MARMARA UNIVERSITY

INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

REMOVAL OF ORGANIC MATTER IN O_3 APPLICATION PRIOR TO PARTICLE AGGREGATION

SERDAR ŞAM

Ph.D. THESIS

Department of Environmental Engineering

Thesis Supervisor

Prof. Dr. Zehra Semra CAN

ISTANBUL, 2025

MARMARA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

Marmara Üniversitesi Fen Bilimleri Enstitüsü Doktora Öğrencisi Serdar ŞAM'ın "Partikül agregasyonu öncesi O_3 uygulamasında organik madde giderimi" başlıklı tez çalışması, 22 Temmuz 2025 tarihinde savunulmuş ve jüri üyeleri tarafından başarılı bulunmuştur.

Jüri Üyeleri

Prof.Dr. Adı SOYADI (Danışman)
Marmara Üniversitesi ..... (İMZA).....

Doç.Dr. Adı SOYADI (Üye)
Marmara Üniversitesi ..... (İMZA).....

Dr. Öğr. Üyesi Adı SOYADI (Üye)
Marmara Üniversitesi ..... (İMZA).....

Dr. Öğr. Üyesi Adı SOYADI (Üye)
Marmara Üniversitesi ..... (İMZA).....

Dr. Öğr. Üyesi Adı SOYADI (Üye)
Marmara Üniversitesi ..... (İMZA).....

ONAY

Marmara Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun ...../...../2025 tarih ve …..... sayılı kararı ile Serdar ŞAM'ın Çevre Mühendisliği Anabilim Dalı Çevre Mühendisliği Programında Doktora derecesi alması onanmıştır.

Fen Bilimleri Enstitüsü Müdürü

Prof. Dr. Bülent MERTOĞLU

MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES IN PURE AND APPLIED SCIENCES

Serdar ŞAM, a Doctor of Philosophy student of Marmara University Institute for Graduate Studies in Pure and Applied Sciences, defended his thesis entitled "Removal of organic matter in O_3 application prior to Particle Aggregation", on July 22, 2025 and has been found to be satisfactory by the jury members.

Jury Members

Prof.Dr. Adı SOYADI (Advisor)
Marmara University ..... (SIGN).....

Assoc.Prof. Adı SOYADI (Jury Member)
Marmara Üniversitesi ..... (SIGN).....

Assist.Prof. Adı SOYADI (Jury Member)
Marmara Üniversitesi ..... (SIGN).....

Assist.Prof. Adı SOYADI (Jury Member)
Marmara Üniversitesi ..... (SIGN).....

Assist.Prof. Adı SOYADI (Jury Member)
Marmara Üniversitesi ..... (SIGN).....

APPROVAL

Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Serdar ŞAM be granted the degree of Doctor of Philosophy in Department of Environmental Engineering, Environmental Engineering Programme on August …., 2025. (Resolution no: ….....…..).

Director of the Institute

Prof. Dr. Bülent MERTOĞLU

ACKNOWLEDGEMENT

I would like to thank my advisor Prof. Dr. Zehra Can and my professor Prof. Dr. Mehmet Ali Yukselen for all the help they have given, also my jury member professors for their valuable times, contributions and guidances, and my wife and family for their existences in my life.

TABLE OF CONTENTS

ÖZET iv

ABSTRACT vi

CLAIM FOR ORIGINALITY viii

LIST OF FIGURES xi

1. INTRODUCTION 1

1.1. Organic Matter 1

1.2. Stabilisation and Destabilisation of Organic Matter 3

1.3. Removal of Organic Matter 4

1.4. Flocculation of Organic Matter 5

1.5. Factors Affecting Organic Matter Flocculation 7

1.6. Hydrolysing Metal Salt Coagulants 9

1.7. Effect of Ozonation on Organic Matter Flocculation 13

1.8. Floc Structure, Breakage and Reformation 17

1.9. Aim of This Investigation 21

2. MATERIALS & METHODS 23

2.1. Methodology 23

2.2. Preperation of Raw Waters Used in Jar Tests 24

2.3. $CaCO_3$ Preparation for Hardness Adjustment 24

2.4. $NaHCO_3$ Preparation for Alkalinity Adjustment 24

2.5. Coagulants 24

2.6. Apparatus 25

2.7. Procedure 28

3. RESULTS & DISCUSSION 33

3.1. Determination of Optimum Coagulant Doses 33

3.1.1. Optimum $Al_2(SO_4)_3$ dose 33

3.1.2. Optimum polyaluminium chloride dose 39

3.2. The Effect of Humic Acid Concentration 40
3.2.1. Experiments with unozonated synthetic raw waters (0 mg/L O_3) 40
3.2.1.1. Experiments with $Al_2(SO_4)_3$ 40
3.2.1.2. Experiments with polyaluminium chloride (PACl) 42
3.2.1.3. Comparison of floc sizes 44
3.2.1.4. Organic carbon removal with $Al_2(SO_4)_3$ 46
3.2.1.5. Organic carbon removal with polyaluminium chloride (PACl) 50
3.2.2. Experiments with 2.5 mg/L pre-ozonated synthetic raw waters 57
3.2.2.1. Experiments with $Al_2(SO_4)_3$ 57
3.2.2.2. Experiments with polyaluminium chloride 59
3.2.2.3. Comparison of floc sizes 61
3.2.2.4. Organic carbon removal with $Al_2(SO_4)_3$ 63
3.2.2.5. Organic carbon removal with polyaluminium chloride (PACl) 66
3.2.3. Experiments with 5 mg/L pre-ozonated synthetic raw waters 73
3.2.3.1. Experiments with $Al_2(SO_4)_3$ 73
3.2.3.2. Experiments with polyaluminium chloride (PACl) 75
3.2.3.3. Comparison of floc sizes 77
3.2.3.4. Organic carbon removal with $Al_2(SO_4)_3$ 79
3.2.3.5. Organic carbon removal with polyaluminium chloride (PACl) 82
3.2.4. Experiments with 10 mg/L pre-ozonated synthetic raw waters 88
3.2.4.1. Experiments with $Al_2(SO_4)_3$ 88
3.2.4.2. Experiments with polyaluminium chloride (PACl) 90
3.2.4.3. Comparison of floc sizes 92
3.2.4.4. Organic carbon removal with $Al_2(SO_4)_3$ 94
3.2.4.5. Organic carbon removal with polyaluminium chloride (PACl) 97
3.3. The Effect of Pre-ozonation Dose 104
3.3.1. Experiments with $Al_2(SO_4)_3$ 104
3.3.1.1. Experiments with synthetic raw waters containing 5 mg/L humic acid .. 104
3.3.1.2. Experiments with synthetic raw waters containing 10 mg/L humic acid 107

3.3.1.3. Experiments with synthetic raw waters containing 20 mg/L humic acid 110
3.3.2. Experiments with polyaluminium chloride (PACl) 114
3.3.2.1. Experiments with synthetic raw waters containing 5 mg/L humic acid .. 114
3.3.2.2. Experiments with synthetic raw waters containing 10 mg/L humic acid 117
3.3.2.3. Experiments with synthetic raw waters containing 20 mg/L humic acid 120
3.3.3. Comparison of floc sizes 123
3.3.4. Organic carbon removal with $Al_2(SO_4)_3$ 128
3.3.4.1. Removals in synthetic raw waters containing 5 mg/L humic acid……128
3.3.4.2. Removals in synthetic raw waters containing 10 mg/L humic acid…....132
3.3.4.3. Removals in synthetic raw waters containing 20 mg/L humic acid…....136
3.3.5. Organic carbon removal with polyaluminium chloride (PACl)……..……140
3.3.5.1. Removals in synthetic raw waters containing 5 mg/L humic acid…..….140
3.3.5.2. Removals in synthetic raw waters containing 10 mg/L humic acid…..…144
3.3.5.3. Removals in synthetic raw waters containing 20 mg/L humic acid…..…148
4. CONCLUSION…….....…….157
REFERENCES 163
APPENDIX……...180

ÖZET

PARTİKÜL AGREGASYONU ÖNCESİ O_3 UYGULAMASINDA ORGANİK MADDE GİDERİMİ

Organik madde içeren suların arıtımı için proses seçenekleri iyi saptanmış ve anlaşılmıştır. Bununla birlikte çoğu arıtma tesisinde (özellikle alkalinitesi düşük, Spesifik UV Absorbansı-SUVA'sı yüksek suları arıtanlarda), yılın çeşitli dönemlerinde ağır yağış ve eriyen kar sularından ötürü organik madde yüklenmelerinde artış gözlenmektedir. Çözünmüş organik karbon (ÇOK) yükü yüksek olan bu dönemlerde, arıtma tesislerindeki su kalitesi ÇOK, renk ve trihalometan (THM) oluşturma potansiyeli (THMOP) bakımından hızla düşmektedir.

Suda bulunan partiküllerin büyüklüğü, yoğunluğu ve sağlamlığı, fiziko-kimyasal arıtma işlemleriyle kirleticilerin giderilmesinde büyük rol oynamaktadır. Genellikle flok olarak adlandırılan bu partiküller, su kaynaklarının çoğunda bulunan askıdaki katılarla ve/veya organik maddeyle anorganik koagülantların tepkimesi sonucu meydana gelmektedir. Temel katı ayrıştırma işlemleri, suya göre yoğunlukları ve büyüklükleri fazla olan bu flokların bertarafına dayanmaktadır. Bu nedenle yoğunluk ve büyüklükteki değişimler flok bertarafını ve dolayısıyla adsorbe olmuş organik maddelerin giderimini etkiler. Organik madde yükünün yüksek olduğu dönemlerde çöktürme ve yüzdürme işlemlerinde başarısızlıklara sebep olan zayıf flokların oluştuğu gözlemlenmiştir.

Ozon, 1970'lerden bu yana su ve atıksu arıtımında dezenfeksiyon, dezenfeksiyon yan ürünlerinin (DYÜ) oluşumunun kontrolü, demir ve mangan oksidasyonu, tat, renk ve koku azaltılması amacıyla kullanılmaktadır. Doğal organik maddenin (DOM) ozonlanması yapısında büyük değişikliklere sebep olmaktadır. Bu sebeple, okside olmuş DOM koagülasyon/flokülasyon prosesinde farklı davranış sergiler. Ön ozonlamanın organik maddenin flokülasyonunu ve giderimini etkilediğini bildiren çokça çalışma bulunmasına rağmen literatürde birbiriyle çelişen pekçok sonuç yeralmaktadır. Kimi çalışmalar, ozonlamanın organik madde giderimini olumsuz etkilediğini söylerken kimi çalışmaların sonuçları da tam tersini

göstermiştir. Bazı çalışmalar ise, etkinin çalışılan şartlara göre değiştiğini bildirmiştir. Literatürde bu kadar farklı sonucun yeralmasının sebebinin çalışılan su örnekleri olduğu düşünülmektedir. Literatürdeki çalışmalar gerçek doğal sularla gerçekleştirilmiştir. Oysa, DOM'un yapısı ve özellikleri bölgesel ve mevsimsel olarak önemli farklılıklar gösterebilmektedir. Bu nedenle, bu çalışmada önerilen gibi, bütün şartların kontrollü tutulduğu bir çalışma, ozonlamanın organik madde giderimine etkisini daha genel sonuçlarla gösterebilmek için önemlidir. Bulgular, düşük hümik asit derişimlerinde, ön ozonlama dozu arttıkça organik karbon gideriminin iyileştiğini; ancak incelenen en yüksek hümik asit derişiminde organik karbon gideriminin azaldığını göstermiştir. Oksitlenmiş daha küçük organik moleküllerin koagülantlarla etkileşime daha yatkın olduğu, oksidasyonla kısmen parçalanmış olsa da aromatik yapılar içeren görece daha büyük moleküllerin, aromatikliği olmayan küçük moleküller kadar iyi giderilemediği düşünülmektedir.

Anahtar Sözcükler: Koagülasyon/flokülasyon, hümik asit, ön ozonlama, organik karbon

ABSTRACT

REMOVAL OF ORGANIC MATTER IN O_3 APPLICATION PRIOR TO PARTICLE AGGREGATION

Process options for the treatment of organic matter containing waters are well established and understood. However, in many treatment plants (especially those treating waters with low alkalinity, and high specific UV absorbance), an increase in organic matter loadings due to heavy rainfall and snowmelt is observed in various periods of a year. In these periods when the dissolved organic carbon (DOC) load is high, the water quality in treatment plants drops rapidly in terms of DOC, colour, and trihalomethane (THM) formation potential (THMFP).

Size, density and strength of particles present in water play a major role in the removal of pollutants by physico-chemical treatment. These particles, commonly referred as flocs, are a result of the reaction between suspended solids and/or organic matter that are present in majority of water resources and inorganic coagulants. Basic solids separation processes are based on the elimination of these flocs, which have larger size and higher density than water. Hence, changes in density and size affect the removal of flocs, hence the elimination of adsorbed organic matter. It has been observed that during periods of high organic matter loads, weak flocs are formed bringing about failures in sedimentation and flotation.

Ozone has been used in water and wastewater treatment since 1970s in the control of disinfection, and disinfection by-products (DBPs), for the oxidation of iron and manganese, and for the reduction of taste, colour and odour. Ozonation of natural organic matter (NOM) yields major changes in its structure. Therefore, oxidised NOM exhibits a different behaviour in the coagulation/flocculation process. Despite the fact that there are many studies in literature reporting the effects of pre-ozonation on organic matter flocculation and removal, many of them contradict one another. Some studies denote that ozone influences the removal of organic matter adversely, whilst others inform the opposite. Some studies have reported that the effect of pre-ozonation depends on the conditions studied. It is thought that the nature of water samples is the

main reason why so many different results are involved in literature. Those studies were carried out with natural waters. However, the structure and characteristics of NOM may exhibit significant regional and seasonal variations. Hence, a study in which all conditions are controlled, as recommended in this study, is essential to expose the effect of ozonation on the removal of organic matter with more general conclusions. Findings showed that at lower humic acid concentrations, organic carbon removals were improved with increasing pre-ozone dose whereas at the highest humic acid concentration studied, organic carbon removal was hindered. Oxidised smaller organic molecules were likely more prone to interact with the coagulants, although shorn by oxidation, relatively larger molecules that still contained aromatic structures might not be removed as well as smaller molecules that lacked aromaticity.

Keywords: Coagulation/flocculation, humic acid, pre-ozonation, organic carbon

CLAIM FOR ORIGINALITY

REMOVAL OF ORGANIC MATTER IN O_3 APPLICATION PRIOR TO PARTICLE AGGREGATION

Ozone has been used in water and wastewater treatment since 1970s in the control of disinfection, and disinfection by-products (DBPs), for the oxidation of iron and manganese, and for the reduction of taste, colour and odour. Ozonation of natural organic matter (NOM) yields major changes in its structure. Since ozonation is usually used coupled with coagulation/flocculation process in drinking water treatment, oxidised thus structurally altered NOM is thought to exhibit a different behaviour in the coagulation/flocculation process. Most of the ozone literature is about disinfection and formation of DBPs and trihalomethanes (THMs) during the process. Similar studies recently focus on oxidation of organics and 'membrane clogging'. There are studies in literature reporting the effects of pre-ozonation on organic matter flocculation and removal, however many of them contradict each other. Some researchers indicated that pre-ozonation diminished the organic matter removal, whilst others claimed the opposite. Some studies have reported that the effect of pre-ozonation depends on the conditions studied. It is thought that the nature of water samples is the main reason why so many different results are involved in literature. All the studies revised have been carried out with natural waters. Raw waters used in those studies are sampled from different regions and climatic conditions. Hence, the structure and characteristics of NOM may exhibit significant regional and seasonal variations. The molecular weight, structure, charge density and acidity of the organic material may vary seasonally and regionally (Edzwald, 1993; Popov et al., 2020). A study in which all conditions are controlled, as done in this study, is essential to expose the effect of ozonation on the removal of organic matter with more general conclusions. As far as known, first time fully synthetic organic matter containing waters were pre-ozonated in order to investigate the effect of ozonation in the subsequent flocculation process where aggregation was also monitored dynamically. Humic acid was chosen as the model NOM because humic acid part of NOM is more aromatic and has a larger molecular size, therefore it is hydrophobic, highly reactive and relatively easily removable by

coagulation. Humic substances constitute the major part of NOM and are more determinative in NOM's behaviour. The chemical composition of raw water used were the same since they were prepared synthetically, only humic acid concentration and ozone dose were different between those waters so to be able to see the effect of ozone on organic matter removal related to aggregation.

ABBREVIATIONS

DBP **:** Disinfection by-product

DOC **:** Dissolved Organic Carbon

FA **:** Fulvic Acid

HA **:** Humic Acid

NOM **:** Natural Organic Matter

PACl **:** Polyaluminium Chloride

PDA **:** Polymetric Dispersion Analyser

SUVA **:** Specific Ultra Violet Absorbance

THM **:** Trihalomethane

TOC **:** Total Organic Carbon

THMFP **:** Trihalomethane Formation Potential

UV **:** Ultra Violet

LIST OF FIGURES

Figure 2.1. Photometric Dispersion Analyser (PDA 2000, Rank Brothers Ltd., Cambridge, UK) 25

Figure 2.2. Flocculator 2000 semiautomatic jar-test device (Kemira Kemwater, Helsingborg, Sweden) 26

Figure 2.3. Peristaltic pump (Watson Marlow) 26

Figure 2.4. pH meter (WTW) 28

Figure 2.5. Ozone Generator (PCI) 29

Figure 2.6. Experimental setup for dynamic monitoring of floc formation in jar-test procedure 29

Figure 2.7. Schematics of the experimental setup for dynamic monitoring of floc formation in jar-test procedure (Yukselen and Gregory, 2002a)..... 30

Figure 2.8. Total Organic Carbon (TOC) Analyser..... 31

Figure 2.9. Shimadzu UV-2450 UV Visible Spectrophotometer..... 31

Figure 3.1. Floc growth with 50 μL and 100 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid..... 33

Figure 3.2. Floc growth with 100 μL and 300 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid..... 34

Figure 3.3. Floc growth with 400 μL and 500 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid..... 34

Figure 3.4. Floc growth with 600 μL and 700 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid..... 35

Figure 3.5. Floc growth with 800 μL and 900 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid..... 36

Figure 3.6. Floc growth with 1000 μL and 1500 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid 36

Figure 3.7. Floc growth with 50 μL - 1500 μL doses of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid..... 37

Figure 3.8. Floc growth with 50 μL - 1500 μL doses of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid (smoothened plot of Figure 3.7)..... 37

Figure 3.9. Alum doses and corresponding residual colour 38

Figure 3.10. Alum doses and corresponding residual TOC 39

Figure 3.11. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw water containing 5 mg/L humic acid 40

Figure 3.12. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw water containing 10 mg/L humic acid 41

Figure 3.13. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw water containing 20 mg/L humic acid 41

Figure 3.14. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw water containing 5 mg/L humic acid 42

Figure 3.15 Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw water containing 10 mg/L humic acid 43

Figure 3.16. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw water containing 20 mg/L humic acid 43

Figure 3. 17. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw waters containing 5, 10 and 20 mg/L humic acid 44

Figure 3.18. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw waters containing 5, 10 and 20 mg/L humic acid 45

Figure 3.19. Floc growth and regrowth with alum (left) and PACl (right) in unozonated (0 mg/L O_3) synthetic raw waters containing 5, 10 and 20 mg/L humic acid 45

Figure 3.20. Residual TOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 47

Figure 3.21. Residual DOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 47

Figure 3.22. Residual absorbance at 254 nm after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 48

Figure 3.23. Specific UV absorbance (SUVA) after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 48

Figure 3.24. E_4/E_6 ratio after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 49

Figure 3.25. Residual TOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 51

Figure 3.26. Residual DOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 51

Figure 3.27. Residual absorbance at 254 nm after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 52

Figure 3.28. Specific UV absorbance (SUVA) after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 53

Figure 3.29. E_4/E_6 ratio after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 53

Figure 3.30. Residual TOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)..... 54

Figure 3.31. Residual DOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)..... 54

Figure 3.32. Residual absorbance at 254 nm after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) 55

Figure 3.33. Specific UV absorbance (SUVA) after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) 56

Figure 3.34. E_4/E_6 ratio after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 56

Figure 3.35. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 57

Figure 3.36. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 58

Figure 3.37. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 58

Figure 3.38. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 59

Figure 3.39. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 60

Figure 3.40. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 60

Figure 3.41. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid..... 61

Figure 3.42. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid..... 62

Figure 3.43. Floc growth and regrowth with alum (left) and PACl (right) in 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 62

Figure 3.44. Residual TOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 64

Figure 3.45. Residual DOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 64

Figure 3.46. Residual absorbance at 254 nm after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 65

Figure 3.47. Specific UV absorbance (SUVA) after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum..... 65

Figure 3.48. E_4/E_6 ratio after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 66

Figure 3.49. Residual TOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 67

Figure 3.50. Residual DOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 67

Figure 3.51. Residual absorbance at 254 nm after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 68

Figure 3.52. Specific UV absorbance (SUVA) after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl..... 68

Figure 3.53. E_4/E_6 ratio after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 69

Figure 3.54. Residual TOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 70

Figure 3.55. Residual DOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 70

Figure 3.56. Residual abs. at 254 nm after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) . 71

Figure 3.57. Specific UV abs. (SUVA) after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) . 71

Figure 3.58. E_4/E_6 ratio after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 72

Figure 3.59. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 73

Figure 3.60. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 74

Figure 3.61. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 74

Figure 3.62. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 75

Figure 3.63. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 76

Figure 3.64. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 76

Figure 3.65. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 77

Figure 3.66. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 78

Figure 3.67. Floc growth and regrowth with alum (left) and PACl (right) in 5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 78

Figure 3.68. Residual TOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 79

Figure 3.69. Residual DOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 80

Figure 3.70. Residual absorbance at 254 nm after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 80

Figure 3.71. Specific UV absorbance (SUVA) after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 81

Figure 3.72. E_4/E_6 ratio after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 81

Figure 3.73. Residual TOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 82

Figure 3.74. Residual DOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 83

Figure 3.75. Residual absorbance at 254 nm after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 83

Figure 3.76. Specific UV absorbance (SUVA) after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 84

Figure 3.77. E_4/E_6 ratio after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 84

Figure 3.78. Residual TOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 85

Figure 3.79. Residual DOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 86

Figure 3.80. Residual absorbance at 254 nm after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) . 86

Figure 3.81. Specific UV abs. (SUVA) after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) . 87

Figure 3.82. E_4/E_6 ratio after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 87

Figure 3.83. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 88

Figure 3.84. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 89

Figure 3.85. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 89

Figure 3.86. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 90

Figure 3.87. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 91

Figure 3.88. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 91

Figure 3.89. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 92

Figure 3.90. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 93

Figure 3.91. Floc growth and regrowth with alum (left) and PACl (right) in 10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid 93

Figure 3.92. Residual TOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 94

Figure 3.93. Residual DOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 95

Figure 3.94. Residual absorbance at 254 nm after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 95

Figure 3.95. Specific UV absorbance (SUVA) after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 96

Figure 3.96. E_4/E_6 ratio after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 96

Figure 3.97. Residual TOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 97

Figure 3.98. Residual DOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 98

Figure 3.99. Residual absorbance at 254 nm after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 98

Figure 3.100. Specific UV absorbance (SUVA) after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 99

Figure 3.101. E_4/E_6 ratio after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 99

Figure 3.102. Residual TOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 100

Figure 3.103. Residual DOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)... 101

Figure 3.104. Residual abs. at 254 nm after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) 101

Figure 3.105. Specific UV abs. (SUVA) after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right) 102

Figure 3.106. E_4/E_6 ratio after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right) 102

Figure 3.107. Floc growth and regrowth with alum in un-ozonated synthetic raw water containing 5 mg/L humic acid 105

Figure 3.108. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 105

Figure 3.109. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 106

Figure 3.110. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 106

Figure 3.111. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid 107

Figure 3.112. Floc growth and regrowth with alum in un-ozonated synthetic raw water containing 10 mg/L humic acid 108

