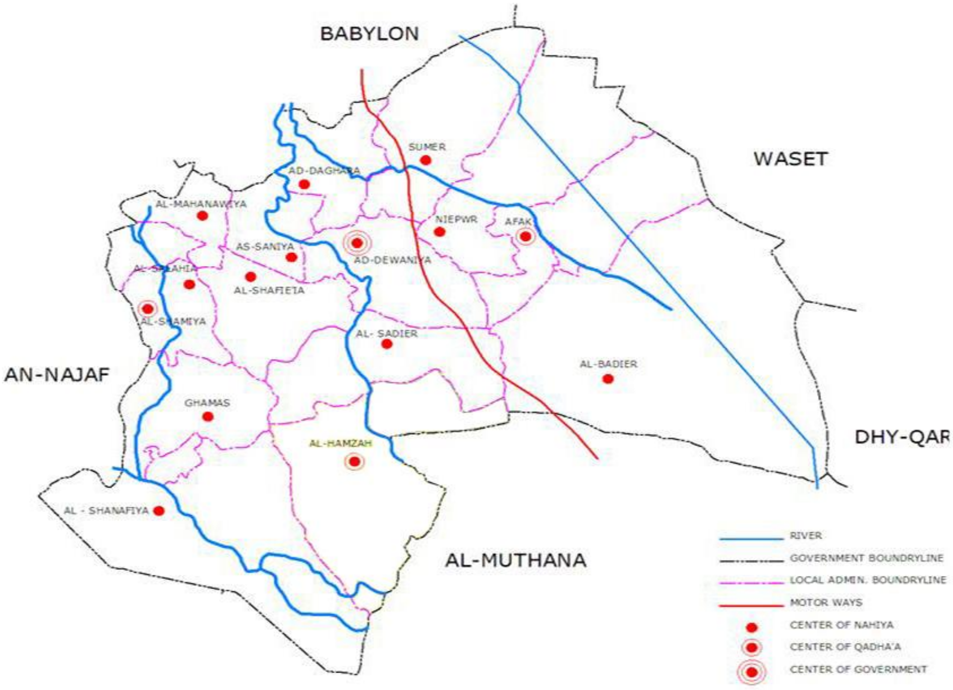

Fig. 2. Al-Dewanyia Rivers Map

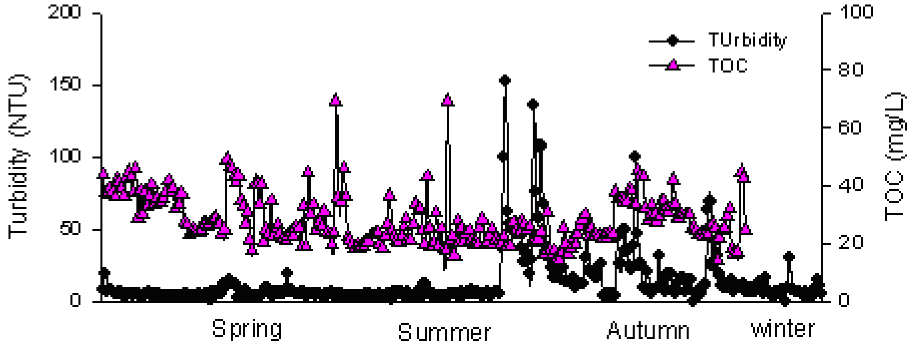

Fig. 3. Seasonal Characteristics of Raw Water Collected from Al-Dewanyia River In 2010

Table 1. Seasonal Characteristics of Water Quality and Limitation of Water Treatment

Season	Water Quality Pattern	Limitation
1~3 month	NOM ↑, Micro Organic Pollutants↑	Mixing/Coagulation Performance Decrease
3~6 month	Algae ↑, Taste & Odor Matter ↑ pH ↑, Residual Chlorine Conc. ↑	DBPs ↑ (Chlorine Dose Increase) Mixing/Coagulation Performance Decrease
6~9 month	Turbidity ↑ Alkalinity ↓	Filtration Bachwashing Interval Decrease Coagulant and pH Controller Increase
9~12 month	Algae ↑ NOM ↑, DBPs ↑	DBPs ↑ (Chlorine Dose Increase) Claim ↑(Taste & Odor Matter)

Table 2. Comparison of Water Quality Criteria between Iraq and US.EPA **[11]**

Items		**Water Quality Criteria- Iraq**	**Water Quality Target Value**	**US.EPA Criteria**
Taste & Odor	Sensory Evaluation	No Taste/Odor	<3TON	<3TON
	Geosmin, MIB	-	<10ng/L	-
Pathogenic Microbes	Giardia	3 log	5 log	5 log
	Cryptosporidium	-	3.5 log	3 ~ 3.5 log
	Turbidity	5 NTU	0.1NTU	0.1NTU
	Particles	-	50/mL	-
Disinfection By-Products (DBPs)	TOC	-	35% Removal	15 ~ 50% Removal
General Items	NH4+	0.5mg/L	0.5mg/L	-
	Fe	0.3mg/L	0.3mg/L	0.3mg/L
	Mn	0.3mg/L	0.05mg/L	0.05mg/L
	pH	5.8 ~ 8.5	7.5 ~ 8.0	6.5 ~ 8.5

MATERIAL AND METHODS

.

Determination of Water Quality Parameters

Colour: Colour (Col), in Hazen units (HU) was determined by measuring the absorbance at 456 nm using UV/VIS spectrophotometer.
Dissolved organic carbon (DOC) analysis: DOC concentrations of water samples (filtered through 0.45 μm) were determined using a total carbon analyser (Model 820, Sievers Instruments Inc., USA) and indirectly by measuring the absorbance at 254 nm using a UV/VIS spectrophotometer with a 1 cm quartz cell.
Turbidity: Turbidity, in nephelometric turbidity units (NTU), was measured using a Hach ratio turbidimeter (Model 2100 AN, Co., USA).
pH: Orion (Model 420A, MA. USA) and WTW pH 340i meters were used.

All instruments located in laboratory of Civil Department in Collage of Engineering Al-Qadissiya University.

Samples

Samples were collected from Al-Dewanyia River during one year in 2010 from Al-Dewanyia River and influent to Al-Dewanyia Water Treatment Plant. Totally ten raw water samples were collected randomly as grab samples. These waters varied in DOC concentration, alkalinity and turbidity.

Coagulant Dose Determination Using Jar Tests.

Jar tests were performed on Al-Dewanyia River water samples (high in turbidity) mixed with other natural waters (low in turbidity) to determine the ferric chloride demand exerted by the turbidity. The coagulants, ferric chloride ($FeCl_3$) were used in jar tests (**Fig. 4**).

Fig. 4. Jar test instrument

A bench-scale jar-testing program that mimicked full-scale operating conditions in Al-Dewanyia 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 **[10].** 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. Curves of pH titrations of raw waters using coagulants and sulphuric acid were determined as described **[10].**
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 **[12].** 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 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.. 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. **Table 3** represents the variation in COD and Turbidity for Water Samples from WTP and River at Different pH

Table 3: Variation in COD and Turbidity for Water Samples from WTP and River at Different pH

pH / Parameter	Sample 1						
	8^x	4.1	5.1	6.1	7	8	10.1
COD mg\l	14.5	4.7	13.6	12.1	2.4	1.8	3.3
Turbidity NTU	130	22	14	2	0.8	1	0.97
pH / Parameter	Sample 2						
	7.5^x	4.4	5.5	6.4	7	7.6	9.1
COD mg\l	40	35	21.6	28.3	17.1	19.4	27.3
Turbidity NTU	40	4.7	3.1	2.3	1.8	2.1	2
pH / Parameter	Sample 3						
	7.5^x	4.4	5.5	6.4	7	7.6	9.1
COD mg\l	22.5	11.7	6.6	7.1	1.4	8.8	7.3
Turbidity NTU	37	30	1.4	1.32	0.6	3.1	0.97
pH / Parameter	Sample 4						
	7.5^x	4.4	5.5	6.4	7	7.6	9.1
COD mg\l	26.5	11.7	7.6	6.1	1.4	8.8	7.3
Turbidity NTU	28	2.7	1.4	1.2	0.5	2	1.97
pH / Parameter	Sample 5						
	7.8^x	4.7	5.9	9.1	10.1	-	-
COD mg\l	15.5	24.7	2.6	2.1	3.4	-	-
Turbidity NTU	15	5.7	0.95	0.7	2.8	-	-