Figure 3.113. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 108

Figure 3.114. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 109

Figure 3.115. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 109

Figure 3.116. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid 110

Figure 3.117. Floc growth and regrowth with alum in un-ozonated synthetic raw water containing 20 mg/L humic acid 111

Figure 3.118. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 111

Figure 3.119. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 112

Figure 3.120. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 112

Figure 3.121. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid 113

Figure 3.122. Floc growth and regrowth with PACl in un-ozonated synthetic raw water containing 5 mg/L humic acid 114

Figure 3.123. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 115

Figure 3.124. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 115

Figure 3.125. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid 116

Figure 3.126. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid 116

Figure 3.127. Floc growth and regrowth with PACl in un-ozonated synthetic raw water containing 10 mg/L humic acid 117

Figure 3.128. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 118

Figure 3.129. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 118

Figure 3.130. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid 119

Figure 3.131. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid 119

Figure 3.132. Floc growth and regrowth with PACl in un-ozonated synthetic raw water containing 20 mg/L humic acid 120

Figure 3.133. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 121

Figure 3.134. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 121

Figure 3.135. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid 122

Figure 3.136. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid 122

Figure 3.137. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid..... 123

Figure 3.138. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid..... 124

Figure 3.139. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid..... 125

Figure 3.140. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid (from left to right)..... 126

Figure 3.141. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid (from left to right)..... 127

Figure 3.142. Residual TOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum 128

Figure 3.143. Residual DOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum 129

Figure 3.144. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum 129

Figure 3.145. SUVA after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum..... 131

Figure 3.146. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum..... 131

Figure 3.147. Residual TOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum 132

Figure 3.148. Residual DOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum 133

Figure 3.149. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum 133

Figure 3.150. SUVA after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum..... 135

Figure 3.151. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum..... 135

Figure 3.152. Residual TOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum 136

Figure 3.153. Residual DOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum 137

Figure 3.154. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum 137

Figure 3.155. SUVA after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum 138

Figure 3.156. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum 138

Figure 3.157. Residual TOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl 140

Figure 3.158. Residual DOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl 141

Figure 3.159. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl 141

Figure 3.160. SUVA after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl 142

Figure 3.161. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl 142

Figure 3.162. Residual TOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl 144

Figure 3.163. Residual DOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl 145

Figure 3.164. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl 145

Figure 3.165. SUVA after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl 147

Figure 3.166. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl 147

Figure 3.167. Residual TOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl 149

Figure 3.168. Residual DOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl 149

Figure 3.169. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl 150

Figure 3.170. SUVA after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl 150

Figure 3.171. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl 151

APPENDIX

Figure 1. TOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 180

Figure 2. DOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 180

Figure 3. UV_{254} removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 181

Figure 4. TOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 181

Figure 5. DOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 182

Figure 6. UV_{254} removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 182

Figure 7. TOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 183

Figure 8. DOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 183

Figure 9. UV_{254} removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 184

Figure 10. TOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 184

Figure 11. DOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 185

Figure 12. UV_{254} removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 185

Figure 13. TOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 186

Figure 14. DOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 186

Figure 15. UV_{254} removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 187

Figure 16. TOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 187

Figure 17. DOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 188

Figure 18. UV_{254} removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 188

Figure 19. TOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 189

Figure 20. DOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 189

Figure 21. UV_{254} removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum 190

Figure 22. TOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 190

Figure 23. DOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 191

Figure 24. UV_{254} removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl 191

Figure 25. Residual TOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right) 192

Figure 26. Residual DOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right) 192

Figure 27. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right) 193

Figure 28. SUVA after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right) 193

Figure 29. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right) 194

Figure 30. Residual TOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right) 194

Figure 31. Residual DOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right) 195

Figure 32. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right) 195

Figure 33. SUVA after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right) 196

Figure 34. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right) 196

Figure 35. Residual TOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right).....197

Figure 36. Residual DOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right) 197

Figure 37. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right) 198

Figure 38. SUVA after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right).....198

Figure 39. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right) 199

Table 1. Parameters measured in raw water.....199

Table 2. Removal efficiencies after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum.....199

Table 3. Removal efficiencies after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum.....200

Table 4. Removal efficiencies after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum.....200

Table 5. Removal efficiencies after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum.....200

Table 6. Removal efficiencies after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl.....201

Table 7. Removal efficiencies after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl.....201

Table 8. Removal efficiencies after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl.....201

Table 9. Removal efficiencies after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl.....202

1. INTRODUCTION

1.1. Organic Matter

Natural Organic Matter (NOM) is formed by climatic conditioning and biodegradation of dead plants and animals (Thurman, 1985, Suffet and MacCarthy, 1989, Chang and Berner, 1998). NOM present in underground and surface waters is defined as a mixture of organic compounds containing both hydrophilic and hydrophobic structures. The complex mixture of humic acids, hydrophilic acids, proteins, oils, amino acids and hydrocarbons present in all drinking water sources is defined as NOM. The constituents of NOM vary depending on the seasonal climate effect and drought. Therefore, the organic matter content of each water resource is unique.

The majority of NOM in water is hydrophobic acids, which generally constitute up to 50% of DOC (Thurman, 1985; Owen et al., 1993). Those acids may be labeled as humic acids, fulvic acids, and aquatic acids composed of humin or humic substances. Those hydrophobic acids are heavy molecules with various structures and molecular weights between 500 and 10,000 Daltons (Thurman, 1985), and their structure is not well known (Speitel et al., 1999).

Up to 90% of NOM can be composed of humic substances such as humic and fulvic acids (Woelki et al., 1997). Humic substance gives water a brown colour, and a muddy taste and odour. In addition to these aesthetic concerns, the fact that humic materials can be used as substrate by microorganisms, promote the transportation of hydrophobic organic and inorganic pollutants via adsorption, enhance the stability of turbidity causing particles such as clay and metal oxides by getting adsorbed on their surfaces resulting in an increase in the coagulant demand, increase disinfectant demand, promote the growth of microorganisms in the distribution lines (Owen et al., 1995), and most importantly they produce harmful disinfection by-products such as trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone during disinfection with chlorine, necessitate their removal from water (AWWA Committee Report, 1979; Kronberg, 1987; Randtke, 1988; White et al., 1997; Richardson, 1998; Dixon et al., 1999). THMs

are carcinogenic to humans after ingestion by mouth and skin (Tate and Arnold, 1990; Andelmann, 1990).

The humic acid fraction is usually designated as the main causes of natural colour of water and the main potential for THM formation (THMFP) (Speitel et al., 1999). Krasner et al. (1996) showed that the hydrophilic acid part constituted 21 μg THM/mg DOC whereas hydrophobic part formed 51 μg THM/mg DOC (humic material constitutes hydrophobic part). Croue et al. (1993) reported that humic and fulvic acid parts were formed of 46 and 27 μg THM/mg DOC respectively and hydrophilic part formed 27 μg THM/mg DOC. Humic acid has a higher molecular weight than fulvic acid and is more aromatic and has lower charge density. It has been found that the typical doses of coagulants applied in water treatment could rather remove humic acid which has a higher molecular weight and lower density (Chow et al., 1999).

Humic acids do not have a definite molecular structure, they are of a very diverse nature and their structure is not well-known (Speitel et al., 1999). Humic acids are heterogeneous anionic macromolecules having low to moderate molecular weight, with weakly acidic functional groups composed of primarily carboxylic and phenolic groups, and containing aromatic and aliphatic structures (Cook and Langford, 1998, Kerc et al., 2004). The reported molecular weights of aquatic humic substances are from 500 Da to more than 100000 Da (Thurman, 1985; Visser, 1985). Molecules with low molecular weight are more prone to utilisation by microorganisms, more mobile, and are adsorbed faster onto the surfaces of minerals due to the fact that they are hydrophilic structures with smaller radii. On the other hand, high molecular weight humic acid molecules are hydrophobic due to their higher aromaticity, their electrostatic potentials and ligand amounts per molecule are higher, their metal binding capacities are high and therefore their mobility is low (Kerc et al., 2004). Humic materials have typical properties of weak anionic polyelectrolytes (Visser, 1985); their functional groups such as carboxylic and phenolic acids promote adsorption of humic matter onto metal ions, metal oxides, minerals such as clay, and organic and inorganic particles and thus affect the electrochemical properties of those particles (Saar and Weber, 1980; Stevenson,

1994). Functional groups were reported to determine the selectivity for natural organic matter during flocculation (Liu et al., 2024).

1.2. Stabilisation and Destabilisation of Organic Matter

The way that an organic surface with carboxyl (COO^-) and amino (NH_3^+) groups become charged as a consequence of ionisation reactions proceeds as follows:

In these reactions, particle's surface charge depends on the proton concentration ($[H^+]$) that is pH (= -log $[H^+]$). As the pH increases ($[H^+]$ decreases) the organic matter gives off H^+ (deprotonated) and negative surface charge increases. Proteins contain both carboxyl and amino groups and they are typically negatively charged when the pH is above about 4. The adsorption of NOM to the surface of particles may occur by such an interaction with a region of surface (Letterman et al., 1999).

Deryaguin, Landau, Verwey and Overbeek (DLVO) theory is concerned with the repulsive electrostatic (double layer) forces and attractive (van der Waals) forces of interaction energy between colloidal particles. This theory can also be applied to humic colloids as an approach (Buffle et al., 1998, Hunter, 1993). Humic molecules can have a high negative charge due to H^+ loss (deprotonation) of the carboxylic and phenolic groups to the water. As a consequence, the cations are collected in a layer (Stern layer) close to the humic surface by the attraction force, and the cation concentration gradually decreases as the distance from the humic surface increases to form the diffuse layer. According to the DLVO theory, coagulation increases by the valence (z) of the cations and by increasing the Debye-Hückel parameter (κ) (ie, decreasing the double layer thickness, 1 / κ), because κ is directly proportional to the square root of the ionic strength. When $I^{1/2}$ increases, κ increases as well, and 1 / κ, that is the thickness of the double layer, decreases (double layer compression). Wall and Choppin (2003) in their study investigating the effect of cationic charge on humic acid coagulation found that the higher the cationic charge and ionic strength were or the smaller the size of the hydrated cations in the double layer was, the more coagulation occured. The radii of hydrated cations are inversely proportional to the ionic radii; i.e. for hydrated cations, the radii are in the following order: $Li^+ > Na^+ > K^+$ and $Mg^{+2} > Ca^{+2}$ (Ong and Bisque,

1968). Wall and Choppin (2003) found that HA coagulation increased when pH was decreased as HA protonation (H^+ gain) occured. In fact, it could be said that this may be the result of the reduction in HA solubility (or precipitation of HA).

1.3. Removal of Organic Matter

Although very high molecular weight organic acids are usually considered to have colloidal properties, dissolved natural organic matter (NOM that filters through 0.45 μm pore size) typically forms the largest part of the NOM (Randtke, 1988; Edzwald, 1993). Humic substances are chemically complex molecules with acidic, aromatic, hydrophilic and hydrophobic fractions. It is thought that the carboxylic and phenolic (and even alcoholic, ketonic, quinonoid and methoxyl) groups present in humic substances determine their reactivity. At around neutral pH (as the pH level of most natural waters), the more acidic group among those functional groups is dissolved bringing about dissolved or colloidal organic molecules that are negatively charged and highly stable (AWWA Committee Report, 1979). High molecular weight fraction of organic material is usually removed easily by coagulation (Collins et al., 1986). Low molecular weight organic matter increases coagulant demand, nonetheless cannot be removed efficiently. For instance, fulvic acid (FA) has a lower average molecular weight than humic acid (HA), with less carbon and nitrogen and more oxygen (AWWA Committee Report, 1979). However, HA removal is more straightforward than that of FA (Vik and Eikebrokk, 1989; Chow et al., 1999). This is attributed to FA's higher charge density due to the fact that it has more carboxylic and phenolic groups. Consequently, FA is more stable in water (Collins et al., 1986, Owen et al., 1995). Functional groups determine the solubility of organic compounds and therefore their removal by coagulation / flocculation. Hydrophobic organic matter has been reported to be more easily removed than hydrophilic (Collins et al., 1986; White et al., 1997; Kim and Yu, 2005). Compared to HA, lower amounts of THM are produced with fulvic acid during chlorine disinfection (Vik and Eikebrokk, 1989, Croue et al., 1993). THM formation has been reported to increase with molecular weight (Collins et al., 1986). Hence, coagulation / flocculation is an effective method for the removal of THM precursors (higher molecular weight organics). In addition, Owen et al. (1995) showed that a significant part of disinfection by-products was formed by the non-humic portion

of the natural organic matter. This non-humic portion is generally more hydrophilic than the humic part, so it is difficult to remove them via coagulation / flocculation.

A detailed method for isolating and decomposing natural organic matter into its fractions has been proposed by Leenheer and Noyes (1984). According to this method, the NOM can be decomposed into as high as eight fractions: fulvic acid, humic acid, weak hydrophobic acids, hydrophilic acids, hydrophobic neutrals, hydrophilic neutrals, hydrophobic bases and hydrophilic bases.

Edzwald (1993) stated that 70% or more DOC removal can be achieved with waters rich in humic substances, whilst much less removal efficiency can be maintained with waters containing non-humic organics. Fearing et al. (2004) studied NOM removal via coagulation using both raw and fractionated NOMs, and reported that whilst 70% of the hydrophobic and hydrophilic acidic fractions were eliminated, only 16% of the non-acidic hydrophilic fraction was removed. Kim and Yu (2005) noted that in the conventional water treatment process, the hydrophobic part is removed more than the hydrophilic part. Chow et al. (2004, 2005) reported that the highly hydrophobic acids fraction of NOM was easily removed by alum whereas the hydrophilic neutrals fraction was almost non-removable. Matilainen et al. (2005) observed that approximately 95% of high molecular weight organic matter were removed with both ferric iron and alum coagulation whilst the removal efficieny of NOM with a molar weight less than 1000 g/mol averaged only 10%.

1.4. Flocculation of Organic Matter

Coagulation/flocculation, active carbon adsorption, oxidation and membrane filtration are applied in organic matter removal from water and wastewater (Edzwald and Tobiason, 1999). Aluminium and iron salts are widely used as coagulants in the removal of organic and inorganic pollutants by coagulation / flocculation in water and wastewater treatment (Boller, 1993; Rebhun and Lurie, 1993). Depending on the concentration of metal ions in solution, flocculation of clay suspensions with hydrolysing metal salts involves mechanisms such as adsorption of dissolved hydrolysis species, accumulation of the hydrolysis precipitate on the clay surface and entrapment of clay particles in the growing hydrolysis precipitate (Packham, 1962, Dentel and

Gossett, 1988, Ching et al., 1994). Flocculation of organic matter with hydrolysing metal salts is generally defined as co-precipitation, charge neutralisation and adsorption mechanisms depending on coagulant dose and DOC concentration (Edwards and Amirtharajah, 1985). Moreover, other interactions such as complex formation between metal ions and humic substance may also be involved (Snoeyink and Jenkins, 1980).

Mechanisms, such as complex formation with coagulant and post-adsorption precipitation, have been mainly proposed in HA coagulation (Edzwald, 1993; Krasner and Amy, 1995; Dennett et al., 1996). The destabilisation mechanism not only involves charge neutralisation and adsorption of organic material onto metal hydroxide flocs but also co-precipitation of metal-organic complexes with metal hydroxides (Edzwald, 1979, Edwards and Amirtharajah, 1985, Narkis and Rebhun, 1977).

In terms of destabilisation, it is advantageous to use the salts of metals with high valence number. For this reason, in the coagulation of humic matter and natural organic matter with frequently utilised Al and Fe (III) salts, as a result of hydrolysis many monomeric and polymeric metal hydroxide products and amorphous metal hydroxide precipitates are formed. There are two main mechanisms which they cause: precipitation and adsorption, each taking place within different pH ranges (Rebhun and Lurie, 1993; Dennett et al., 1996, Chow et al., 1999).

Application of coagulation in the treatment of NOM has been studied widely (Edzwald, 1993, Dennett et al., 1996, Volk et al., 2000). Colloid destabilisation, sedimentation, co-precipitation, or adsorption mechanisms are implemented to remove NOM (Gregor et al., 1997; Volk et al., 2000). Performance of the process depends on the pH of coagulation, type and dose of the coagulant. The optimum pH for coagulation varies with water source, but typical values are around pH 4-6 for iron-containing coagulants and around 6 for aluminium-containing coagulants. There is not much evidence to support that a coagulant is superior to the other. Some authors promote iron-based coagulants (Dennett et al., 1996) whilst others rally around aluminium-based coagulants (Lind, 1995) and polymers (Bolto et al., 2001). Consequently, it is a fact that chemical nature of a water source is important in coagulant selection.

The most frequently preferred method in the treatment of waters containing high TOC is coagulation with aluminium or iron-based coagulants. Optimum coagulant dose increases with NOM concentration whilst optimum pH for coagulation decreases (Hall and Peckham, 1965; Dempsey et al., 1984). An alternative option is tapering coagulation (Chow et al., 1999, Wahlroos, 1991, Carlson and Gregory, 2000, Billica and Gertig, 2000).

Cheng and Chi (2002) studied the flocculation of humic acid with Fe (III) coagulant and adsorption of humic acid onto pre-coagulated $Fe(OH)_3$ and found that out of the two types of flocs formed, the one resulting from adsorption dissolved when pH was decreased, whilst the other resulting from coagulation did not, indicating that charge neutralisation is the main mechanism in HA flocculation. A similar result was obtained by Cheng (2002). Jung et al. (2005) observed that hydrolysed Fe species combined with carboxylic groups of humic colloids at pH 6 and pH 8 and upon not detecting any Fe hydroxide precipitate in the coagulated precipitate they concluded that charge neutralisation/complex formation was the predominant flocculation mechanism.

1.5. Factors Affecting Organic Matter Flocculation

Flocculation of HA with hydrolysing metal salts depends on solution conditions. It is well-known that when aluminium based coagulants are used, temperature and pH affect the mechanisms (Dempsey et al., 1984, Hundt and O'Melia, 1988). Effect of temperature on coagulation has not been fully understood, but it is known that removing turbidity with alum is more difficult at low temperatures (Morris and Knocke, 1984). Removal efficiency of colour and especially low-molecular weight organic substances (<1000 g/mol) via coagulation was reported to be adversely affected by low temperatures, yet TOC removal was reported not to be affected at all (Knocke et al., 1986). Temperature may have influences on many factors. Increased water viscosity at low temperatures may diminish coagulation and sedimentation (Amirtharajah and O'Melia, 1990). Temperature may also affect hydrolysis equilibrium kinetics and metal hydroxide formation (AWWA Committee Report, 1989; Knocke et al., 1986; Matsui et al., 1998). It is a well-known, observable, measurable fact that smaller-sized flocs are formed at low temperatures (Morris and Knocke, 1984).

In order to model natural organic matter (NOM), Exall and vanLoon (2000) studied flocculation of four organic compounds (tannic, humic, lignosulphonic, and salicylic acids) with three coagulants (aluminium sulphate, polyaluminium chloride and polyaluminium hydroxysulphate) at two different temperatures (5 ^{o}C and 22 ^{o}C), and found out that organic matter removal reduced at low temperature. Of the organic materials used in that study, humic acid required the least coagulant dose. They also found that low-molecular weight salicylic acid was hard to remove and the addition of organic material diminished the efficiency of turbidity removal.

In the adsorption of organic matter onto particles, pH determines the surface charges of humic matter and particles and therefore the interaction between them. It is well-known that humic acid adsorbs to the surfaces of particulate matter (such as clay minerals and other oxides) present in the water. Au et al. (1999) revealed that the adsorption of humic acid to the hematite surface was significantly altered by pH. It decreased with increasing pH. As pH increases, the negative charge density of humic acid also increases by deprotonation (release of H^{+}). The point zero net proton charge, pH_{pznpc}, of hematite particles was found to be 8.1. In the absence of organic material and other specifically adsorbing ions, charge of the hematite particles is negative in the case of pH> pH_{pznpc}, and it is positive when pH <pH_{pznpc} (Au et al., 1998). The interaction between HA and hematite particles is attractive when pH < 8.1, whereas it is repulsive when pH > 8.1. This explains extensive adsorption of HA to the hematite surface at low pH values. Adsorption observed at pH > 8.1 could not be attributed solely to electrostatic interaction, it was claimed that hydrophobic properties of HA contributed to the adsorption (O'Melia et al., 1999).

The effect of pH is important in the determination of flocculation mechanism. Semmens and Field (1980) reported that when pH was higher than 6, the predominant mechanism was the adsorption of organic species onto the $Al(OH)_3$ (s) precipitate and in cases where pH was lower than 5, precipitation of soluble organic molecules with soluble cationic polymeric metal hydroxide species dominated. Both mechanisms occur between pH 5 and 6 simultaneously. Dempsey et al. (1984) proposed similarly with a slight difference; they reported slightly higher pH values (less than 5, 5 to 7 and higher than 7). Similarly, Lu et al. (1999) reported that humic material formed soluble complex

molecules with Al^{3+} at low pH values (< 4.5), whilst adsorption of it to $Al(OH)_3$ surface became dominant at higher pH values (> 5) achieving maximum removal of humic material. In adsorption, the carboxylic group of humic molecule first forms a ligand or a coordination via anion exchange with the Al core at the surface of $Al(OH)_3$, and then the rest of the molecule adsorbs to the $Al(OH)_3$ surface with forces such as van der Waals and H bonds. Proposed pH values are essentially close to the pH level at which Al solubility is minimum and $Al(OH)_3$ precipitation is maximum (pH 6.3). Duan et al. (2002) studied the flocculation of humic acid in distilled water (DW), tap water (TW) and synthetic seawater (SSW) and observed that the minimum Al solubility was at pH 6 in all three water samples. Due to high ionic strength of SSW, a severe charge neutralisation was observed and HA flocculation occurred at a much lower alum dose compared to DW and TW.

1.6. Hydrolysing Metal Salt Coagulants

In water treatment, hydrolysing metal salts which are aluminium and iron based are widely used. Alum has been used for clarification of water since ancient times and was first mentioned by Pliny in around 77 AD (Cohen and Hannah, 1971). Hydrolysing coagulants have been routinely used since the early 20th century and played a vital role in eliminating many pollutants including clay, pathogenic microorganisms and dissolved natural organic matter. Aluminium sulphate (alum), ferric chloride and ferric sulphate are the most commonly used coagulants.

As mentioned previously, many colloids in water are negatively charged and therefore they can be stabilised by electrostatic repulsion. These particles have to be destabilised in order to be eliminated from water efficiently. This can be accomplished by adding salt in relatively large amounts or by adding a small amount of specifically interacting cations. In this sense, cations such as highly charged Al^{+3} and Fe^{+3} are effective. However, in the normal pH range of natural waters (5-8) those cations are not present in significant amounts to hydrolyse and give various hydrolysis products. Many hydrolysis products are cationic and they cause destabilisation and coagulation at the correct dose and pH due to strong interaction with negatively charged colloids.

The solubilities of Al (III) and Fe (III), which plays a very important role in coagulation/flocculation processes, are limited to around neutral pH due to amorphous hydroxide precipitation. Further information on the role of hydroxides can be found in the article by Bache and Papavasilopoulos (2003). The deposition of positively charged precipitate particles on pollutant particles (heterocoagulation) leads to the possibility of charge neutralisation and destabilisation. Another possibility is the precipitation of hydroxide on the surface of particle in order to produce similar results. In practice, precipitation of excess amount of hydroxide is a more important flocculation mechanism. This flocculation mechanism, which is essentially the entrapment of pollutant particles within the growing precipitate, is called sweep flocculation.

Hydrolysing coagulants also help to remove dissolved natural organic matter (NOM) by destabilising it via charge neutralisation, or by its adsorption on the metal hydroxide precipitate.

Al and Fe (III) coagulants are thought to have similar coagulation/flocculation mechanisms by adsorption or polymerisation by hydrolysis. However, Yu et al. (2002) observed that there were some differences between Al and Fe (III) coagulations by comparing their E_4/E_6 ratios (Chen et al. (1977), Gressel et al. (1995), and Maartens et al. (1999) introduced in their studies that structural information about humic substances can be obtained by taking the ratio of light absorbance at 465 nm (E_4) to 656 nm (E_6). A high E_4/E_6 ratio indicates the presence of small molecules in solution, whilst a low value points out large molecules). According to their results, at optimum doses of both coagulants smaller HA molecules were removed with the aid of Fe whereas larger ones were eliminated by Al.

It is clear that type of organic material plays a crucial role in the effectiveness of coagulant in flocculation. SUVA can be used to specify hydrophilic and hydrophobic composition of water; SUVA < 3 essentially represents the hydrophilic matter (Edzwald and Tobiason, 1999) whilst SUVA > 4 points out hydrophobic and particularly aromatic matter. Although there is no specific relationship between SUVA and removal, it is observed that the higher the SUVA is, the better the removal of DOC gets.

Lindqvist et al. (2002) found that the Fe (III) salts were better than the Al salts in dissolved organic matter removal, and the best removal was obtained with $FeCl_3$. They reported that the difference between the efficiencies of coagulants most obviously arose in the removal of dissolved organic matter in the molecular weight range 1000-4000 Da. They found that turbidity removal was highly dependent on pH and more dependent on pH than dissolved organic matter removal for all coagulants tested. Lovins et al. (2003) reported that the DOC removal of iron-based coagulants was 10-15% higher than the aluminium-based coagulants and that the maximum DOC removal efficiencies were 77% with Fe and 65% with Al.

In addition to simple hydrolysing salts, a number of pre-hydrolysed coagulants are commercially available. Pre-hydrolysed metal-based coagulant types, such as polyaluminium chloride, polyiron sulphate and polyiron chloride, have become widespread. They contain highly-charged cationic hydrolysis products and are generally more effective than aluminium and iron salts.

There is conflicting information in the literature about the superiority of the monomeric and polymeric coagulant types to each other. This issue results from the fact that working conditions highly determine the performance of coagulants.

In coagulation/flocculation process, hydrolysis of metal ion is an important reaction for destabilisation of suspended particles and organic matter, and complex formation. It has been reported that the hydrolysis of monomeric and polymeric coagulants is quite different (Rebhun and Lurie, 1993). Right after the monomeric salt is added to the water, a series of complex hydrolysis reactions begin. This makes coagulation difficult to control (Tang and Stumm, 1987). Subsequently, a metal hydroxide precipitate forms rapidly. On the other hand, polymeric salt contains metal hydroxide complexes having different charges. Degree of hydrolysis of polymeric salt is kept under control during production, this minimises complicated reactions caused by metal salt hydrolysis. For this reason, it has been claimed that the use of polymeric salt is simpler in terms of coagulation control (Tenny and Derka, 1992, Jiang et al., 1993, Jiang and Graham, 1998a). Jiang and Graham (1998b) examined the zeta potentials and isoelectric points of precipitates formed in the polyferric sulphate and ferric sulphate coagulations and reported that the rate of floc formation was higher with monomeric

coagulants. However, in their studies, the difference between hydrolysis of two coagulants only in distilled water was shown. On the contrary, many studies have reported that polymeric metal salt coagulants cause more rapid floc formation (Matsui et al., 1998; Yukselen and Gregory, 2002a and b; Yukselen and Gregory, 2004a and b; Şam and Yükselen, 2006; Sam and Yukselen, 2007; Yukselen et al., 2007; Sam et al., 2010).

The question of how to improve the efficiency of coagulation/flocculation process in removal of organic pollutants is still of interest. So far, the mechanism for removing organic contaminants via coagulation/flocculation process has not been satisfactorily revealed. Whilst a number of reports have focused on coagulants which provide colloid destabilisation (e.g., Gray et al., 1995) and neutralise the charge of organic anions (e.g., Østerhus and Eikebrokk, 1994), some others have concentrated on polymeric species formed by hydrolysis (Eikebrokk and Fettig, 1990; Fettig et al., 1990). Studies have shown that unpre-hydrolysed coagulants (such as alum) provide the best organic matter removal in acidic media (pH <6.0). The low pH medium was provided by adding acid to the raw water or by overdosing the hydrolysing coagulants. However, both methods add abrasive properties to the water. To minimise this effect, coagulants such as alum were replaced with pre-hydrolysed coagulants such as polyaluminium chloride (PACl). The pre-hydrolysed coagulants contain polymerised species resulting from the hydrolysis of metal (aluminium, in the case of PACl) and have a high positive charge. Superior performance of those inorganic polymeric coagulants are attributed to their highly charged pre-hydrolysed metal species (like Al_{13}) content. Al_{13} has been reported to exhibit a broader effective dosage range and pH range compared with $AlCl_3$, form floc with a more compact crystalline structure and higher strength and show significantly higher efficiency in removing particulate matter and organic substances (Liu et al., 2025). However, there is disagreement among researchers on the use of PACls in the remediation of organic pollutants. Eikebrokk (2000) and Edzwald et al. (2000) reported that PACls were more effective than alum, whilst Yao and O'Melia (1989) and Diamadopoulos and Vlachos (1996) disagreed. Swiderska-Bróz and Rak (2002) studied organic matter removal with five different PACl coagulants with different basicities and alum, and found that the removal efficiency increased in accordance with increasing basicity. They observed that as well as the undissolved part

of the organic carbon, some dissolved part was removed but the removal efficiency is reduced when the ratio of DOC in TOC increased. Another finding of their work was that PACls were more effective in removing not only the undissolved portion, but also the dissolved portion of organic matter, and could work at wider pH and temperature ranges compared to alum. Increasing the pH from 6.0 to 6.8 increased the TOC and DOC removal efficiency, which was more pronounced with alum. The reason is probably that the minimum Al solubility is at pH 6.3 and since PACls are pre-hydrolysed they are not as much affected as alum by pH change in that range. Increasing the pH to 8.5 adversely affected the organic removal, at that pH mostly undissolved portion of the organic material was removed. The reason might be that organic matter may become more soluble through deprotonation as pH increases.

In a study investigating the effect of B ratio (OH/Al) in the flocculation of organic matter, $AlCl_3$ was found to be the lowest performance coagulant and it was observed that floc formation increased with increasing B value (Hailong et al., 2007).

Cheng (2002) stated that it was easier to control coagulation with polyferric sulphate than $FeCl_3$, but that there was no difference between the adsorption of humic acid to the $Fe(OH)_3$ precipitate obtained from both coagulants and therefore the physical and chemical structures of flocs formed with both coagulants were similar.

1.7. Effect of Ozonation on Organic Matter Flocculation

Ozone is used for a number of purposes in water treatment. The oxidising property of ozone is used to disinfect, to oxidise iron and manganese, to reduce colour, to reduce taste and odour compounds, and to control DBP formation (Langlais et al., 1991, Liao et al., 2025), especially to prevent trihalomethane (THM) formation during chlorination of still surface water resources such as lakes and dams is a common practice of ozonation. Such still water bodies usually contain low particulate matter concentration and relatively high amount of natural organic matter (NOM). Organic loads on treatment plants receiving raw water from these resources may get significantly elevated during periods of heavy precipitation, in spring months when snow melt waters reach and spring/autumn months when thermal stratification changes. These circumstances give rise to dissolved organic carbon (DOC), colour and THM formation

potential (THMFP) in water prior to disinfection, drastically. Coagulant doses used in practice are capable in tolerating small changes in water quality. However, significant increases in organic loading and employing pre-ozonation may increase coagulant demand. Under such circumstances, the coagulant dose routinely applied may not provide enough flocculation, the organic matter removal efficiency may decrease dramatically, the filter operating times may decrease and the risk of organic matter escapes to the disinfection units may arise. NOM can cause serious problems in water treatment since it is converted into disinfection by-products (DBPs) when chlorine is used as a disinfectant (Krasner et al., 1989). For this reason, the most important point in preventing the formation of DBPs is to remove the organic matter before disinfection, i.e. in flocculation, sedimentation and filtration processes. Ozonation is also applied for elimination of organic matter before chlorine disinfection, either as pre-ozonation or intermediate ozonation.

Ozonation of humic acid results in a decrease in UV absorbance at 254 nm and may slightly decrease TOC content. Kerc et al. (2004) found that the molecular weight of humic acid between 500 and 450000 Da is reduced to 500-100000 after ozonation. The shift of the molecular distribution towards smaller molecules is the cause of the reduction of UV absorbance. In unozonated waters, organic matter molecules have a distribution of different molecular sizes, large and small. Ozone is a very strong oxidant. Ozonation of water containing organic matter disintegrates organic molecules with large structures and shifts the size distribution to small molecules. When the coagulant is added at appropriate dose, a metal hydroxide precipitate forms. Organic matter flocculates by adsorbing on the surface of this precipitate and becomes separable.

It is known that ozone significantly alters the structure of organic matter. Organic matter reacting with ozone is transformed from large molecular weight structures into smaller molecular weight structures, and polarity also increases due to oxidation. Besides, ozonation breaks the double bonds in the molecules and therefore the UV absorption of the water at 254 nm wavelength is reduced. (Amy et al., 1991, Miltner et al., 1992, Tobiason et al., 1993). As a result of these structural changes, it is thought that ozonation will change the mechanism of flocculation, thus affecting floc formation, strength and reformation. Some studies in the literature show that there is a

relationship between structural characterisation of organic matter in the water and its removal. For example, Edwards and Benjamin (1992) have reported that as the molecular weight of DOC increases, the efficiency of removal by flocculation increases. Similarly, Lindqvist et al. (2002) found that in the removal of organic matter the effect of molecular weight on flocculation efficiency was greater than the effect of pH.

Bose and Reckhow (2007) found that the adsorption tendency of NOM fractions to aluminium hydroxide surface increased as the specific charge of those fractions increased. However, this did not apply to fulvic acid and hydrophilic acids, which were the two highest charge density fractions. The tendency of adsorption also increased as the specific UV absorbance (SUVA) of organic parts increased. It was also reported that pre-ozonation changes the adsorption tendency of NOM fractions on the aluminium hydroxide surface significantly. Ozonation of the fulvic acid and humic acid fractions, which constitute the major part of the NOM, reduced their adsorption tendencies, whilst ozonation of the second most part, the hydrophilic neutrals fraction, increased the adsorption tendency. In flocculation with alum, as the amount of ozone dose increased, the removal of DOC was found to decrease. It was thought that ozone first reacted with the humic components of NOM (fulvic acid and humic acid), so the raw water was coagulated before ozonation to separate the humic part. It was observed then that the adsorption of the non-humic part of NOM to aluminium hydroxide surface increased when precoagulated water is ozonated.

O'Melia et al. (1999) found that ozonation of waters containing high TOC had a detrimental effect on alum coagulation and DOC removal. Ozonation broke down the organic matter and shifts the size distribution towards smaller, oxidised molecules. These compounds had a higher charge and more reactive metal hydroxide surface was required to achieve DOC removal similar to the unozonated case. For this reason, the optimum alum dose was increased, or the amount of DOC that is removed by a certain alum dose is reduced after ozonation. In the same study, it was found that when alum was used as coagulant, ozonation of water containing low TOC reduced the optimum alum dose. It was claimed that this was caused by the change of the adsorption of organic matter and its placement on particles. It was stated that the optimal coagulant dose was determined by turbidity (particles and organic matter adsorbed on them).

Hailong et al. (2007) investigated the effects of ozone and B ratio (OH / Al) on organic matter flocculation. They found that as the ozone dose was increased, floc formation was inhibited, and turbidity, DOC and UV_{254} removals are reduced. $AlCl_3$ was found to be the coagulant with the lowest performance; floc formation increased with increasing B value and PACl with a B value of 2.5 was found not to be significantly influenced by ozone.

The results of researches in literature examining the effect of ozone on the removal of NOM by coagulation / flocculation are complicated and specific to the conditions studied (Reckhow and Singer, 1984; Colin et al., 1986; Farvardin and Collins, 1989; Marhaba and Pipada, 2000; Singer et al., 2003).

Ozonation imposes a substantial alteration in the structure of organic matter. After ozonation, organic matter of high molecular weight is converted into organic compounds with smaller molecular weight, yet no significant change occurs in TOC concentration (Miltner et al., 1992, Tobiason et al., 1993). Oxidised organic matter is expected to act in a different way during coagulation. Consequently, turbidity and efficiency of organic carbon removal are expected to change. The interaction between ozone and organic matter is rather complicated, mainly because neither the structure of organic matter nor reactions that occur are definitely known. In literature there are numerous articles reporting the effect of ozonation on organic matter removal that contradict one another (Xie et al., 2016). Some researchers indicated that pre-ozonation diminished the organic matter removal (Schneider and Tobiason, 2000; Hailong et al., 2007; Bose and Reckhow, 2007), whilst others claimed the opposite (Marhaba and Pipada, 2000; Singer et al., 2003; Yukselen et al., 2007; Pei et al., 2007; Jasim et al., 2008). And some informed that effect of ozonation depended on the concentration of organic matter (O'Melia et al., 1999) and ozone dose (Singer, 1990; Edwards et al., 1993) (For instance, Edwards et al., (1993) reported that “pre-ozonation directly removed organic matter by mineralisation, volatilisation and/or stripping reactions, improving removal in comparison to unozonated systems. On the other hand, pre-ozonation decreased the surface charge of floc formed after coagulation with hydrolysing metal salts, hindering adsorptive removal of the anionic organic molecules by floc surfaces and/or inducing stabilised floc formation; changes that decrease

removal in comparison to unozonated systems."). The contradictory statements in literature might have arisen from the use of characteristically different waters. Raw waters used in those studies are sampled from different regions and climatic conditions. The molecular weight, structure, charge density and acidity of the organic material may vary seasonally and regionally (Edzwald, 1993; Popov et al., 2020). Substantially, humic substances of different origins may not react identically with ozone (Gilbert, 1988). This necessitates a study in which experiments are conducted with synthetic model suspensions under controlled operating conditions so as to better understand the effect of ozone on organic matter flocculation and removal. In this study, humic acid was chosen as the model NOM because humic acid part of NOM is more aromatic and has a larger molecular size, therefore it is hydrophobic, highly reactive and relatively easily removable by coagulation (Randtke, 1988; Owen et al., 1995). Humic substances constitute the major part of NOM and are more determinative in NOM's behaviour (Sharp et al., 2006, Bose and Reckhow, 2007). Also, humic acid serves as the main cause of THMFP (Speitel et al., 1999), thus its efficient removal and elimination of THMFP is crucial.

1.8. Floc Structure, Breakage and Reformation

In the absence of particulate matter, flocs of humic matter and inorganic metal salts may be quite fragile and light thus difficult to settle. The fragile structure of flocs may cause easy disintegration of flocs at the subsequent stages of the treatment and consequently the efficiency of treatment may be adversely affected. Floc rupture may affect whole treatment process negatively, hence it has a vital importance for the effectiveness of treatment. Broken flocs may regrow to some extent if agitation after fracture is reduced, or they may return to their size before breakage. The latter occurs generally when polyelectrolytes are used, whilst floc regrowth is limited in case of hydrolysing coagulants in sweep flocculation. The ability of the broken flocs to regrow their size before breakage is also seen in cases where the flocculation mechanism is charge neutralisation. Where aggregation is primarily electrical, broken bonds may reform, but in sweep flocculation, in which other factors are thought to be involved and whose structure is not yet fully understood, broken bonds cannot be formed to the same extent. In this regime, degree of floc reformation, or the extent to which disintegrated

flocs can reform depends on factors such as coagulant type, organic matter concentration and ozone dose.

Strength of a floc depends on the inter-particle forces and the number of contacts among particles. The application of fluid shear to increase collision efficiency in orthokinetic flocculation also leads to the possibility of floc breakage. Under certain shear conditions, it has been found that flocs usually grow to a certain size, whilst in the case of larger growth they split into smaller units. When the shear rate is increased, the maximum size that flocs can reach is reduced. This has led to the most empirical definition of floc strength; the larger the flocs grow in a given shear condition, the stronger they are.

A difficulty encountered in flocculation in stirred tanks is that the regional energy dissipation and thus the effective shear rate (determined by the total energy dissipation or the mixer rotational speed) are considerably larger than the average value. The shear rate near the tips of the propellers can reach ten times the tank average. The maximum size that flocs can reach is based on the maximum shear rate they are exposed to, whilst the rate of floc growth is determined by the average shear rate.

Floc strength is a rather poorly understood feature because of lack of proper techniques for making adequate measurement. It is known that flocs break up from their weakest point. Floc strength is related to floc size and structure. Deformation and fracture for large flocs can be the result of dynamic pressure change. In case of flocs smaller than microscale (100 μm) viscous forces prevail and may cause erosion of primary particles or small floccules from a larger floc, or break-up of a larger floc into smaller flocs of similar size. In most cases, collisions of particles with each other have a small effect on the fracture process.

Fractal nature of flocs has some interesting points about floc strength and breakage. The number of contacts between the particles is higher for more compact (higher d_F) structures, so these flocs are stronger than those with smaller fractal dimensions. However, according to an empirical definition of floc strength, floc size under a given shear condition can be taken as a measure of floc strength. For a given particle mass, floc size depends on the fractal dimension, so interpretation of such

measurements is not entirely accurate. Additionally, one of the factors that cause more compact flocs is low collision efficiency, which means that there is less attraction among particles and hence lower floc strength. Studies that consistently combine interactions between particles and fractal character are important.

Intuitively, it is expected that flocs formed by cluster-cluster flocculation should be separated in the original clusters when they break up. There is not much information in this regard, but it reminds of old ideas based on a hierarchical flocculation that suggests that the flocs of primary particles are different from the aggregates of those flocs of primary particles. In these ideas, only the aggregates are thought to break into resistant flocs.

Almost all applications with hydrolysing coagulants are under turbulent fluid motion conditions. Coagulant mixing is carried out in a mixing tank or a type of hydraulic structure for a short period of time with very intense agitation (rapid mixing) and usually followed by lighter mixing (slow mixing) for a longer period of time. The aim of the latter phase is to encourage collisions of particles and floc growth. Flocs grow initially at a rate dependent on the applied shear rate as well as the particle concentration and collision efficiency. As the flocs grow, more growth is limited by the applied shear, mainly due to the following two reasons: Existing flocs can be broken by the action of shear forces (Matsuo and Unno, 1981), and in a shear environment collision efficiency diminishes as the particle size increases (Brakalov, 1987). The dynamic equilibrium between floc growth and breakage usually determines the steady-state floc size distribution, in which the largest size flocs can reach is dependent on the shear applied (Mühle, 1993; Serra et al., 1997).

Bache et al. (1999) suggest an electrostatic bridge model in which the positive charge of precipitate is shared by the negative charge of the primary particles. They suggest that the durability of this bridge depends on the negative charges of primary colloids. To prove this, they used four different suspensions with different particle surface charges (zeta potential), and found that the flocs of the primary particles with the lowest zeta potential had the highest, whilst the flocs of the primary particles with the highest zeta potential had the lowest strength.

The flocs formed by hydrolysing coagulants are rather weak and breakage is already possible. In sweep flocculation, floc breakage is not completely reversible, i.e. after fracture, when the shear rate is decreased to the rate before floc breakage, flocs cannot grow back to their previous size. This effect is known in practice, but has attracted more systematic attention (Francois and Van Haute, 1984; Francois, 1987; Spicer et al., 1998). Although the more recent studies (Yukselen and Gregory, 2002a and b; Yukselen and Gregory, 2004a and b; Şam and Yükselen, 2006; Sam and Yukselen, 2007; Yukselen et al., 2007) provide detailed information on this issue, the underlying causes are not yet known.

Yukselen and Gregory (2002a and b; 2004a and b) used the dynamic monitoring of floc formation and found that breakage of flocs formed in the flocculation of kaolin suspensions with aluminium sulphate, iron (III) sulphate, polyaluminium chloride and polyiron chloride was irreversible, and the extent of breakage depended on the duration of rupture (i.e. rapid mixing time to break fully grown flocs). According to this, flocs cannot reach their size before breakage when they reformed after breakage, and the maximum size they regrow to also gets smaller as the breakage time increases.

So far, no model has been developed to explain all these findings. This effect appears to be specific to sweep flocculation, since it has been found that floc breakage is almost completely reversible in studies with polyelectrolytes which destabilise particles by charge neutralisation and electrostatic "patch" effect (Yukselen and Gregory, 2002a and b, Alizadeh and Pawlik, 2024). When the interaction between the particles is only electrical, there is no reason for the broken flocs to grow back to their original size. It has been shown that flocs formed by electrostatic interaction can grow to their former size after breakage (Yukselen and Gregory, 2004a).

In studies researching floc strength, many different model suspensions, jars, stirrers, and shear apparatus have been used. Although these studies are in agreement on some issues, they differ from each other in many respects due to the differences in the techniques and equipment used in determining floc strength (Jarvis et al., 2005).

1.9. Aim of This Investigation

The results of researches in literature examining the effect of ozone on the removal of NOM by coagulation / flocculation are complicated and specific to the conditions studied (Reckhow and Singer, 1984; Colin et al., 1986; Farvardin and Collins, 1989; Marhaba and Pipada, 2000; Singer et al., 2003).

Ozonation imposes a substantial alteration in the structure of organic matter. After ozonation, organic matter of high molecular weight is converted into organic compounds with smaller molecular weight, yet no significant change occurs in TOC concentration (Miltner et al., 1992, Tobiason et al., 1993). Oxidised organic matter is expected to act in a different way during coagulation. Consequently, turbidity and efficiency of organic carbon removal are expected to change. The interaction between ozone and organic matter is rather complicated, mainly because neither the structure of organic matter nor reactions that occur are definitely known. In literature there are numerous articles reporting the effect of ozonation on organic matter removal that contradict one another (Xie et al., 2016). Some researchers indicated that pre-ozonation diminished the organic matter removal (Schneider and Tobiason, 2000; Hailong et al., 2007; Bose and Reckhow, 2007), whilst others claimed the opposite (Marhaba and Pipada, 2000; Singer et al., 2003; Yukselen et al., 2007; Pei et al., 2007; Jasim et al., 2008). And some informed that effect of ozonation depended on the concentration of organic matter (O'Melia et al., 1999) and ozone dose (Singer, 1990; Edwards et al., 1993) (For instance, Edwards et al., (1993) reported that "pre-ozonation directly removed organic matter by mineralisation, volatilisation and/or stripping reactions, improving removal in comparison to unozonated systems. On the other hand, pre-ozonation decreased the surface charge of floc formed after coagulation with hydrolysing metal salts, hindering adsorptive removal of the anionic organic molecules by floc surfaces and/or inducing stabilised floc formation; changes that decrease removal in comparison to unozonated systems."). The contradictory statements in literature might have arisen from the use of characteristically different waters. Raw waters used in those studies are sampled from different regions and climatic conditions. The molecular weight, structure, charge density and acidity of the organic material may vary seasonally and regionally (Edzwald, 1993; Popov et al., 2020). Substantially,

humic substances of different origins may not react identically with ozone (Gilbert, 1988). This necessitates a study in which experiments are conducted with synthetic model suspensions under controlled operating conditions so as to better understand the effect of ozone on organic matter flocculation and removal. In this study, humic acid was chosen as the model NOM because humic acid part of NOM is more aromatic and has a larger molecular size, therefore it is hydrophobic, highly reactive and relatively easily removable by coagulation (Randtke, 1988; Owen et al., 1995). Humic substances constitute the major part of NOM and are more determinative in NOM's behaviour (Sharp et al., 2006, Bose and Reckhow, 2007). Also, humic acid serves as the main cause of THMFP (Speitel et al., 1999), thus its efficient removal and elimination of THMFP is crucial.