pH / Parameter	Sample 6						
Parameter	8^{x}	6.1	7.1	8.1	10	-	-
COD mg\l	14.8	1.7	3.6	6.1	8.4	-	-
Turbidity NTU	5	1.0	0.9	1.7	2.8	-	-
pH / Parameter	Sample 7						
Parameter	7.5^{x}	4.4	5.5	6.4	7	7.6	9.1
COD mg\l	40	35	21.6	28.3	17.1	19.4	27.3
Turbidity NTU	50	5.7	3.1	2.3	2.8	2.1	2
pH / Parameter	Sample 8						
Parameter	7.5^{x}	4.4	5.5	6.4	7	7.6	9.1
COD mg\l	28.5	15.7	6.3	7.1	2.4	8.8	7.3
Turbidity NTU	90	35	4.4	3.32	1.6	3.1	1.97
pH / Parameter	Sample 9						
Parameter	8^{x}	7.4	8.5	9	-	-	-
COD mg\l	16.5	11.7	12.6	12.1	-	-	-
Turbidity NTU	58	1.7	1.74	1.2	-	-	-
pH / Parameter	Sample 10						
Parameter	7.8^{x}	5.4	6.5	7.4	8.5	9.6	10.6
COD mg\l	12	1.7	1.9	4.1	7.1	7.3	11.3
Turbidity NTU	45	22	0.9	1.7	1.8	1	0.88

RESULTS AND DISCUSSIONS

Graph showing the relationship between turbidity, pH, alkalinity, organic matter and coagulant dose with time shown in **Figure 5**. Turbidity, pH, Coagulant dose, tends to decrease (**Fig. 2b 2c, and 2e**). As for alkalinity, and organic matters slightly tends to increase (**Fig. 2a** and **2d**).