2. MATERIALS & METHODS

2.1. Methodology

Flocculation tests with fully synthetic raw waters whose hardness and alkalinity is maintained by pre-added $CaCO_3$ and $NaHCO_3$ (into deionised water) and pH was preset (to around neutral pH) and containing different concentrations of humic acid consisted of orthokinetic aggregation experiments by hydrolysing metal salts and pre-hydrolysed metal coagulants were conducted in jar test equipment. Monomeric metal salt $Al_2(SO_4)_3$ and polymeric metal salt polyaluminium chloride (PACl) were used as coagulants. For the purpose of examining the effect of ozone, some of the prepared suspensions were used as unozonated and the others were pre-ozonated at different doses before flocculation. Flocs obtained in flocculation process were allowed to settle for a 20 min., and samples were collected from the clear zone (supernate). Residual total organic carbon (TOC), dissolved organic carbon (DOC) (filtered through membranes of 0.45 μm), absorbances at 254 nm, 465 nm and 656 nm were measured. The UV absorbance at 254 nm enables us to compare between the concentrations of organic matter present, and it is also used in the calculation of Specific UV absorbance (SUVA) by taking the ratio of it to DOC amount. SUVA gives insight into hydrophobicity/hydrophilicity of humic matter. It was attempted to find evidences for the molecular size distribution of humic material by taking the ratio of absorbances at 465 nm and 656 nm. High E_4/E_6 ratio indicates that small molecules are present in the solution, whilst low E_4/E_6 ratio indicates that large molecules are present (Maartens et al., 1999).

The phases of flocculation were monitored dynamically using a Photometric Dispersion Analyser (PDA). This device operates on the basis of optical principles which are used to determine the relative floc size. The PDA device does not measure the actual floc size but gives a Flocculation Index (FI) for the relative floc size, which allows the comparison of floc dimensions. Consistency of FI value with the course of flocculation has been introduced by Gregory and Nelson (1986). The FI value is obtained by proportioning the average light intensity (dc value) passing through and the positive average (rms) of fluctuating component (ac value) (FI = rms/dc). As the floc

size increases, rms value also varies in a direct proportion. Since the device is sensitive to the slightest change that may occur in floc size, floc breakage and re-formation after the breakage can be monitored.

2.2. Preperation of Raw Waters Used in Jar Tests

In order to maintain a controlled experimental media and better reproducibility raw waters to be used in the jar tests were prepared synthetically by adding designated amount of hardness, alkalinity and humic acid to deionised water and the pH was set. Hardness and the alkalinity of waters were adjusted to 100 mg/L by adding appropriate amount of 0.1 M $CaCO_3$ (Merck) and 0.1 M $NaHCO_3$ (Merck). pH of the raw waters was kept around 7.0 by addition of necessary amount of 0.1 N H_2SO_4 (Merck). Flocculation experiments were performed with suspensions containing 5, 10 and 20 mg/L humic acid (HA) concentrations used unozonated and pre-ozonated with 2.5, 5 and 10 mg/L applied ozone doses.

2.3. $CaCO_3$ Preparation for Hardness Adjustment

0.1 M $CaCO_3$ solution was prepared as described in the Standard Methods, as follows: 5000 mg of $CaCO_3$ was weighed and dried in oven at 103-105 ^oC. After it was cooled in a desiccator, it was transferred into 500 mL Erlenmeyer flask or beaker. 1+1 HCl was added until all $CaCO_3$ in the flask dissolves. Then, 300 mL of deionised (DI) water was added and the solution was boiled for a few minutes until all CO_2 is expelled. Finally, prepared solution was cooled and transferred into a 1 L graduated flask and diluted to 1000 mL with DI water.

2.4. $NaHCO_3$ Preparation for Alkalinity Adjustment

8400.65 mg of $NaHCO_3$ was weighed and diluted to 1000 mL with DI water. This 0.1 M $NaHCO_3$ solution is used to add alkalinity to synthetic raw waters.

2.5. Coagulants

Alum [Aluminium sulphate octadeca hydrate ($Al_2(SO)_4$ **.** $18H_2O$; Merck)] is one of the coagulants used for flocculation experiments. For preparation, alum was

dried in oven at 103-105 ^{o}C and dissolved in deionised water at a concentration of 0.1M. Stock alum solution was kept in refrigerator at +4 ^{o}C.

Commercial polyaluminium chloride (PACl) product (PAX-XL9) (Kemira Kemi AB, Helsingborg, Sweden) was also used for the flocculation experiments. PACl has a density of 1.192 g/mL and supplied as 4.29 weight % Al solution. This solution was used without any dilution.

2.6. Apparatus

The dynamics of flocculation were monitored using a Photometric Dispersion Analyser (PDA) (Photometric Dispersion Analyser - PDA 2000, Rank Brothers Ltd., Cambridge, UK) in order to compare the flocculation rates.



Figure 2.1. Photometric Dispersion Analyser (PDA 2000, Rank Brothers Ltd., Cambridge, UK)



Figure 2.2. Flocculator 2000 semiautomatic jar-test device (Kemira Kemwater, Helsingborg, Sweden)



Figure 2.3. Peristaltic pump (Watson Marlow)

800 mL of synthetic waters were contained in 1000 mL jars, each was stirred with pedal mixers connected to a Flocculator 2000 semiautomatic jar-test device (Kemira Kemwater, Helsingborg, Sweden).

On the menu of this device or by a software through computer connection rapid and slow mixing times and speeds can be preset.

Sample from one beaker was circulated for dynamic monitoring of floc growth through transparent plastic tubing (3 mm i.d.) by a peristaltic pump (Watson Marlow).

The peristaltic pump was located after the Photometric Dispersion Analyser (PDA) instrument to prevent floc breakage since flocs are likely to be broken in the pinch portion of pump. The tubing was clamped in the PDA instrument so that the flowing sample was illuminated by a narrow light beam (850 nm wavelength). The PDA 2000 measures the average transmitted light intensity (dc value) and the root mean square (rms) value of the fluctuating component. The ratio of the latter to the former (rms/dc), which is the Flocculation Index (FI), gives a sensitive index of particle aggregation (Gregory and Nelson, 1986).

The FI value is not an exact measure of the floc sizes, it can only be used as comparative information on floc properties under different coagulation kinetics conditions such as different mixing intensities and times, different coagulant types and doses, etc.

The FI value was shown to be in good correlation with mean floc size and residual turbidity after sedimentation (Gregory and Nelson, 1986; McCurdy *et al*., 2004). As flocs under shear grow, a corresponding increase in the FI value is observed, and the rate of increase is a good indication of flocculation rate. By the same way, floc breakage is apparent by a reduction in the FI value, and so is re-growth of flocs by a following increase.

Considering the difficulties in determining the absolute floc sizes under dynamic conditions using currently available methods, this ‘turbidity fluctuation technique’ used by PDA is very practical in many circumstances. The experimental

setup for dynamic monitoring of floc growth is presented in Figure 2.6 and illustrated in Figure 2.7.

2.7. Procedure

Synthetic raw waters were prepared by adding designated amount of humic acid to deionised water. Before humic acid addition 0.1 M $CaCO_3$ and 0.1 M $NaHCO_3$ were added to deionised water. Finally, necessary amount of H_2SO_4 was added to keep pH around 7.0 (WTW pH 730 pH meter).

Ozone Generator (PCI Ozone & Control Systems, Inc West Caldwell, N.J.) was used for pre-ozonation of the synthetic raw waters.

For standard jar tests, 800 mL of synthetic waters containing humic acid (alkalinity and hardness was each set to 100 mg/L as $CaCO_3$) was placed in a 1000 mL jar. The sample was circulated from the stirred jar at a flow rate about 25 mL/min through a transparent plastic tubing which was attached to the PDA instrument. After allowing a 60 seconds for steady-state readings to be established, coagulant was dosed and immediately after dosing, the sample was stirred at 400 rpm (G = 518 s^{-1}) for 10 seconds to provide complete mixing of the coagulant.



Figure 2.4. pH meter (WTW)



Figure 2.5. Ozone Generator (PCI)



Figure 2.6. Experimental setup for dynamic monitoring of floc formation in jar-test procedure

After rapid mixing, the stirring speed was reduced to 50 rpm (G = 23 s^{-1}) and kept at this value for 10 minutes to allow flocs grow. In order to achieve floc breakage, the stirring speed was increased to 400 rpm for 10 seconds. After floc breakage the stirring speed was reduced back to the previous slow mixing condition which was 50 rpm for 10 minutes. At the end of each jar test, the flocculated sample was allowed to rest for 20 minutes to leave flocs to settle. The G values given above were average shear rates and calculated according to Mejia and Cisneros (2000), who used a similar jar test device.

Illustration of the experimental setup for dynamic monitoring of floc is as follows:

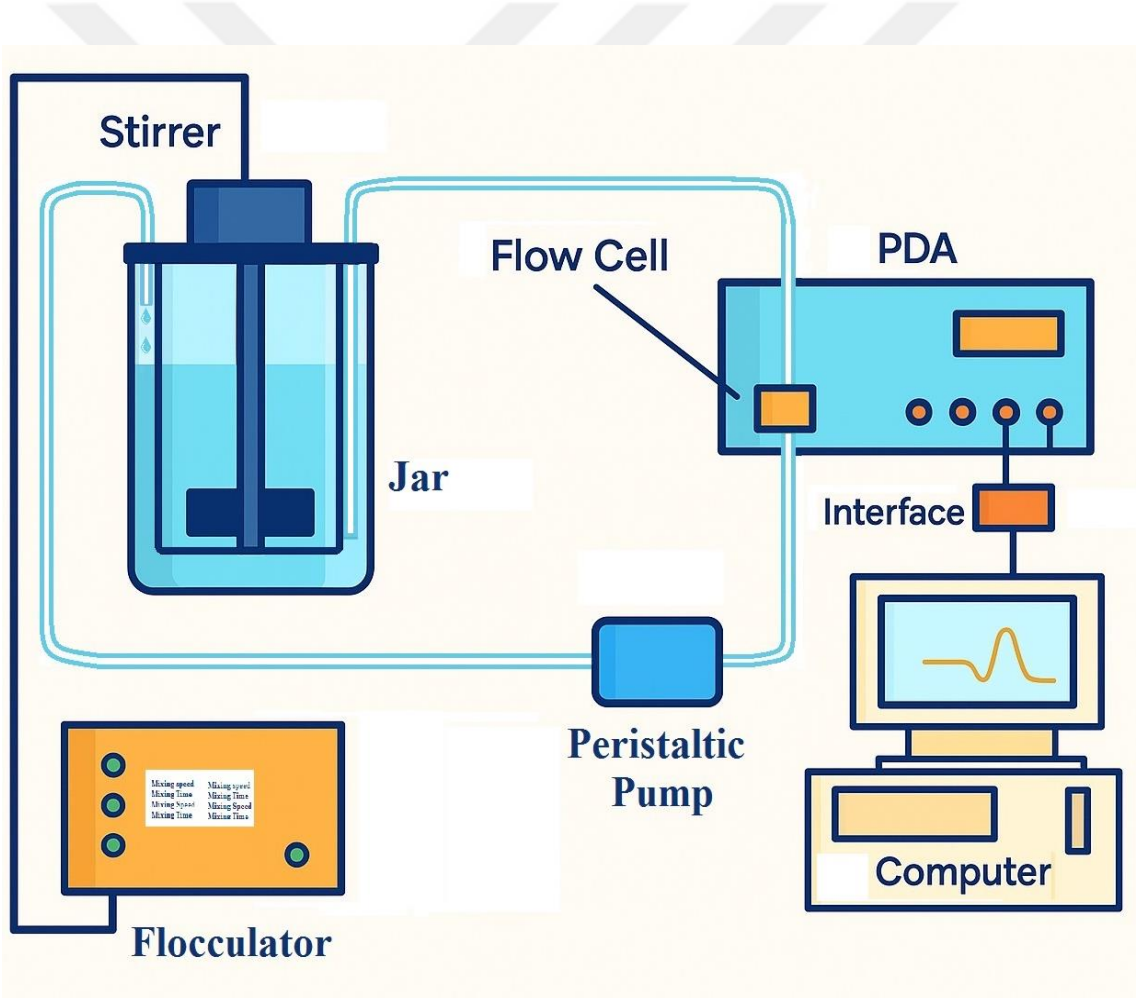

Figure 2.7. Schematics of the experimental setup for dynamic monitoring of floc formation in jar-test procedure (Yukselen and Gregory, 2002a)

At the end of 20 min. settling period, a 50 mL sample was withdrawn from the top clear phase for total organic carbon (TOC), dissolved organic carbon (DOC) and UV absorbance measurements.



Figure 2.8. Total Organic Carbon (TOC) Analyser



Figure 2.9. Shimadzu UV-2450 UV Visible Spectrophotometer

Total organic carbon and dissolved organic carbon measurements was performed by Tekmar Dohrmann Apollo 9000 TOC Analyser, which uses high temperature combustion technique with catalyst.

The residual absorptions of samples were measured in the UV visible range by a Shimadzu UV-2450 UV Visible Spectrophotometer.

All experiments were carried out at least three times for reproducibility of data.

3. RESULTS & DISCUSSION

3.1. Determination of Optimum Coagulant Doses

3.1.1. Optimum $Al_2(SO_4)_3$ dose

Using 0.1 M alum stock solution a series of jar test experiments were performed adding different alum doses. Optimum dose was determined as the dose achieving the optimal colour and TOC reduction.

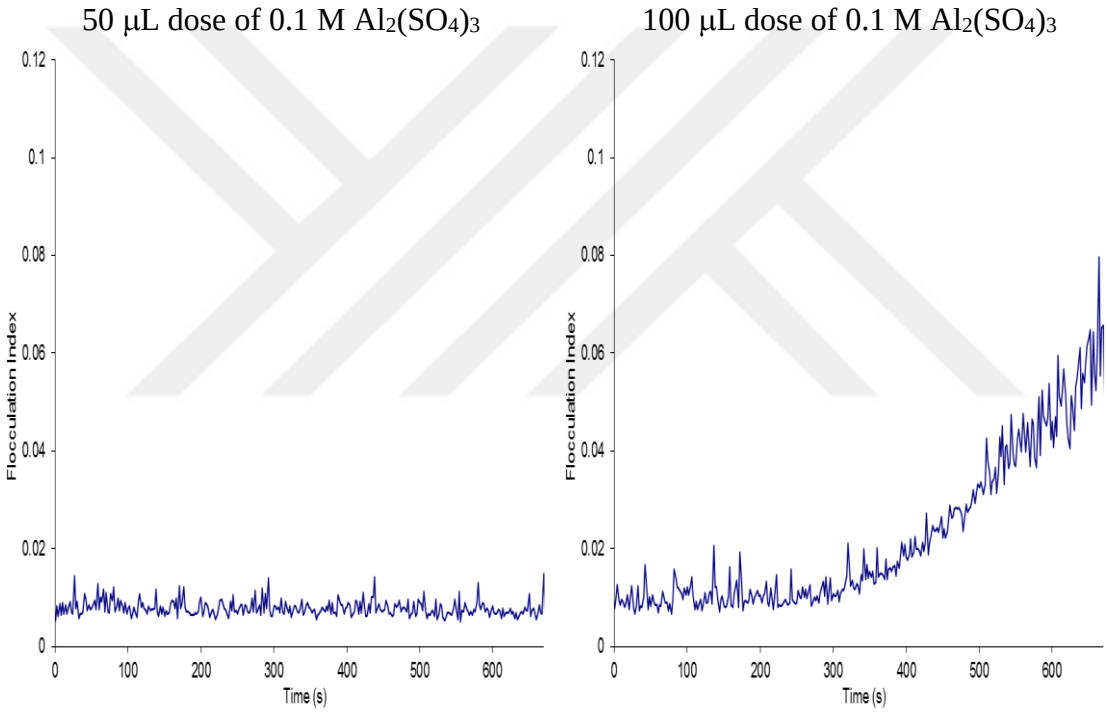

Figure 3.1. Floc growth with 50 μL and 100 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

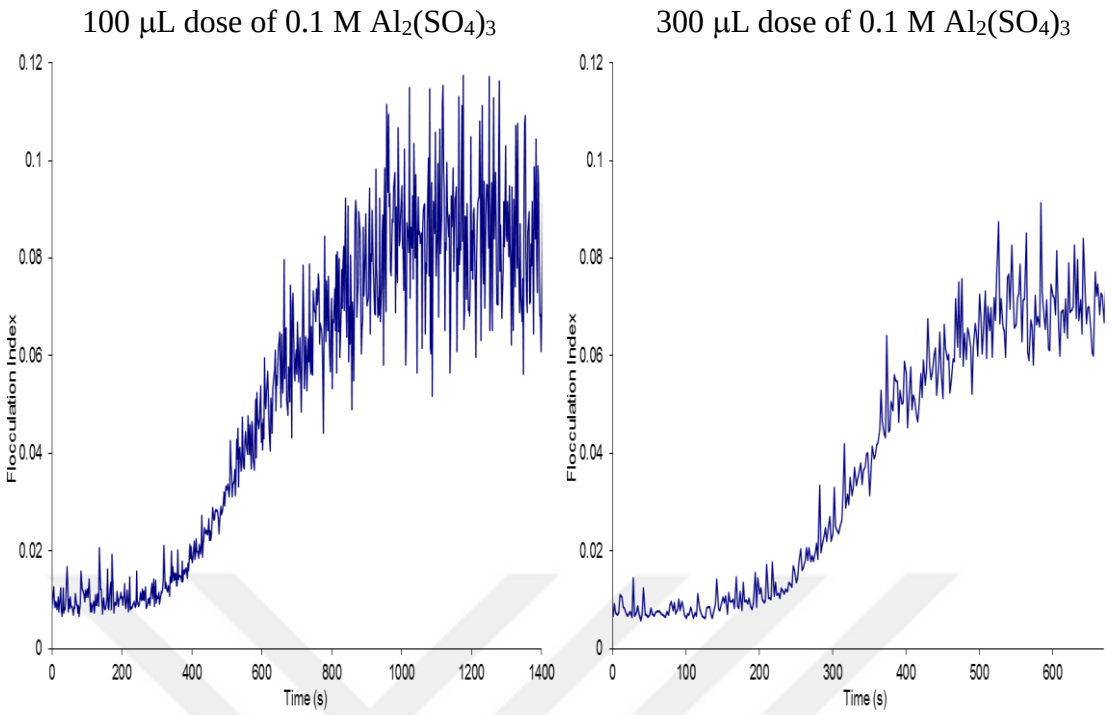

Figure 3.2. Floc growth with 100 μL and 300 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

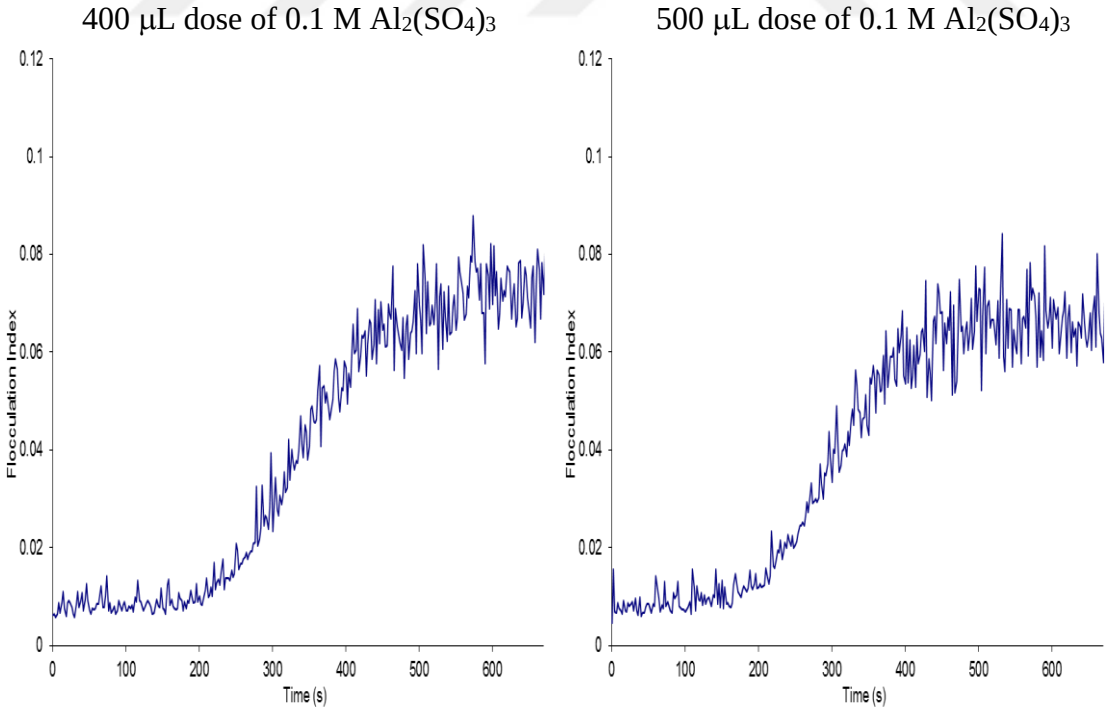

Figure 3.3. Floc growth with 400 μL and 500 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

600 μL dose of 0.1 M $Al_2(SO_4)_3$ 700 μL dose of 0.1 M $Al_2(SO_4)_3$

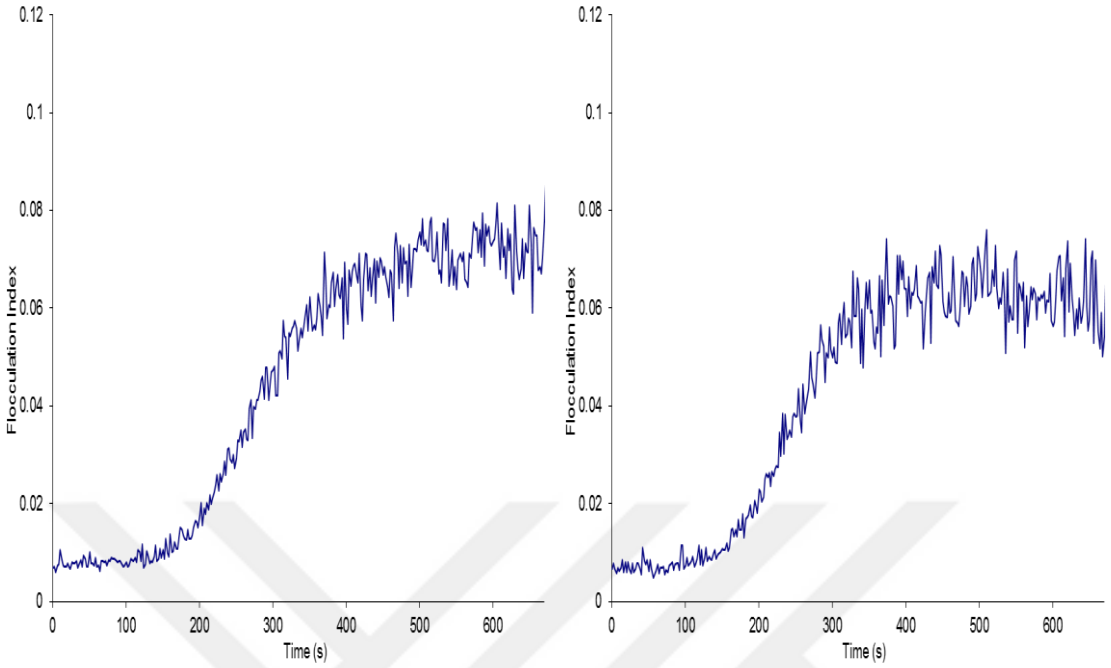

Figure 3.4. Floc growth with 600 μL and 700 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

Examining Figures 3.1 and 3.2 shows that aggregation starts when alum dose is increased from 50 μL to 100 μL. However, at 100 μL of 0.1 M $Al_2(SO_4)_3$ dose 10 minutes of slow mixing is not long enough to obtain fully grown flocs; steady-state floc size distribution can only be reached after 16-17 minutes of slow mixing. Further increasing 0.1 M $Al_2(SO_4)_3$ dose makes aggregation start earlier but does not change steady-state floc size distribution significantly. Moreover, increasing alum dose more than 600 μL causes a slight decrease in floc size. These observations can be comparatively seen when Figures 3.1-3.6 are depicted together as in Figure 3.7.

When Figure 3.7 is examined it is seen that the onset of floc formation gets earlier with increasing alum dose. For instance, the onset of aggregation is about the 3rd minute (2 minutes after dosing) when the alum dose is 300 μL of 0.1 M alum solution but it is about the 2nd minute (1 minute after dosing) when the dose is 1500 μL. This indicates an increase in aggregation rate when alum dose is increased.

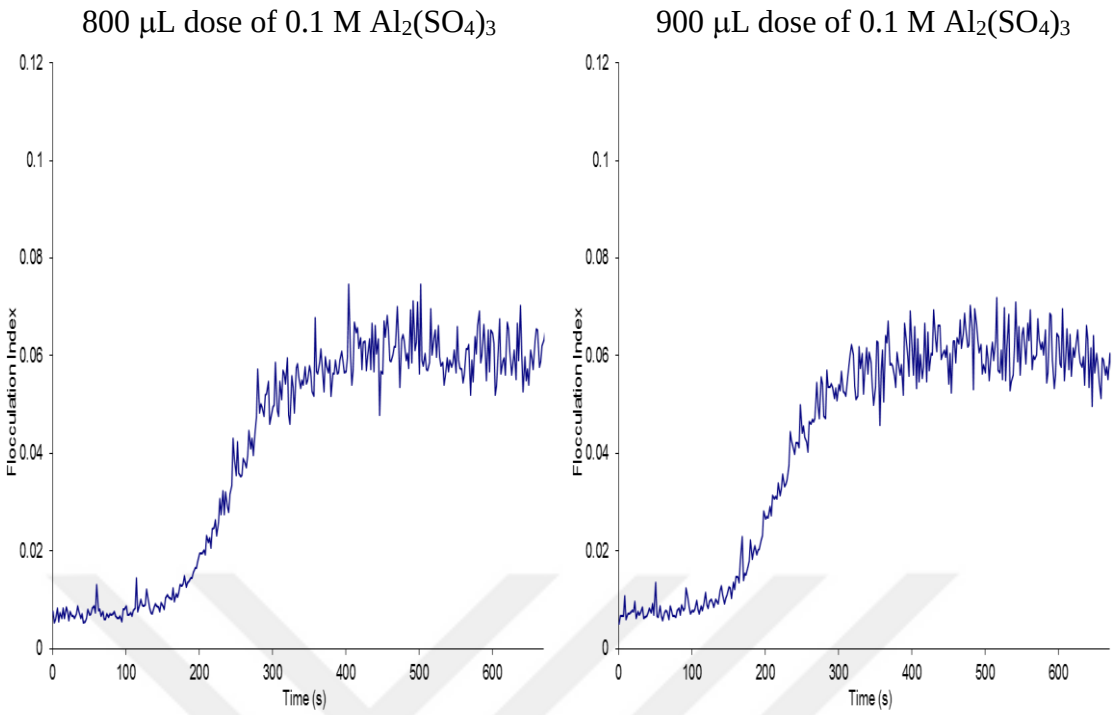

Figure 3.5. Floc growth with 800 μL and 900 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

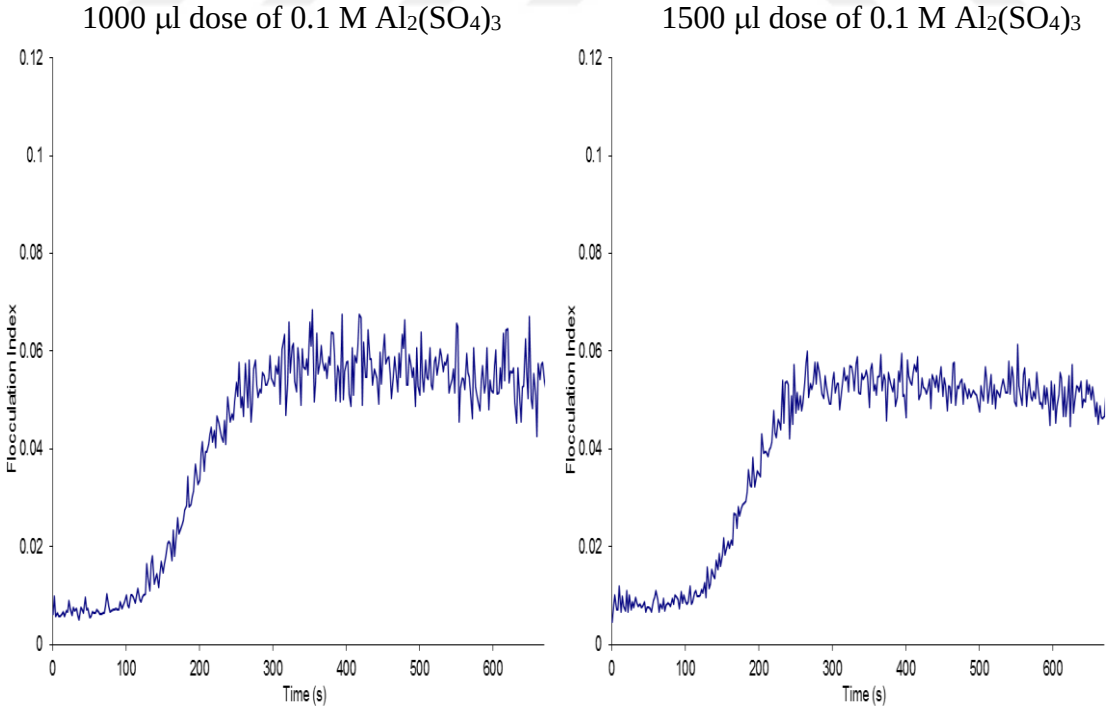

Figure 3.6. Floc growth with 1000 μL and 1500 μL dose of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

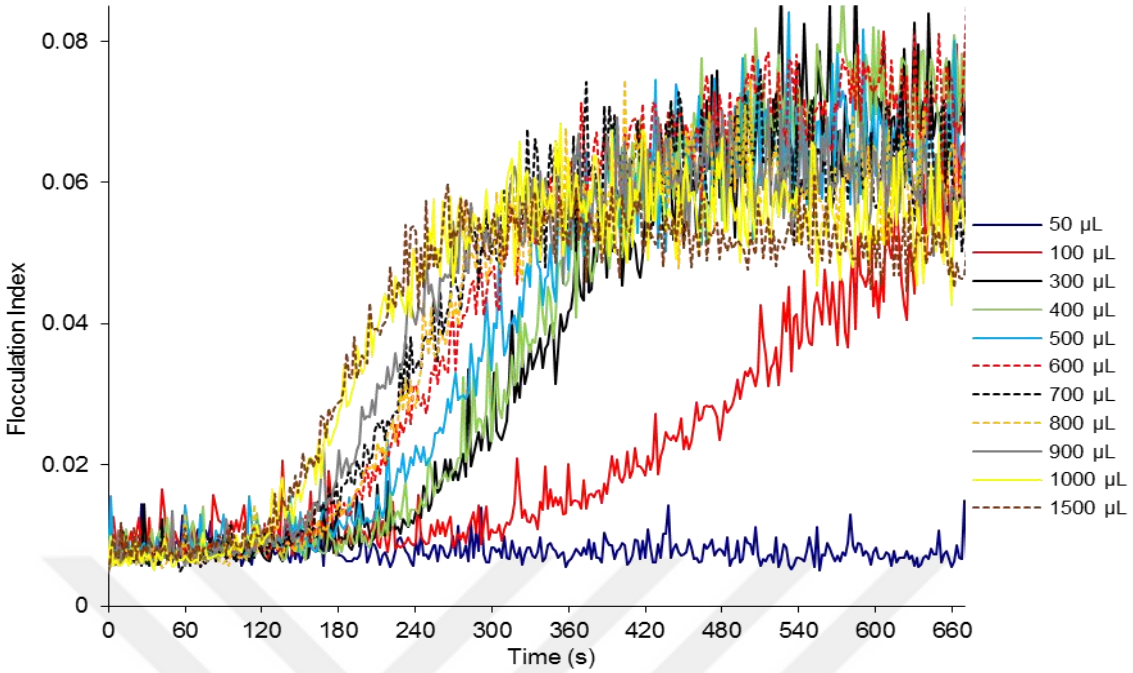

Figure 3.7. Floc growth with 50 µL - 1500 µL doses of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid

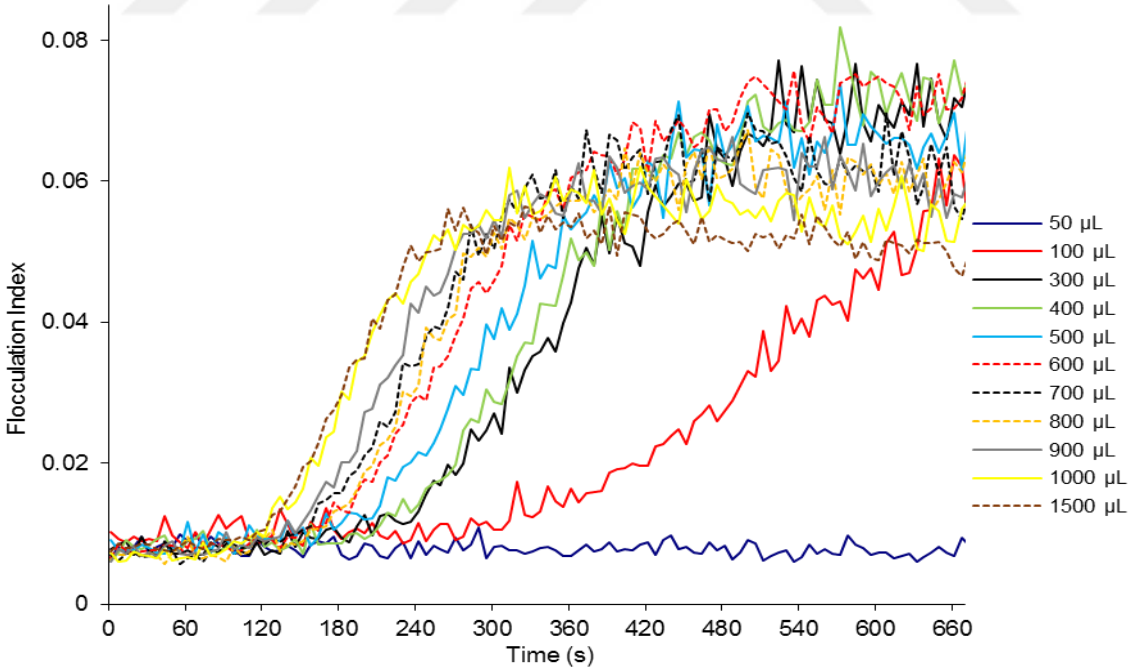

Figure 3.8. Floc growth with 50 µL - 1500 µL doses of 0.1 M alum in unozonated (0 mg/L O_3) synthetic raw waters (800 mL) containing 5 mg/L humic acid (smoothened plot of Figure 3.7)

On the other hand, the change in floc size with increasing alum dose is not of a significant measure solely. Further increase in alum dose after 300 µL does not change relative floc size (FI value) much. Removal parameter should also be considered.

Residual colour does not change significantly by dosing more than 400 µL alum. More importantly, TOC removal is not improved much after 500 µL alum dose, further dosing of the coagulant would be an unnecessary waste chemical in terms of amount, health and environment issues and costly. According to the results of experiments the optimum alum dose was determined as 500 µL of 0.1 M alum which corresponds to 3.373 mg/L Al concentration.

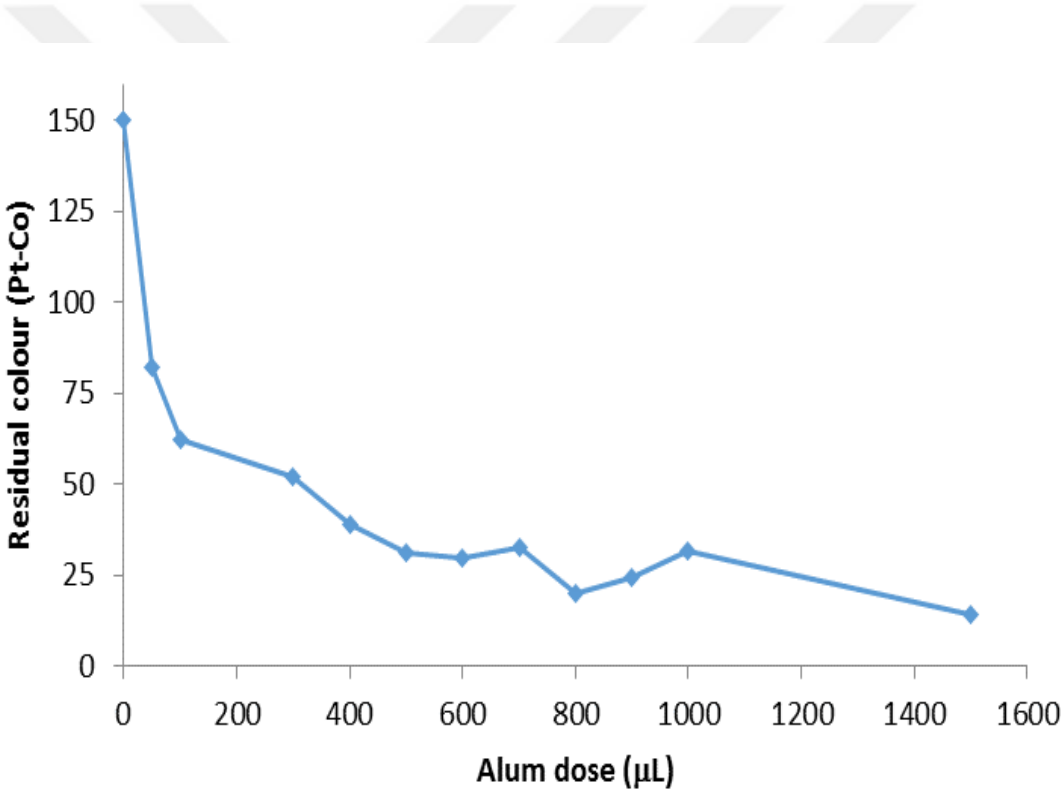

Figure 3.9. Alum doses and corresponding residual colour

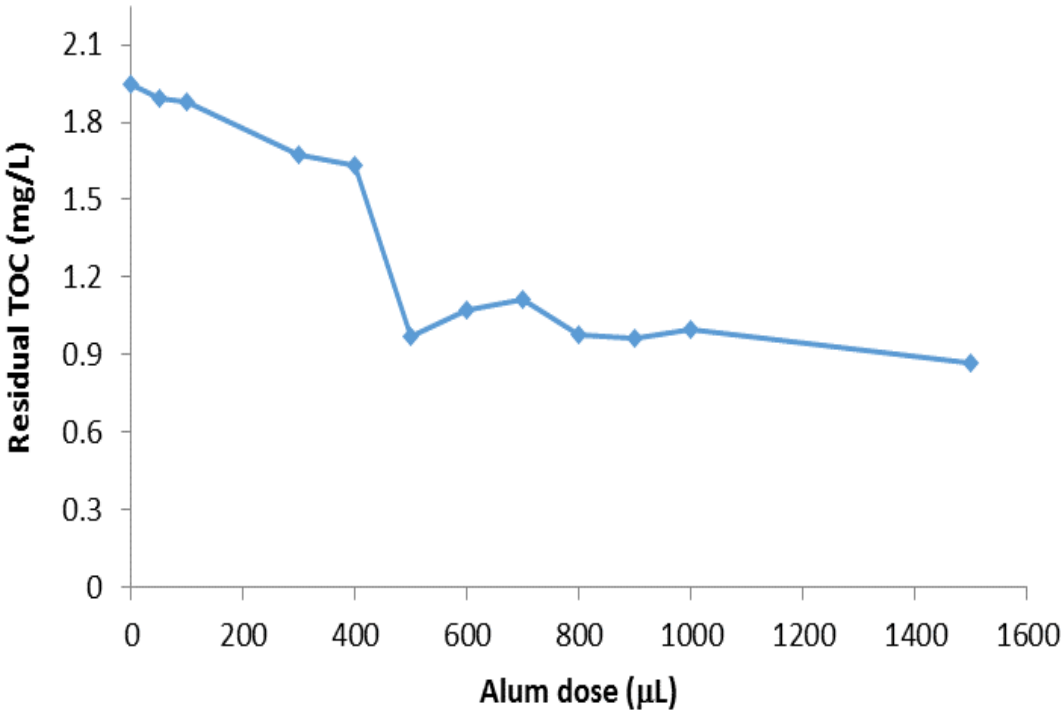

Figure 3.10. Alum doses and corresponding residual TOC

3.1.2. Optimum polyaluminium chloride dose

The pre-hydrolysed coagulant polyaluminium chloride was dosed to give the same Al concentration, i.e. 3.373 mg/L Al.

The further experiments were performed using these coagulant doses. All the experiments were repeated at least three times for reproducibility of data.

Preliminary tests of this work were performed with lower humic acid concentrations and ozone doses. In order to see clearer differences in the results of experiments under different conditions, humic acid concentrations and ozone doses were modified to those used in this research. The data are not included here because they have been thoroughly presented in Sam et al. (2010).

3.2. The Effect of Humic Acid Concentration

3.2.1. Experiments with unozonated synthetic raw waters (0 mg/L O_3)

Flocculation experiments performed with aluminium sulphate and polyaluminium chloride in unozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid are presented:

3.2.1.1. Experiments with $Al_2(SO_4)_3$

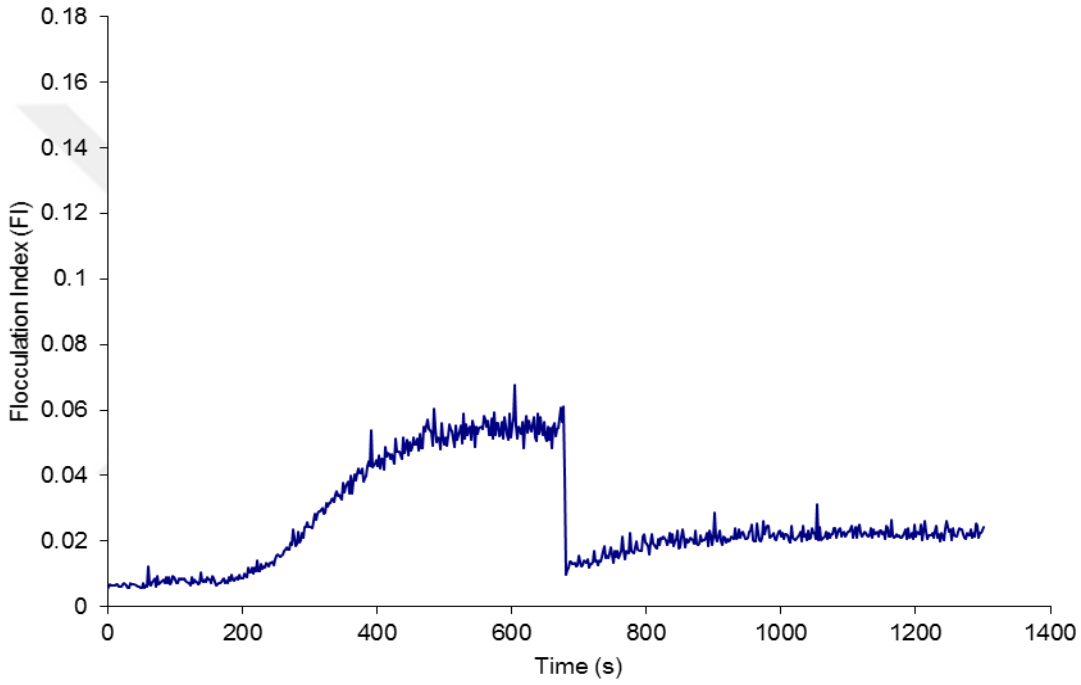

Figure 3.11. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw water containing 5 mg/L humic acid

As seen in Figures 3.11-3.13, with increasing humic acid concentration larger flocs were formed. This can be attributed to higher collision efficiency. When fully grown flocs are exposed to rupture it is known that in sweep flocculation regime flocs cannot grow back to their sizes before break-up. It is thought that in sweep flocculation the aggregation is in the form of entrapment of particles/adsorption of dissolved organic molecules in growing amorphous metal hydroxide precipitates rather than electrostatic

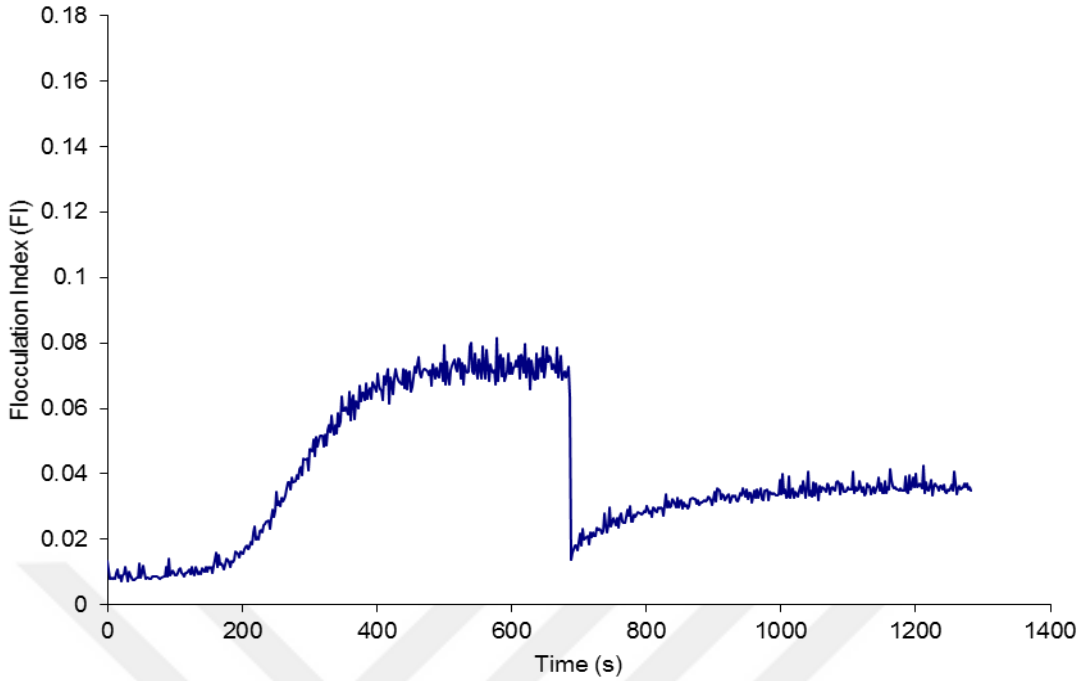

Figure 3.12. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw water containing 10 mg/L humic acid

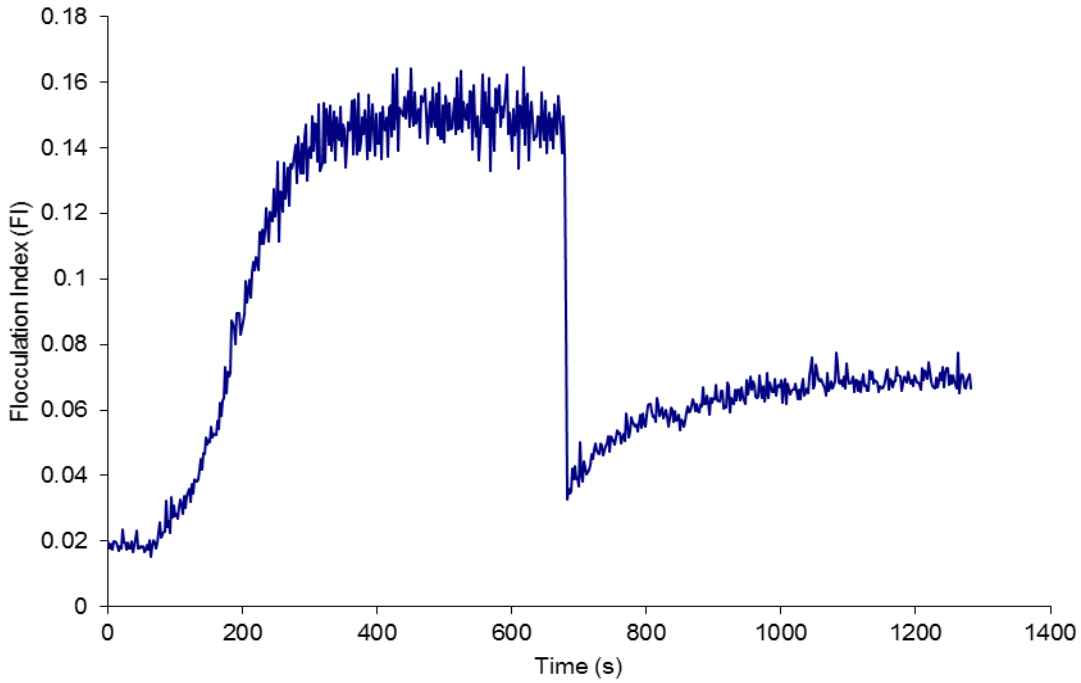

Figure 3.13. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw water containing 20 mg/L humic acid

attraction between destabilised particles. It was observed in all the experiments performed where fully grown flocs were exposed to high shear and breakage.