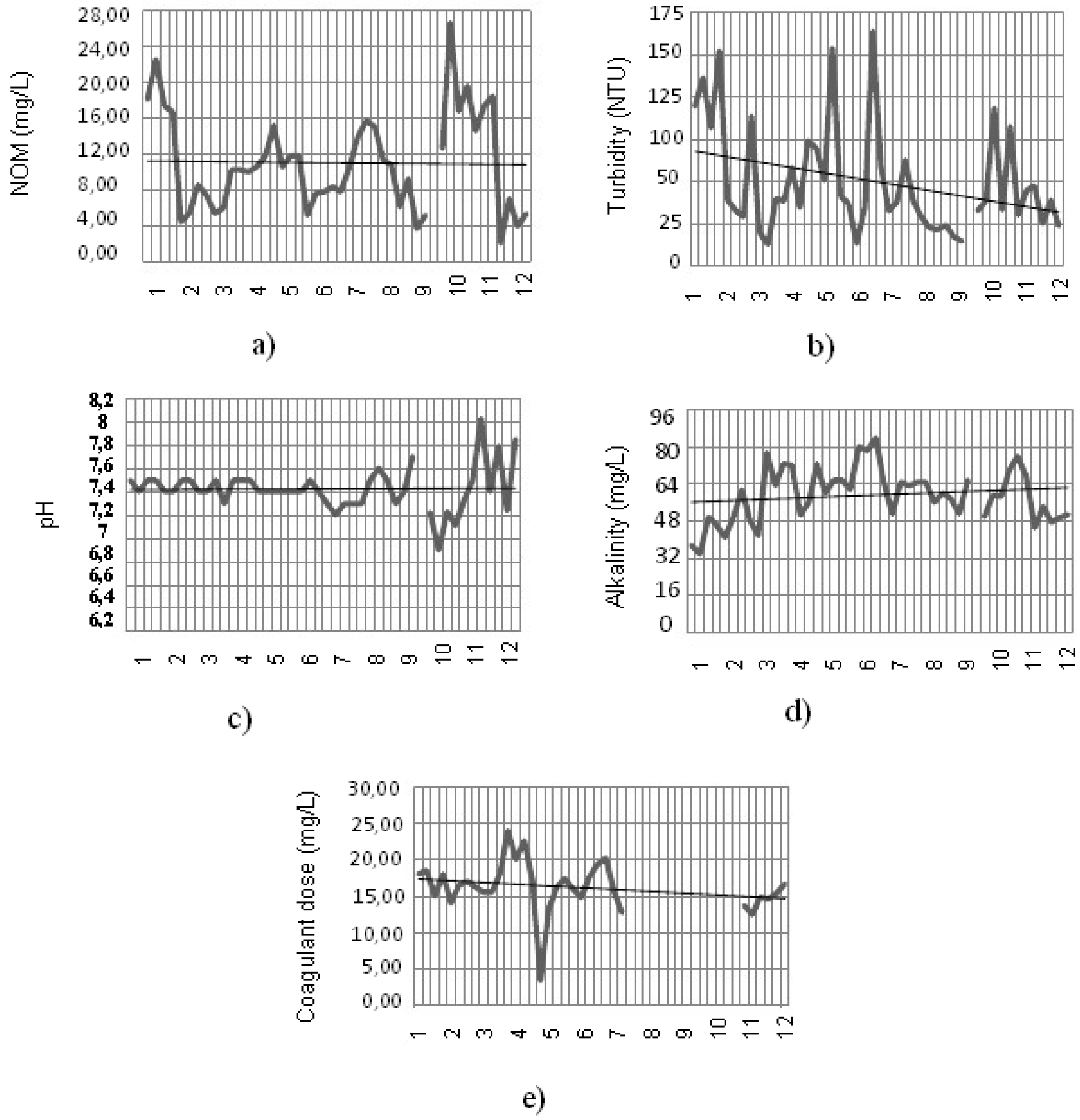

Figure 5. Relations between time and (a) coagulant dose, (b) turbidity, (c) pH, (d) alkalinity, and (e) organic matters

Figures 6 and **7** summarize the jar-testing results for improved coagulation conditions of water samples from Al-Dewanyia River and influent to Al-Dewanyia Water Treatment Plant by ferric chloride for each pH of treatment. These tests were conducted using constant coagulant dosage (11 mg/L and 19 mg/L $FeCl_3$, respectively) with varied pH of treatment **[7].** 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.

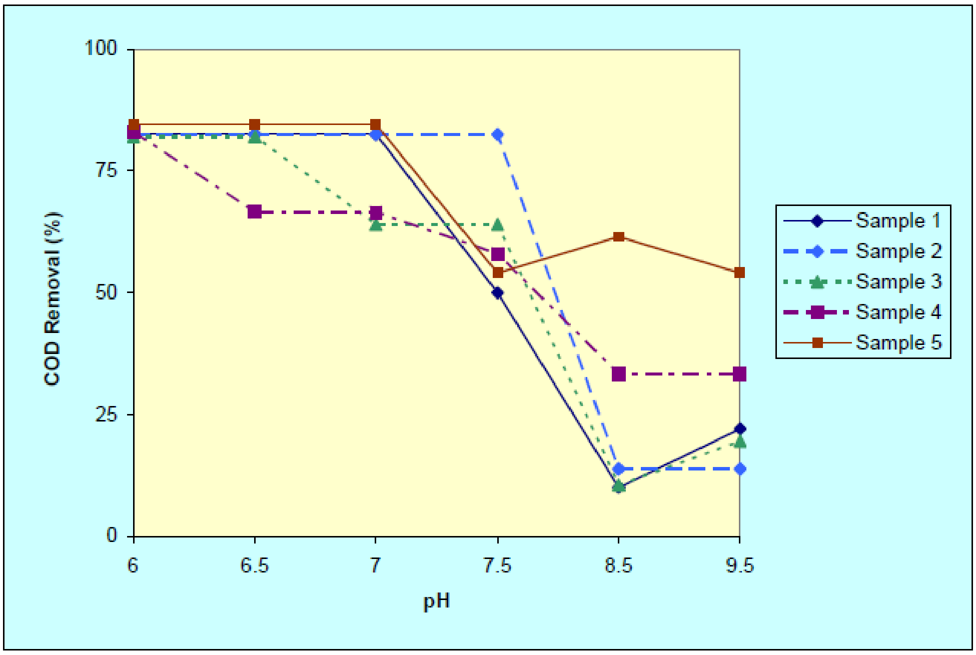

Fig. 6. Removal percentage of organic matter in various pH of water coagulation with 11 mg/l ferric Chloride**, (samples from River)**