Another feature attracting attention is that the onset of flocculation was delayed as the concentration of humic acid was decreased. The onset of flocculation was about 75th second for 20 mg/L humic acid containing water, 120th second for 10 mg/L humic acid containing water and 150th second for 5 mg/L humic acid containing water. This could also be evaluated as a result of higher collision efficiency.

3.2.1.2. Experiments with polyaluminium chloride (PACl)

As seen, with increasing humic acid concentration larger flocs were formed (Figures 3.14-3.16). This can, as afore mentioned, be attributed to higher collision efficiency. The onset of flocculation was about 120th second for 5 mg/L humic acid containing water, 90th second for 10 mg/L humic acid containing water and about 70th second (almost immediately) for 20 mg/L humic acid containing water. This could be considered as another proof of increased collision efficiency with increasing humic acid

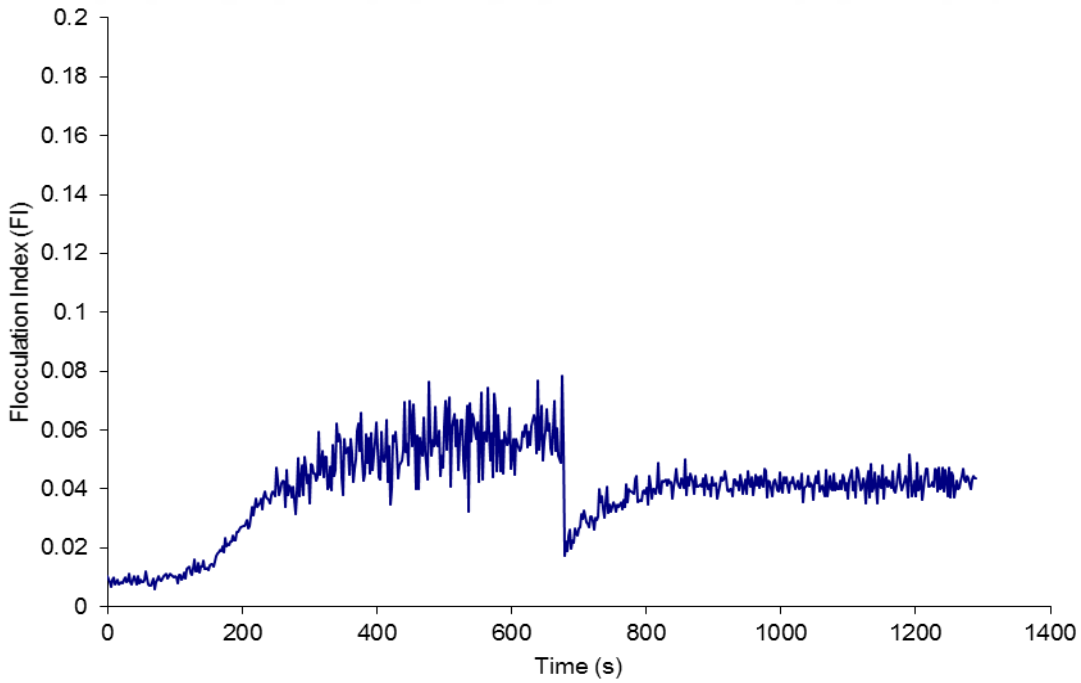

Figure 3.14. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw water containing 5 mg/L humic acid

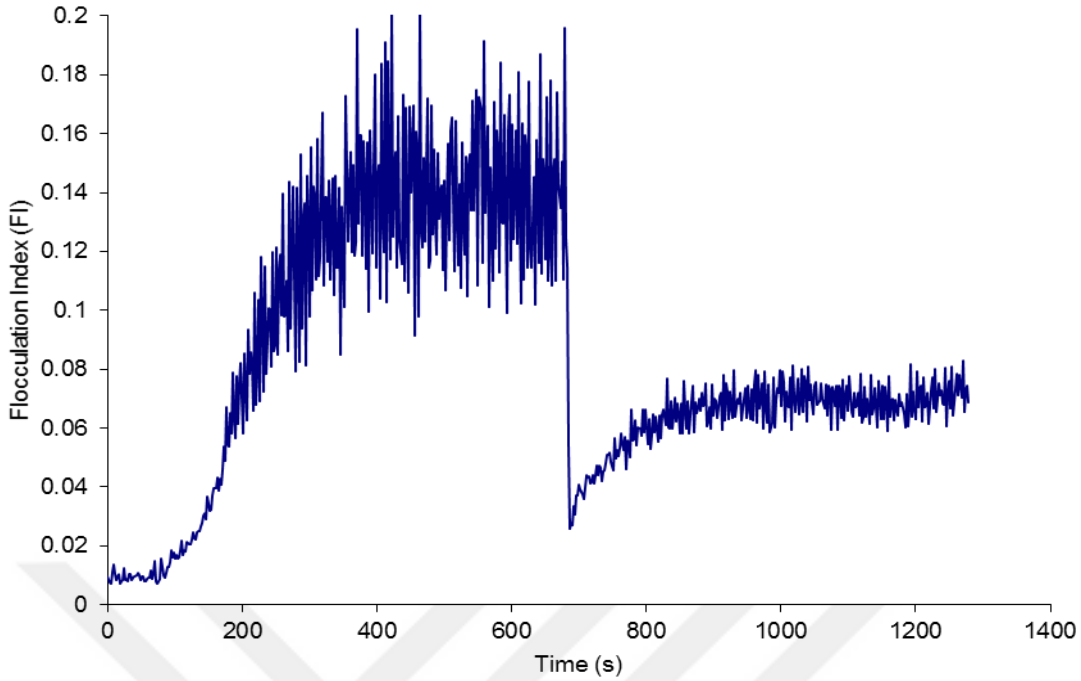

Figure 3.15. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw water containing 10 mg/L humic acid

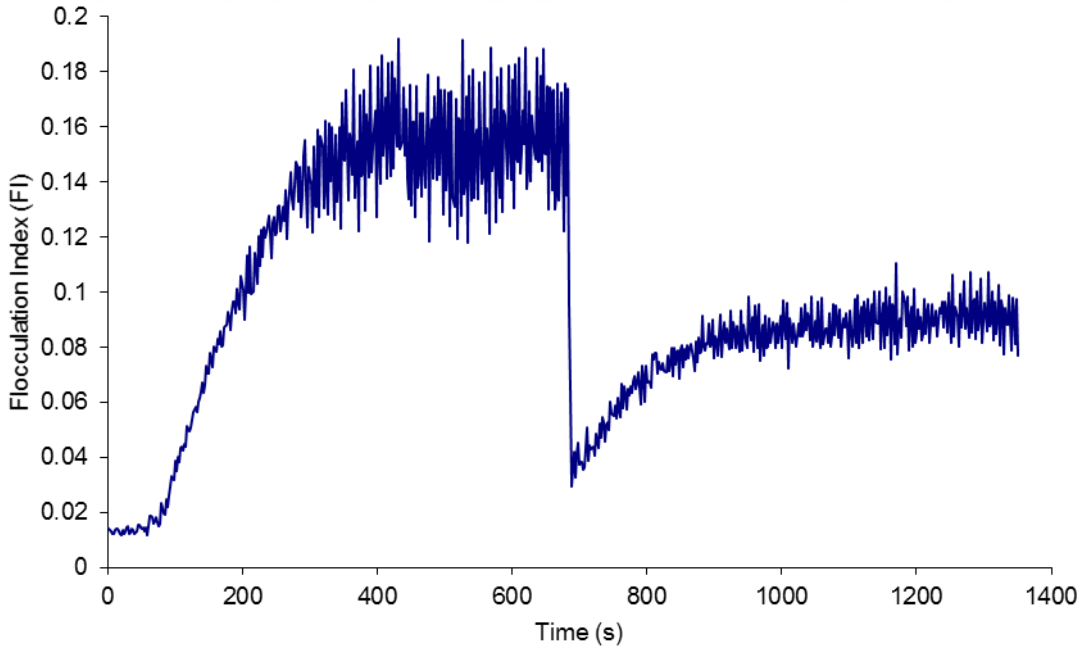

Figure 3.16. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw water containing 20 mg/L humic acid

concentration. The onsets of aggregations were rather quick compared to those with alum, which is thought to be because of higher valence of pre-hydrolysed metal hydroxide species of polyaluminium chloride coagulant. Because of the same reason, PACl exhibited better performance compared to alum in terms of forming larger flocs.

3.2.1.3. Comparison of floc sizes

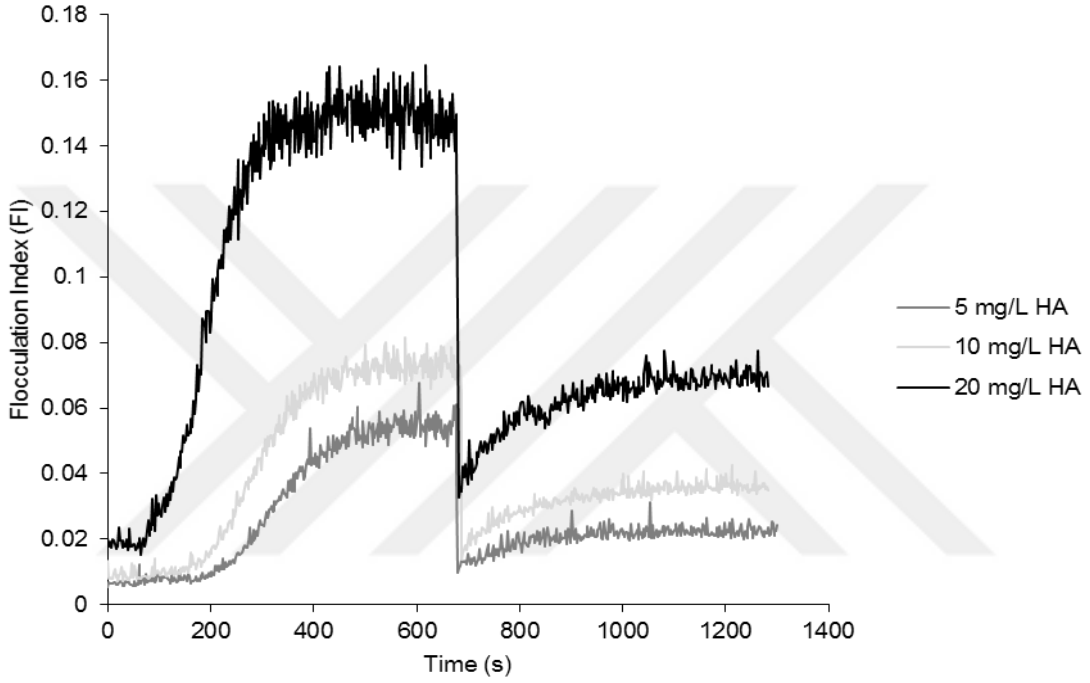

Figure 3.17. Floc growth and regrowth with alum in unozonated (0 mg/L O_3) synthetic raw waters containing 5, 10 and 20 mg/L humic acid

Floc growth with alum and PACl exhibited a similar pattern; larger flocs were formed with increasing humic acid concentration. This can be attributed to higher collision efficiency.

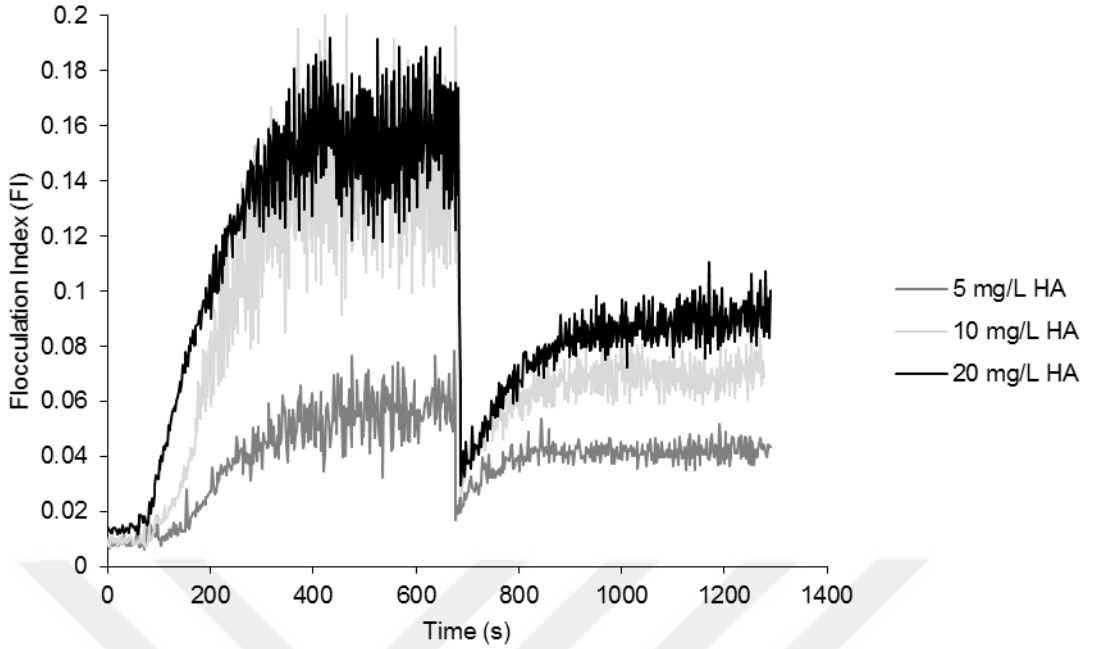

Figure 3.18. Floc growth and regrowth with PACl in unozonated (0 mg/L O_3) synthetic raw waters containing 5, 10 and 20 mg/L humic acid

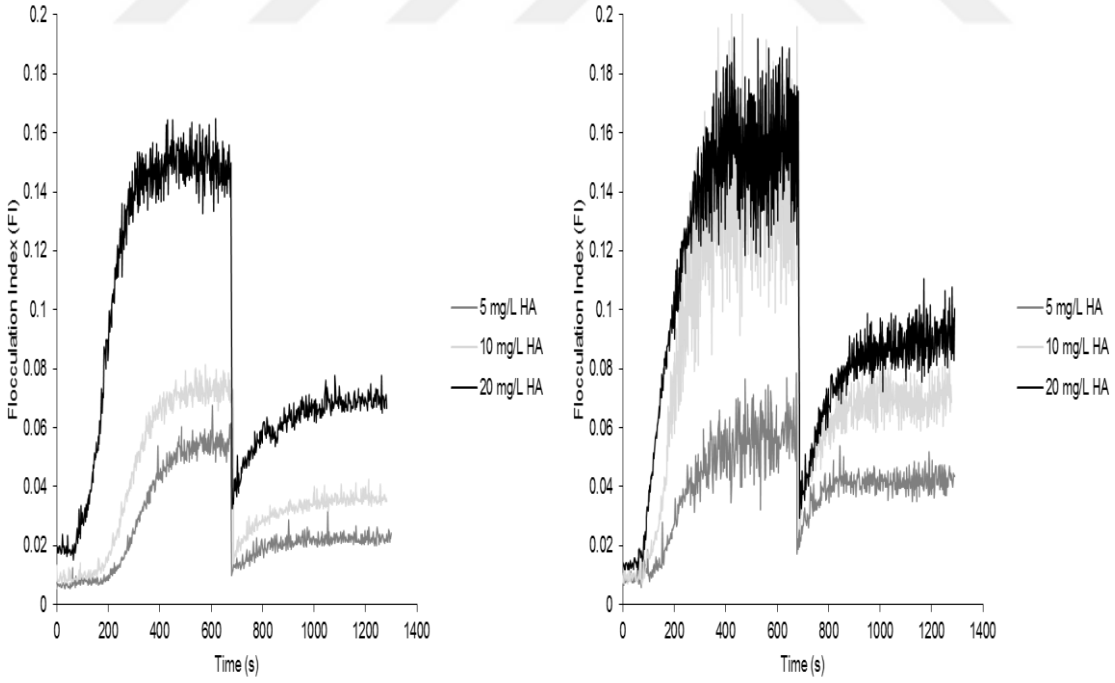

Figure 3.19. Floc growth and regrowth with alum (left) and PACl (right) in unozonated (0 mg/L O_3) synthetic raw waters containing 5, 10 and 20 mg/L humic acid

Another feature correlating this suggestion is that floc growth began sooner as the concentration of humic acid was increased. It was shown that when enough coagulant dose is used, aggregation starts earlier in waters with higher particulate concentration because of higher collision efficiency (Şam and Yükselen, 2006; Sam et al., 2010).

Formation of larger flocs was observed with PACl compared to alum, this is attributed to higher positively charged Al species contributed by PACl, which is a pre-hydrolysed coagulant. With both of the coagulants, it was observed that broken flocs could only recover to some extent of their sizes before breakage. Better floc size recovery after breakage was observed with PACl, probably due to the same reason. As the humic acid concentration was increased, the characteristics of Flocculation Index (FI) curves of both coagulants showed similarities; larger flocs and earlier onset of flocculation were observed with PACl (Figures 3.17-3.19).

3.2.1.4. Organic carbon removal with $Al_2(SO_4)_3$

In the case of flocculation with alum, as the concentration of humic acid was increased, floc size also increased. This could be attributed to higher collision efficiency with increasing humic acid concentration. Residual total organic carbon and dissolved organic carbon concentrations increased with increasing humic acid concentration. This might seem to contradict with the floc size data when residual organic matter concentration is examined, though it is not. One might think since the optimum coagulant dose was determined for 5 mg/L humic acid containing unozonated synthetic water, as the humic acid concentration was gradually increased, that dose of coagulant became more and more insufficient, leading to the observation of increasing residual organic matter concentrations but when removal efficiency is taken into account, it is seen that organic matter removal improved with increasing humic acid concentration (Appendix Figure 1 and Figure 2), which correlates with increasing floc size.

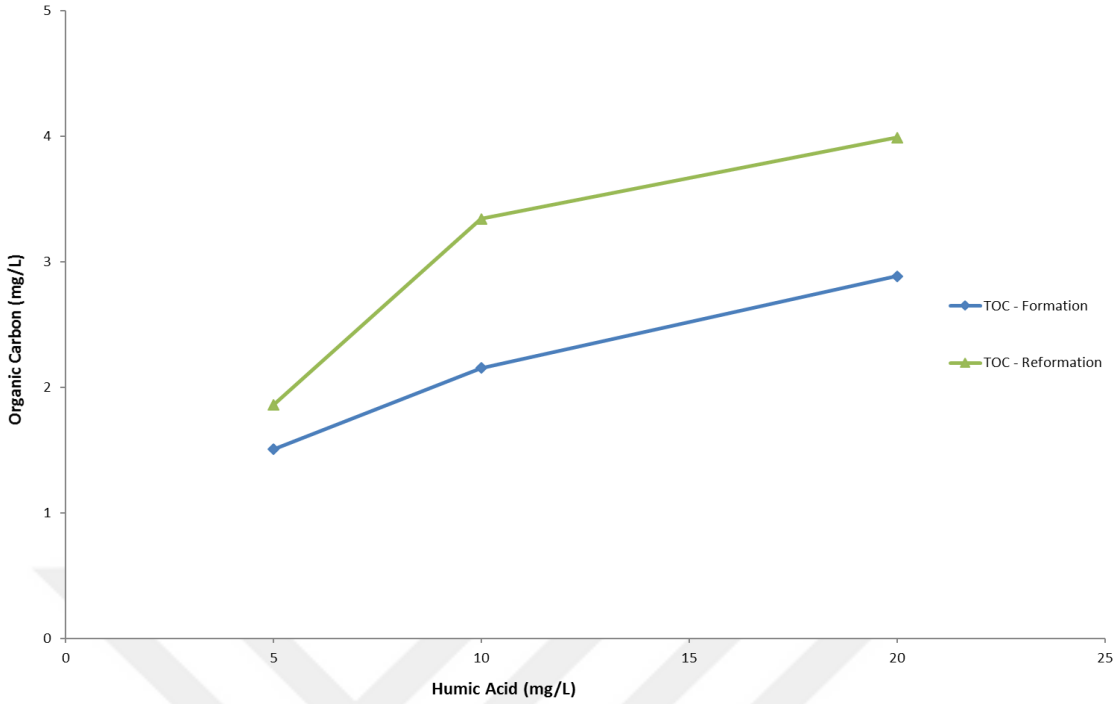

Figure 3.20. Residual TOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

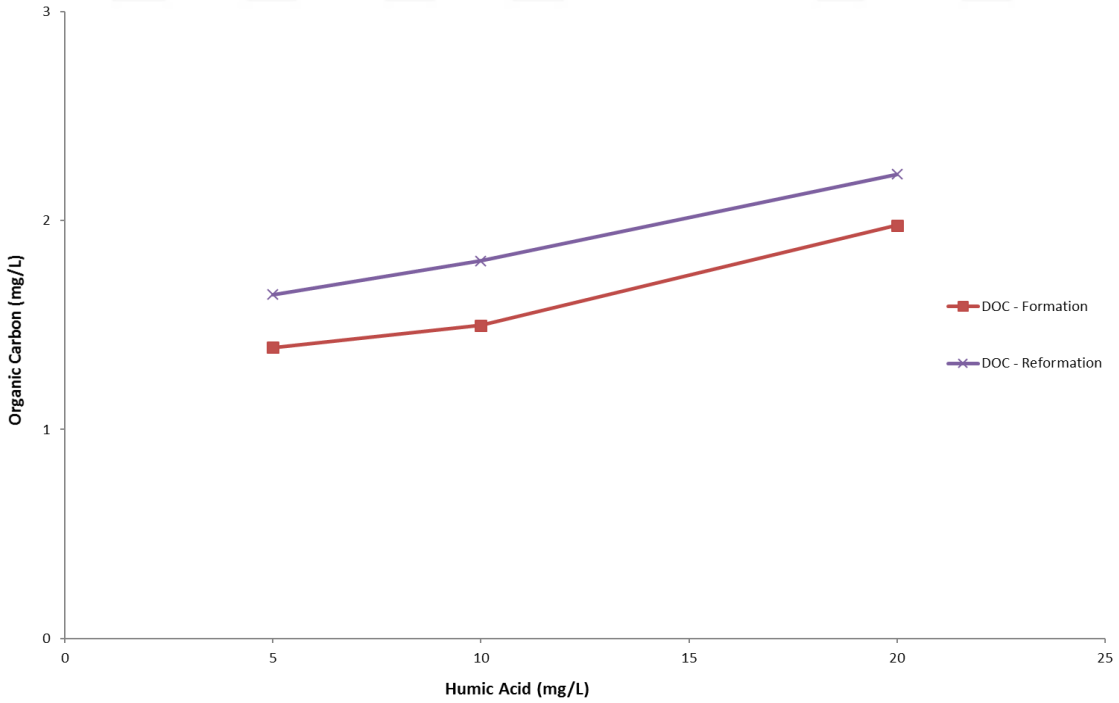

Figure 3.21. Residual DOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

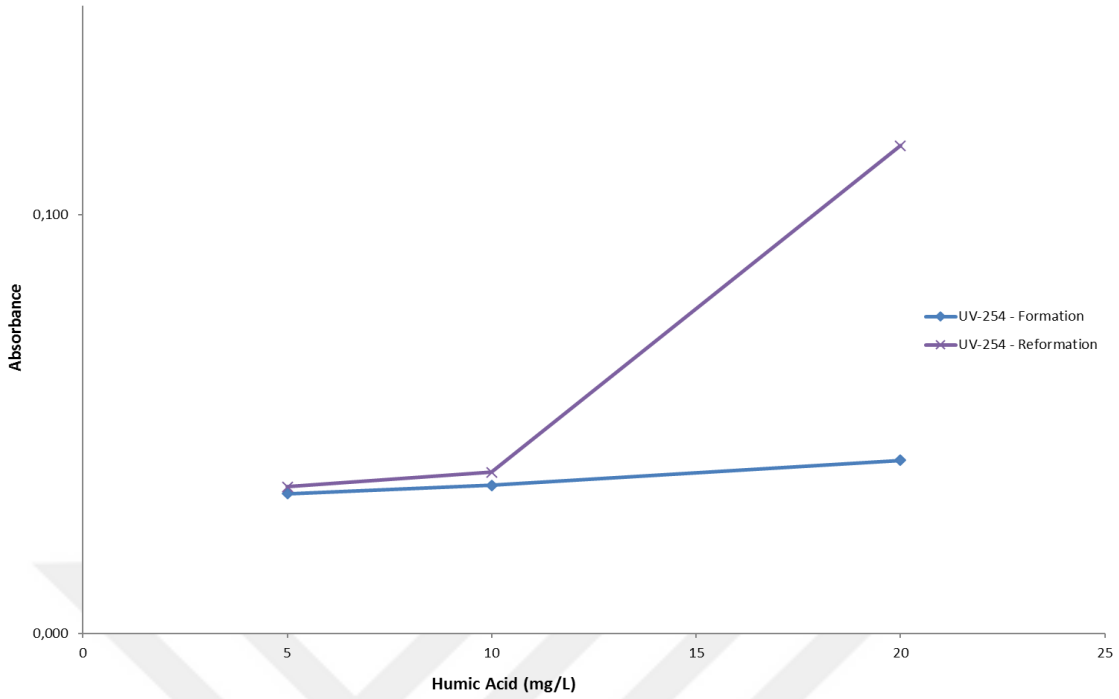

Figure 3.22. Residual absorbance at 254 nm after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

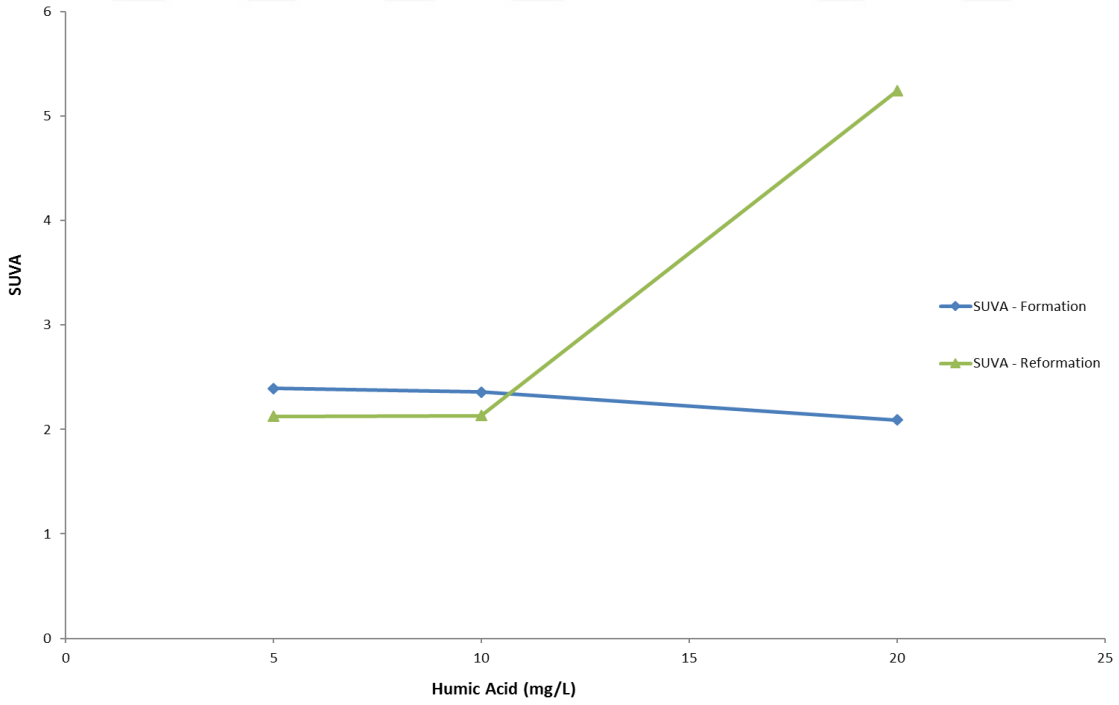

Figure 3.23. Specific UV absorbance (SUVA) after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

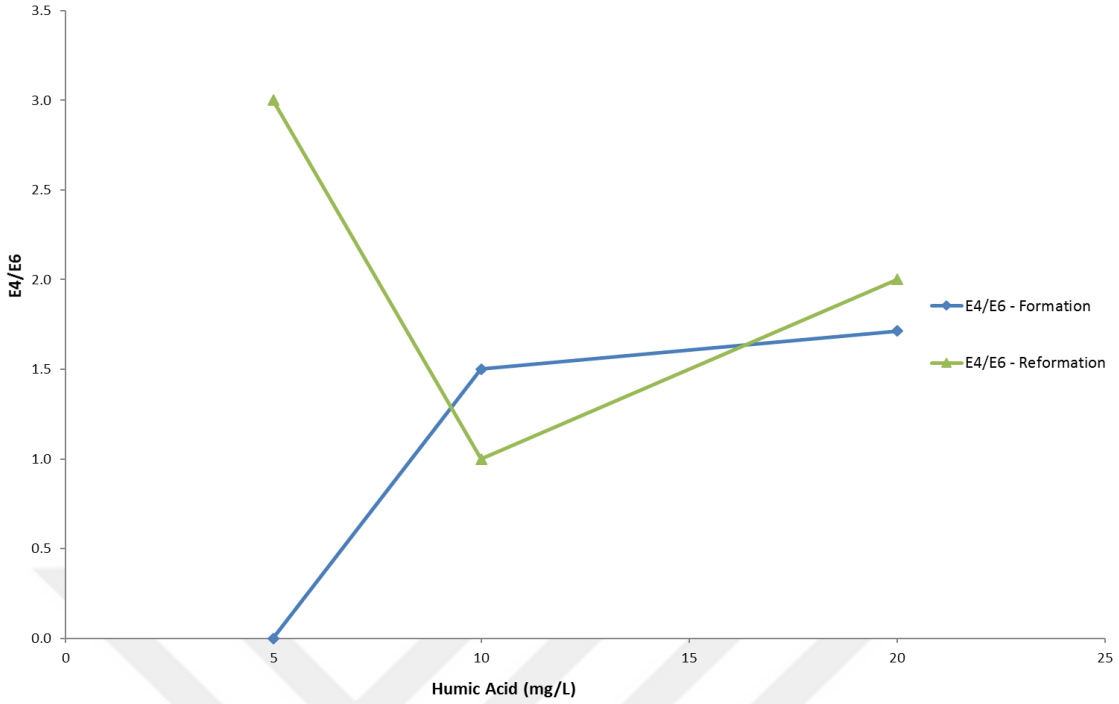

Figure 3.24. E_4/E_6 ratio after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

UV_{254} data (Figure 3.22) are also in correlation with these findings; although residual UV absorbance increased with higher humic acid concentrations, which might suggest a decrease in flocculation performance, removal was found to be improved (Appendix Figure 3), which correlates with floc size data.

The UV absorbance at 254 nm enables us to compare between the concentrations of organic matter present, and it is also used in the calculation of Specific UV absorbance (SUVA) by taking the ratio of it to DOC amount. SUVA gives insight into hydrophobicity/hydrophilicity of humic matter. SUVA can be used to specify hydrophilic and hydrophobic composition of water; SUVA < 3 essentially represents the hydrophilic matter (Edzwald and Tobiason, 1999) whilst SUVA > 4 points out hydrophobic and particularly aromatic matter. Although there is no specific relationship between SUVA and removal, it is observed that the higher the SUVA is, the better the removal of DOC gets.

It was attempted to find evidences for the molecular size distribution of humic material by taking the ratio of light absorbance at 465 nm (E_4) to 656 nm (E_6). A high E_4/E_6 ratio indicates the presence of small molecules in solution, whilst a low value points out large molecules (Maartens et al., 1999).

When SUVA data are examined, it is seen that for fully grown flocs SUVA decreased slightly gradually with increasing humic acid concentration, indicating that the hydrophilicity of the untreated organic matter increased. Considering the raw water SUVAs were measured as 6.88, 7.20 and 7.58 for 5, 10 and 20 mg/L humic acid concentrations, respectively (Appendix Table 1), it can be said that the hydrophobic and aromatic fraction of organic matter were removed mostly, probably leaving increasing amounts of small organic molecules in suspension, unflocculated.

The increasing trend in E_4/E_6 ratio when the humic acid concentration was increased suggests that smaller molecules were dominant in the residue, which is consistent with the finding mentioned above. So, it can be said that larger flocs were formed when the humic acid concentration was increased and consistently, improved organic carbon removals were observed, the organics removed were mainly more readily removable part of humic acid; possibly more aromatic and colour giving part of organic matter, and smaller molecules were not removed that well.

3.2.1.5. Organic carbon removal with polyaluminium chloride (PACl)

As previously mentioned, similar to results observed with alum, floc size in the flocculation experiments with PACl was observed to increase with increasing humic acid concentration, which could be attributed to higher collision efficiency when the humic acid concentration was increased. Similarly, residual total organic carbon (Figure 3.25) and dissolved organic carbon (Figure 3.26) concentrations increased when the humic acid concentration was increased. It might be thought that residual organic carbon concentration increased as the concentration of humic acid to be treated with the same dose of coagulant was increased, that is, coagulant dose might have become insufficient to flocculate increased concentrations of humic acid. This might seem to contradict with the floc size data nevertheless, when the removal data was evaluated in the efficiency perspective, it is seen that both the total and the dissolved organic carbon

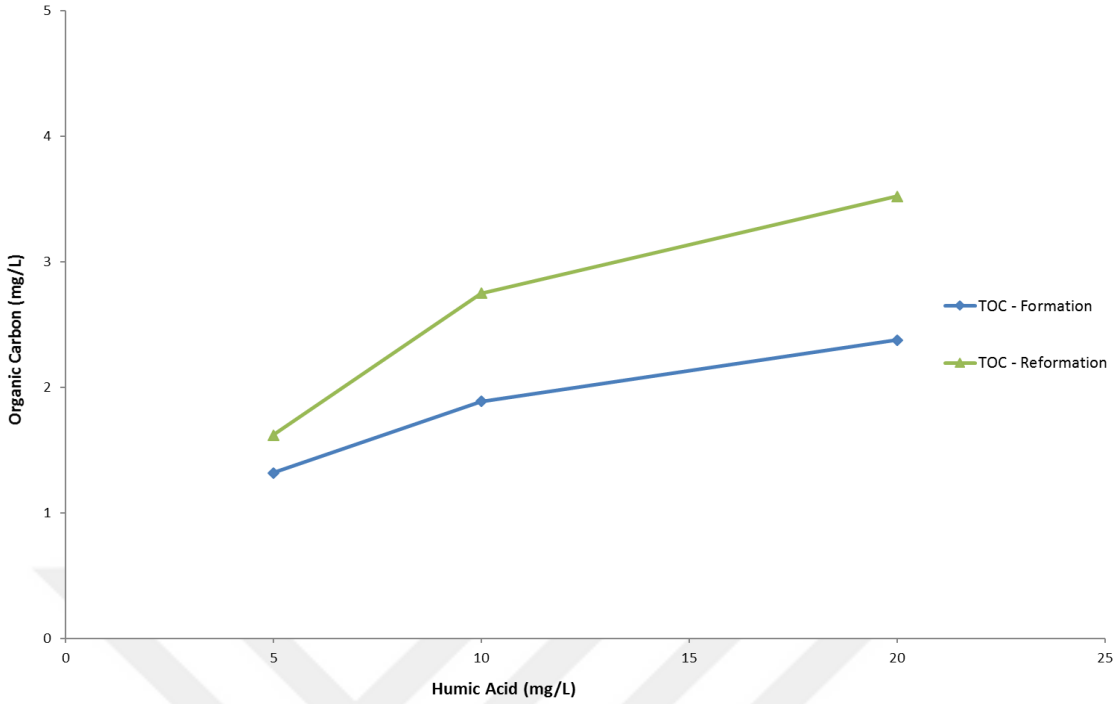

Figure 3.25. Residual TOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

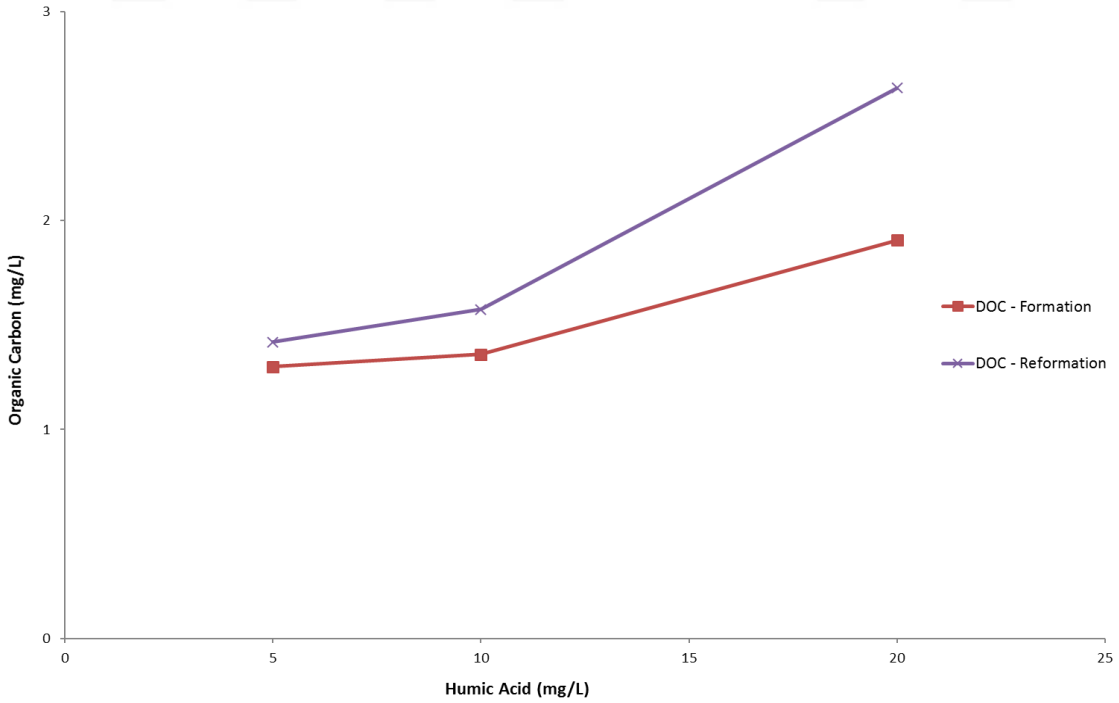

Figure 3.26. Residual DOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

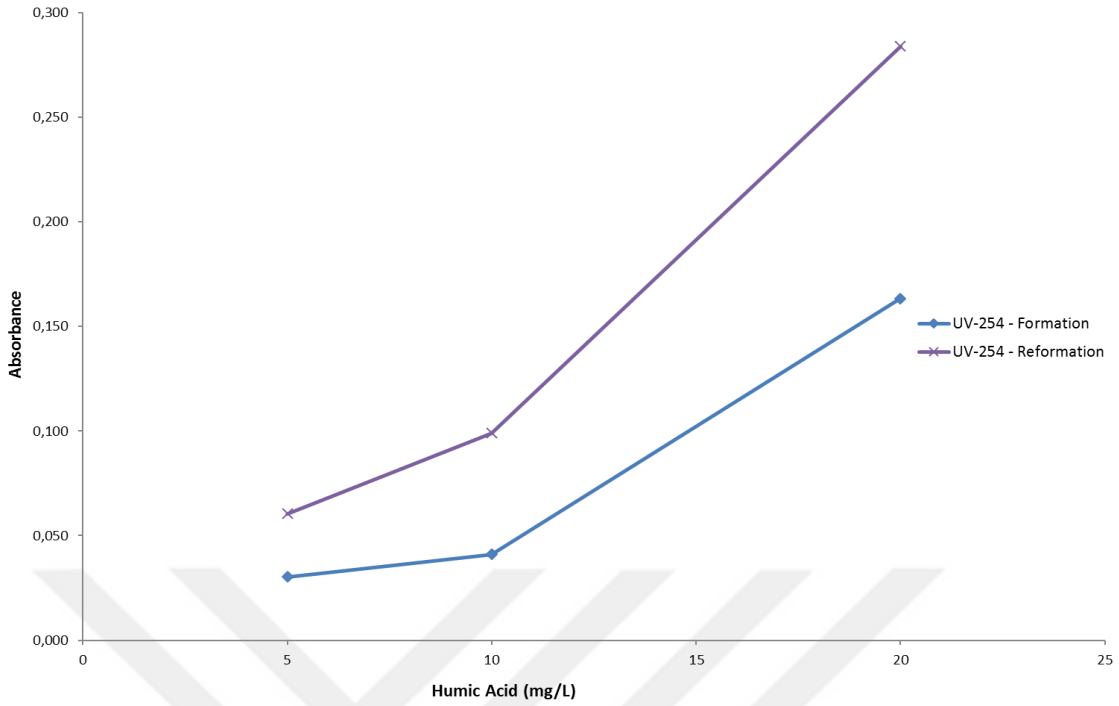

Figure 3.27. Residual absorbance at 254 nm after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

removal efficiencies increased as the humic acid concentration was increased (Appendix Figure 4 and Figure 5), which is well correlating with floc size data. UV data (both the residual UV_{254} – Figure 3.27 and UV_{254} absorbance removal – Appendix Figure 6) are also in good correlation with these findings.

When SUVA data (Figure 3.28) are examined in the light of the knowledge (Edzwald and Tobiason, 1999) that 'SUVA < 3 essentially represents the hydrophilic matter whilst SUVA > 4 points out hydrophobic and particularly aromatic matter', for fully grown flocs it can be said that in cases of 5 mg/L and 10 mg/L humic acid concentrations hydrophobic or more readily removable part of organic matter was removed by PACl flocculation and mainly hydrophilic part was left unremoved in the residue. However, when the humic acid concentration was further increased to 20 mg/L, the coagulant dose likely became insufficient to remove some portion of the hydrophobic part. In correlation with that, E_4/E_6 ratio (Figure 3.29) suggests that smaller molecules became dominant in the suspension supernate as the humic acid concentra-

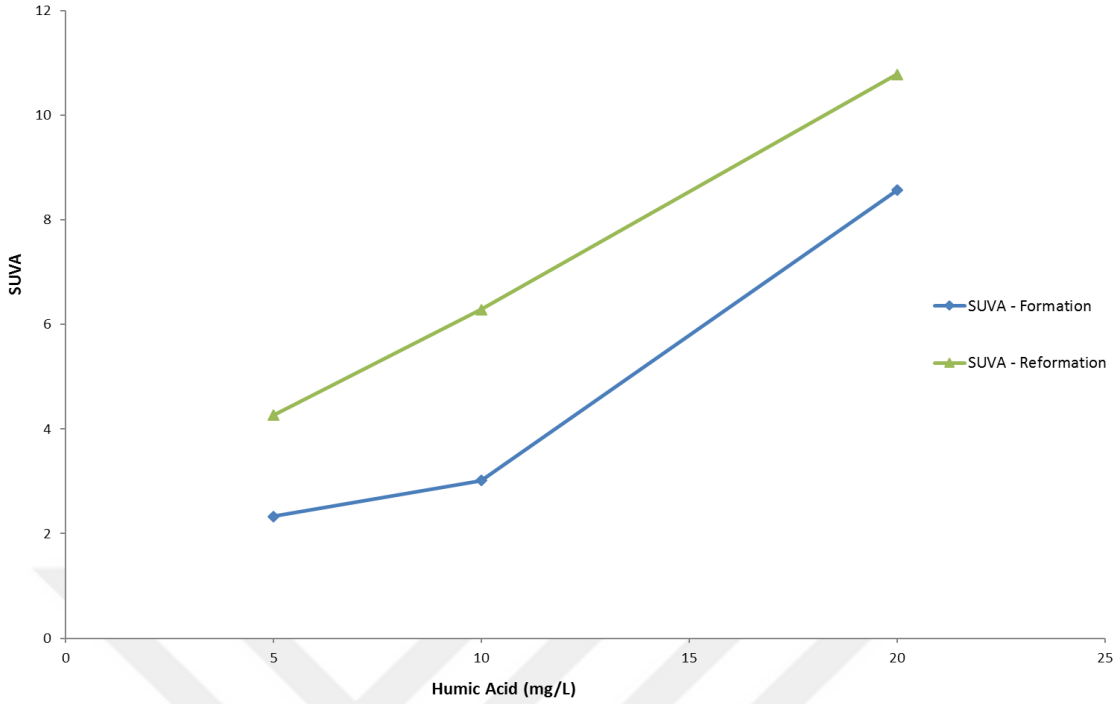

Figure 3.28. Specific UV absorbance (SUVA) after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

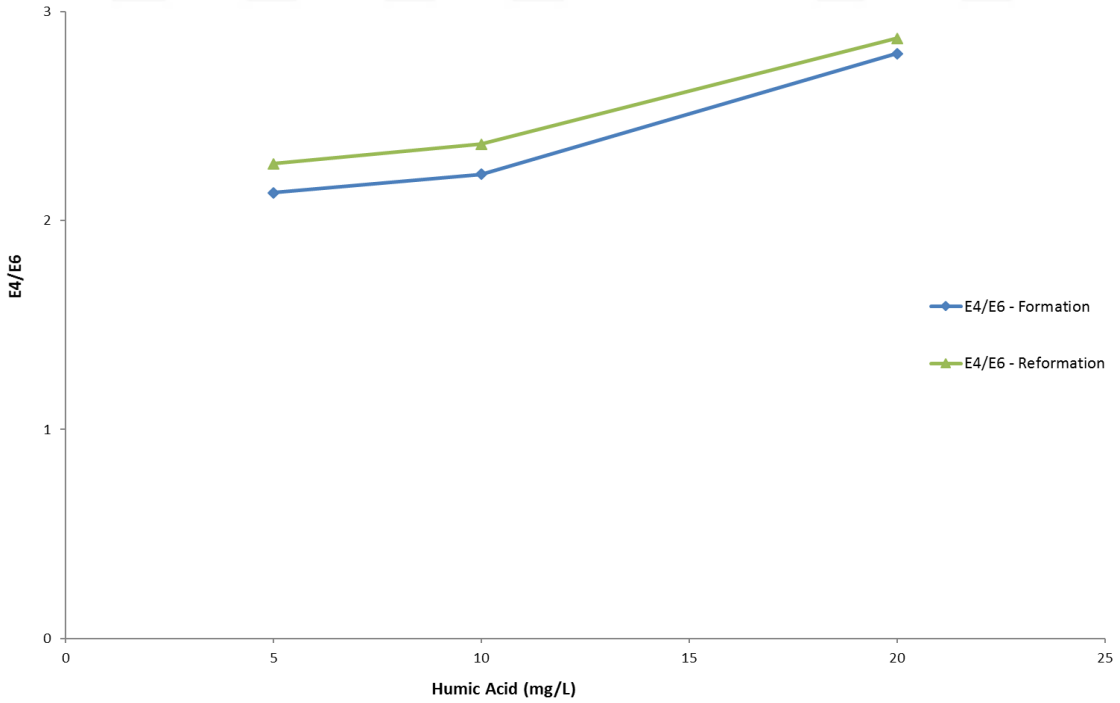

Figure 3.29. E_4/E_6 ratio after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