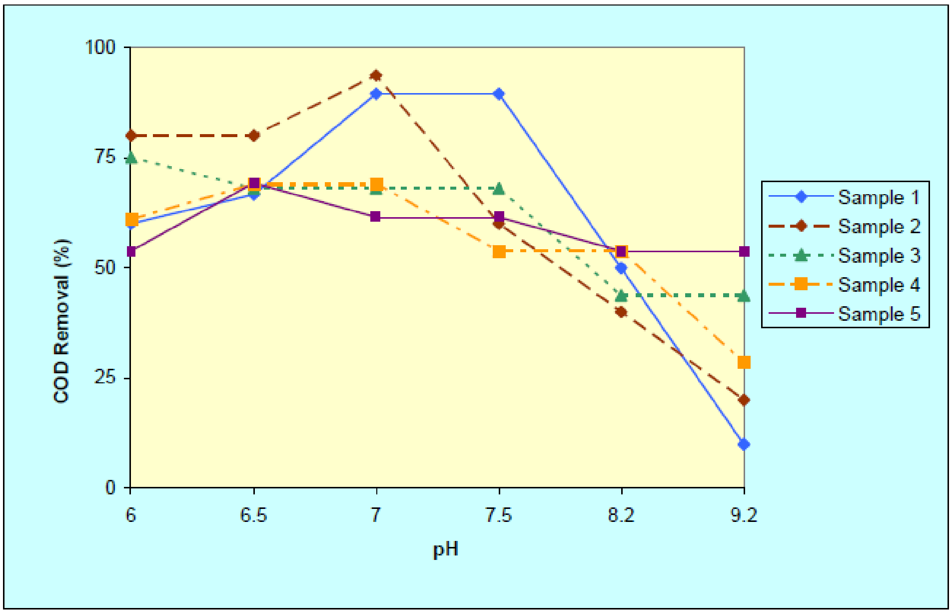

Fig. 7. Removal percentage of organic matter in various pH of water coagulation with 19 mg/l ferric chloride, **(samples from Water Treatment Plant)**

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. 6** and **7**, 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 9 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 Al-Dewanyia 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 Al-Dewanyia might be better coagulated in pHs less than the position source (water treatment intake), and without need to much increase in coagulant dose and subsequent sludge increase.

CONCLUSIONS

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 level (maximum increase to be 0.5 NTU and for all treated samples turbidity values were remained less than 2.5 NTU).. 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. 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 Al-Dewanyia water samples at less pH with ferric chloride. The results indicated that a modified coagulation process without need to much increasing the amount of coagulant can be developed for these water samples.

ACKNOWLEDGEMENTS

The author wish to thank the Al-Dewanyia Water Treatment Plant staff for accessing to the required data.

REFERENCES

1. Bachi, A., E. Puech-Coste, R. Ben Aim and J.L. Probst. Mathematical modelling of optimum coagulant dose in water treatment plant, Revue Des Sciences De L'eau. 3,

377-397, 1990.

2. Ellis, G.W., A.G. Collins, Xi Ge and C.R. Ford Chemical dosing of small water utilities using regression analysis, J. Environ. Engng. 117(3), 308-319, 1991.
3. Girou, A., M. Franceschi, E. Puech-Costes and L. Humbert. Modelisation des phenomenes de coagulation et etude de la morphologie des flocs : optimisation du taux de coagulant, Recents Prog. Genie Procedes 6(20), 373-385, 1992.
4. Ratnaweera, H., and H. Blom. Optimisation of coagulant dosing control using real-time models selective to instrument errors, Water Supply 13(3/4), 285-289, 1995.
5. van Leeuwen, J., C.W.K. Chow, D. Bursill and M. Drikas. Empirical mathematical models and artificial neural networks for determination of alum doses for treatment of southern Australian surface waters, J. Water SRT-Aqua 48(3) 115-127, 1999a.
6. Edwards, M. Predicting DOC removal during enhanced coagulation. J. AWWA 89(5) 78-89. 2003.
7. Urfer, D., P. M. Huck, G. A. Gagnon, D. Mutti and F. Smith. Modeling enhanced coagulation to improve ozone disinfection, J. AWWA. 91(3) 59-73, 1999.
8. Baxter, C. W., Stanely, S. J. and Zhang, Q. Development of a full-scale artificial neural network model for the removal of natural organic matter by enhanced coagulation. J Water SRT – Aqua 48(4) 129-136, 1999.
9. Ghaly, A.E., A. Snow and B.E. Faber. 2007. Effective coagulation technology for treatment of grease filter washwater. Am. J. Environ. Sci., 3: 19-29. DOI: 10.3844/ajessp.2007.19.29
10. Guida, M., M. Mattei, C. Della Rocca, G. Melluso and S. Meric,. Optimization of alumcoagulation/ flocculation for COD and TSS removal from five municipal wastewater. Desalination, 211: 113-127. DOI: 10.1016/j.desal.2007.02.086
11. United States Environmental Protection Agency. Office of Water. January, National Water Quality Inventory: Report to Congress Reporting Cycle. EPA 841-R-08-001. Washington, DC. 2009.
12. APHA, AWWA, WPCF,. Standard Methods for the Examination of Water and Wastewater, APHA, 19th Ed, Washington. 1995.