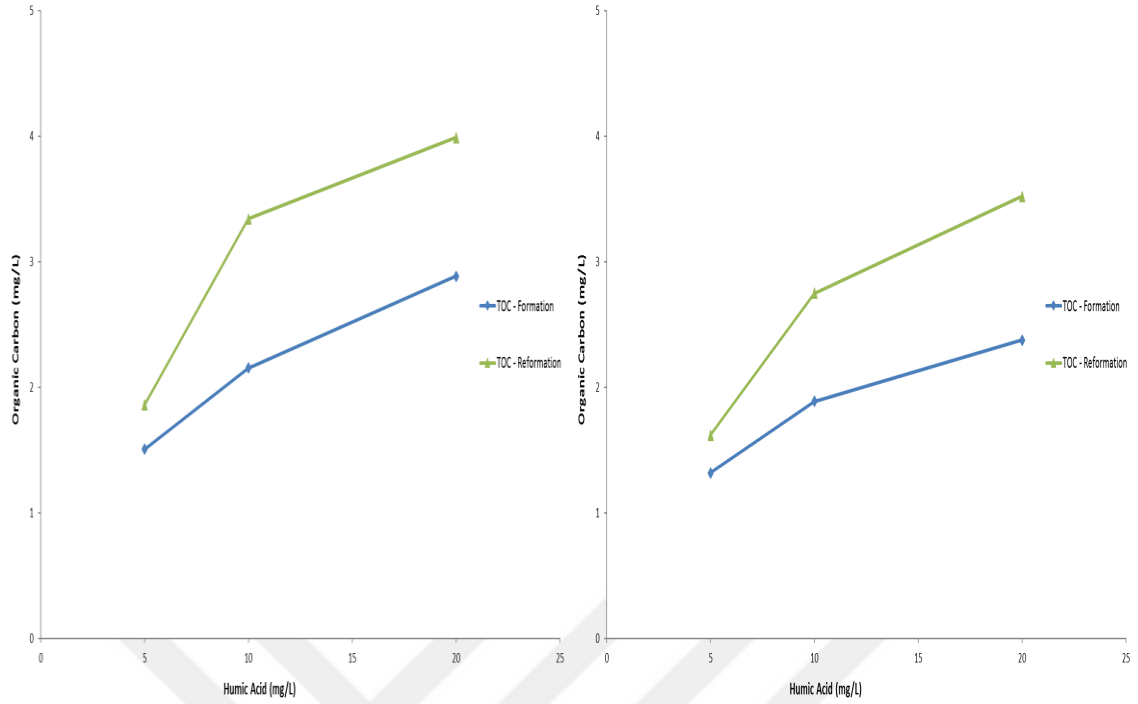

Figure 3.30. Residual TOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

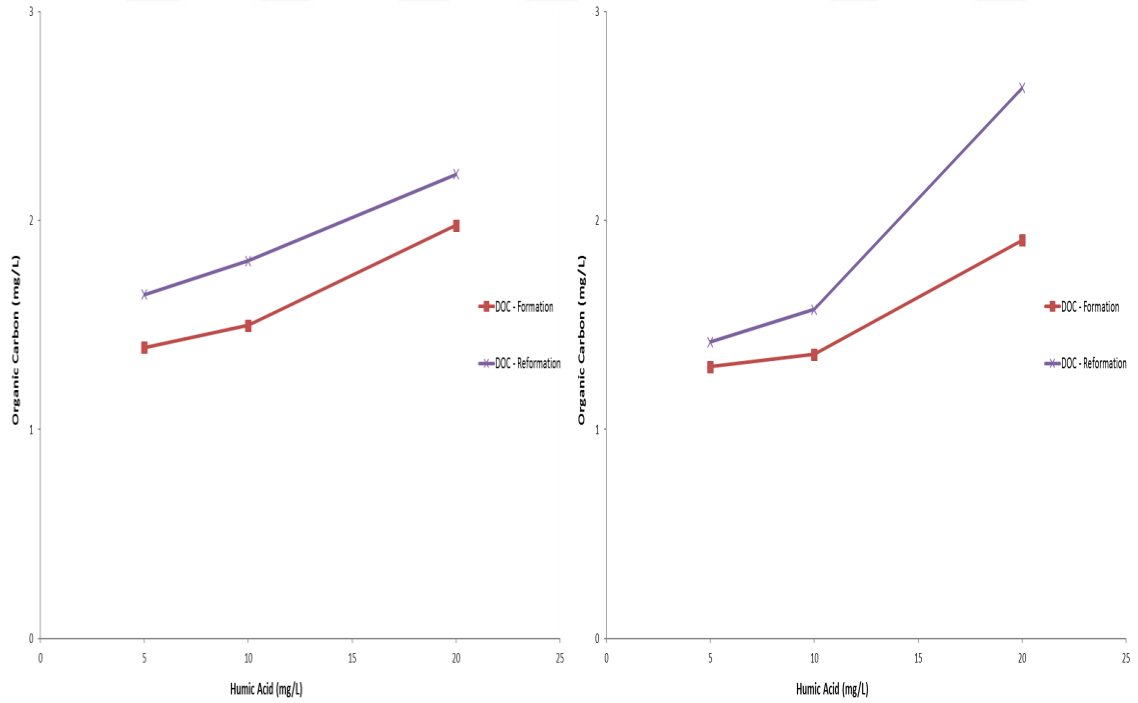

Figure 3.31. Residual DOC after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

tion was increased.

PACl showed better performance in the removal of organic matter compared to alum since larger flocs were formed with PACl (Figure 3.19), which is attributed to its higher positively charged Al species content. At 5 mg/L humic acid concentration similar floc sizes were obtained with both coagulants (slightly larger flocs with PACl), so residual total and dissolved organic carbon concentrations were similar (slightly lower residual concentrations with PACl). At 10 mg/L humic acid concentration PACl exhibited better flocculation performance, so residual total and dissolved organic carbon concentrations were higher with alum. At 20 mg/L humic acid concentration, again larger flocs were obtained with PACl, so residual total and dissolved organic carbon concentrations were lower with PACl (Figures 3.30 and 3.31). Consistent with relative floc size data, total and dissolved organic carbon removals in general were better with regrown flocs of PACl. When the humic acid concentration was increased further from 5 mg/L, higher residual UV_{254} absorbance measurements were observed with PACl. Examination of SUVA data and E_4/E_6 ratio (Figures 3.33 and 3.34) suggests that alum

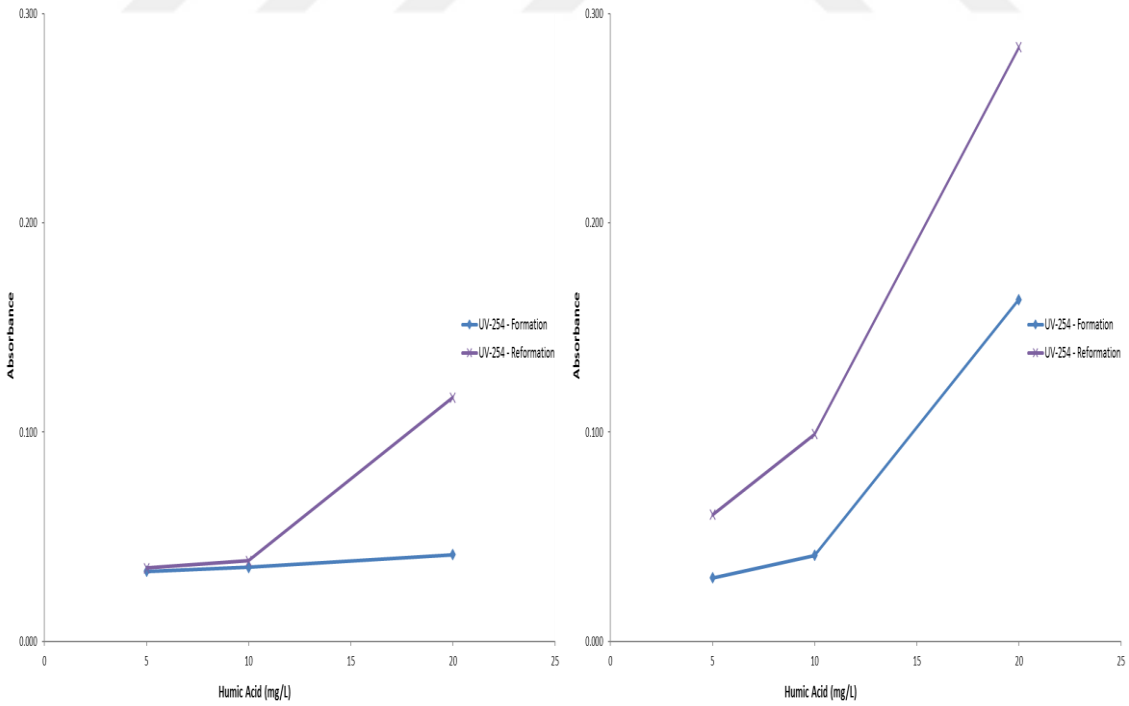

Figure 3.32. Residual absorbance at 254 nm after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

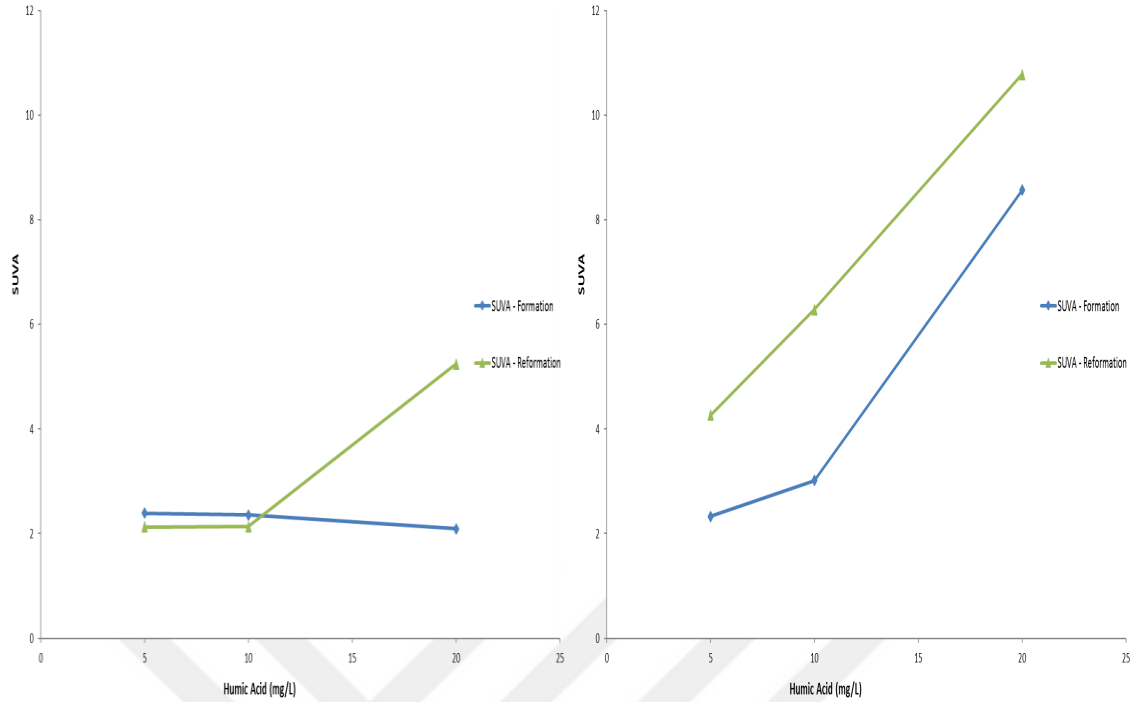

Figure 3.33. Specific UV absorbance (SUVA) after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

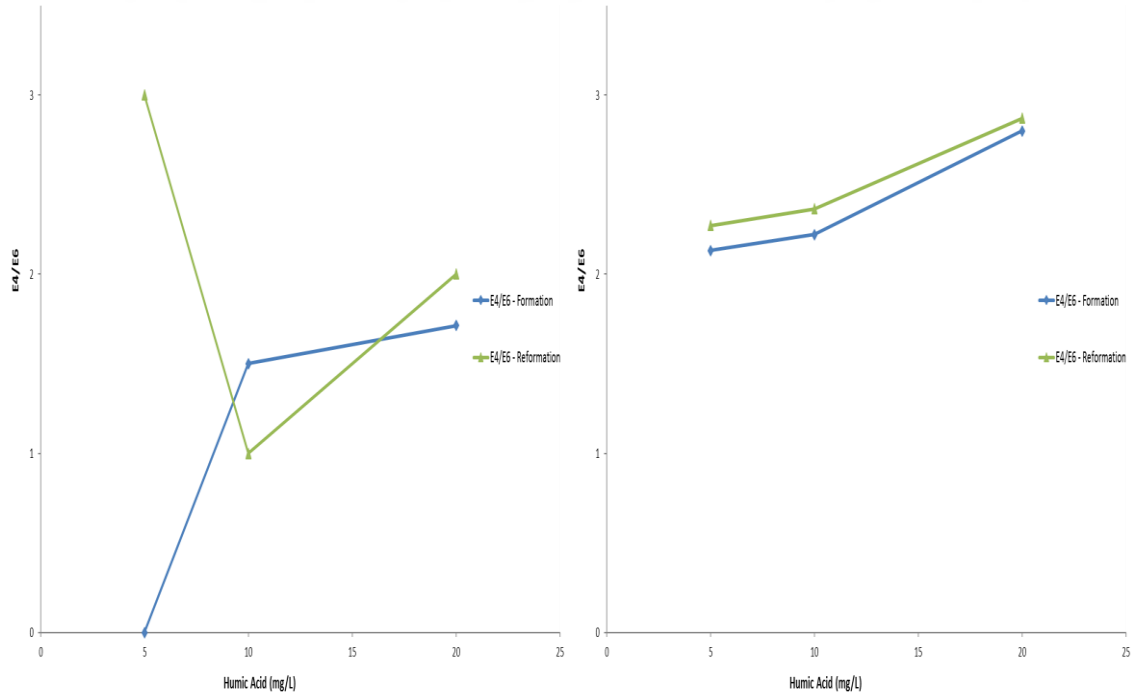

Figure 3.34. E_4/E_6 ratio after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

showed better performance in flocculating hydrophobic portion and smaller molecules of organic matter at 20 mg/L humic acid concentration.

3.2.2. Experiments with 2.5 mg/L pre-ozonated synthetic raw waters

Following the experiments with unozonated raw waters flocculation experiments with aluminium sulphate and polyaluminium chloride were performed using 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid:

3.2.2.1. Experiments with $Al_2(SO_4)_3$

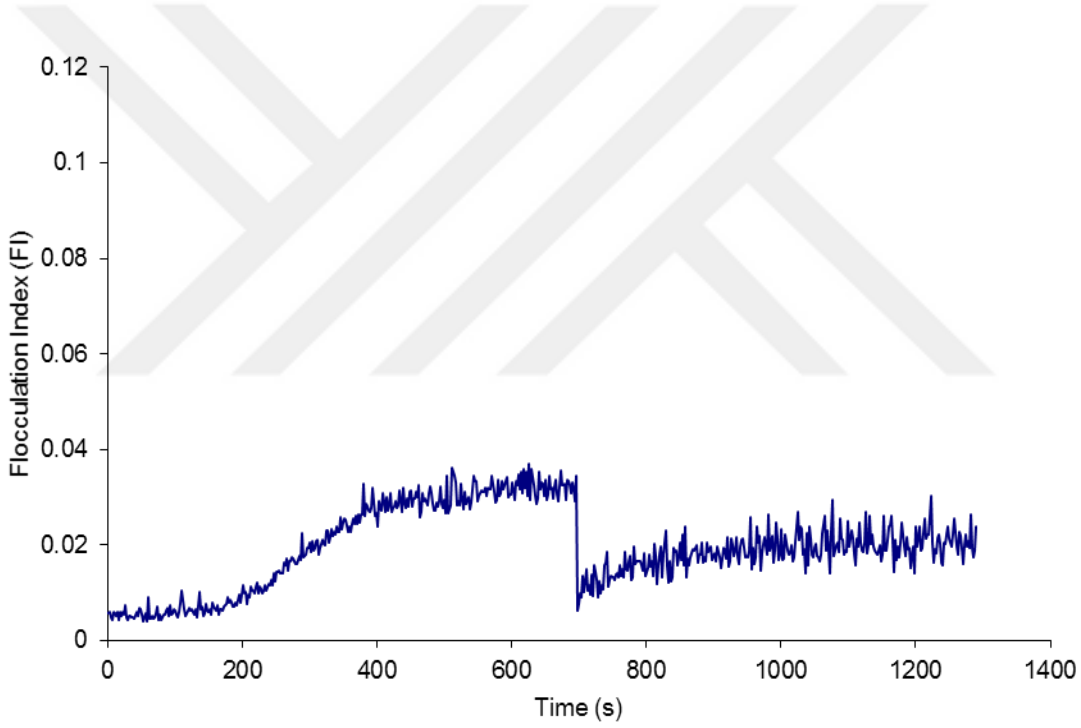

Figure 3.35. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

Larger flocs were formed as the humic acid concentration was increased in unozonated synthetic raw waters. The same observation prevails also in flocculation tests with 2.5 mg/L pre-ozonated synthetic raw waters. This can be attributed to higher collision efficiency with increasing humic acid concentration.

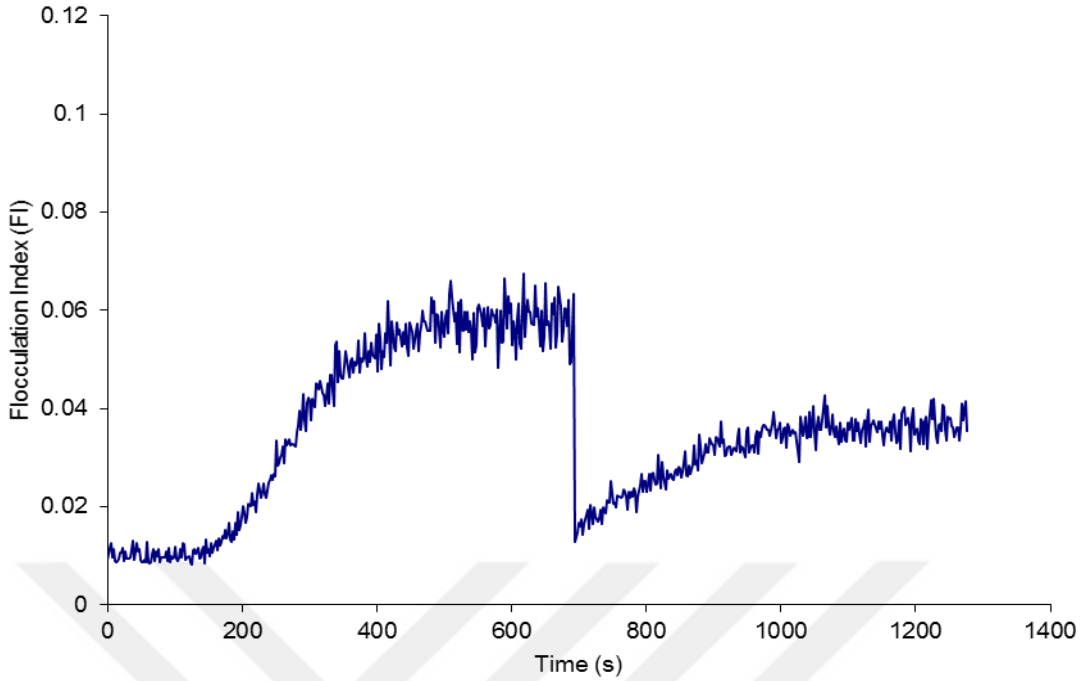

Figure 3.36. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

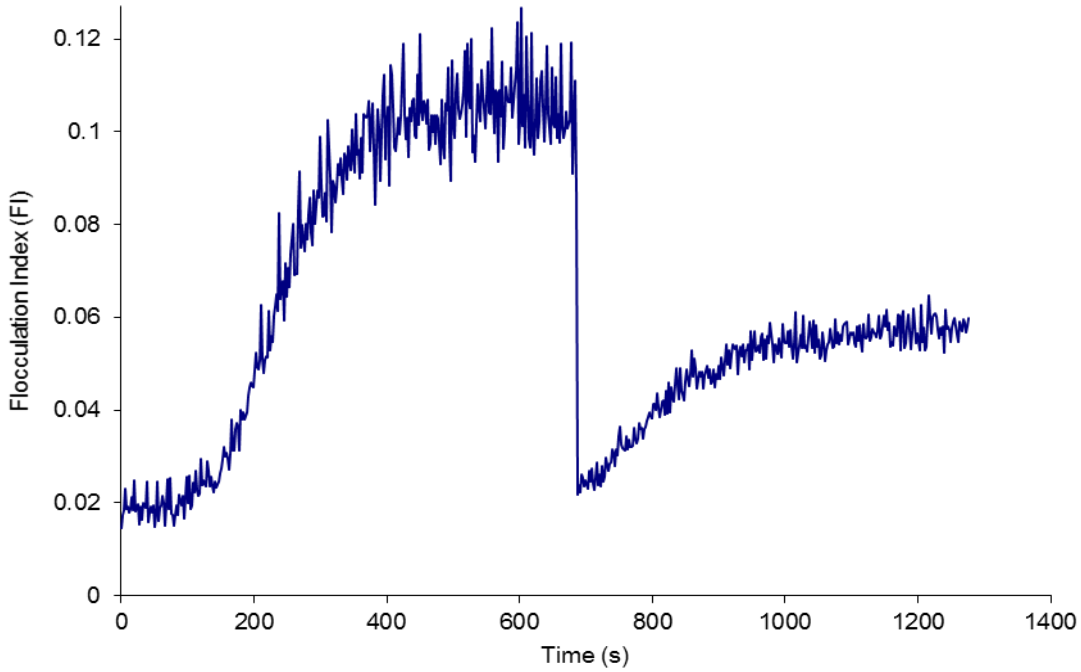

Figure 3.37. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

Similar to the results found in flocculation experiments performed with unozonated synthetic raw waters using alum, in jar tests with 2.5 mg/L pre-ozonated synthetic raw waters the onset of flocculation was delayed as the concentration of humic acid was decreased. The onset of flocculation is about 160th second for 5 mg/L humic acid containing water, 130th second for 10 mg/L humic acid containing water and 90th second for 20 mg/L humic acid containing water; as the humic acid concentration was increased, flocculation started earlier. It also results in shorter time to reach steady-state (fully grown) floc size as the humic acid concentration was increased (narrower or steeper S-curve). This is another finding to show that it could be attributed to higher collision efficiency with increasing humic acid concentration.

3.2.2.2. Experiments with polyaluminium chloride

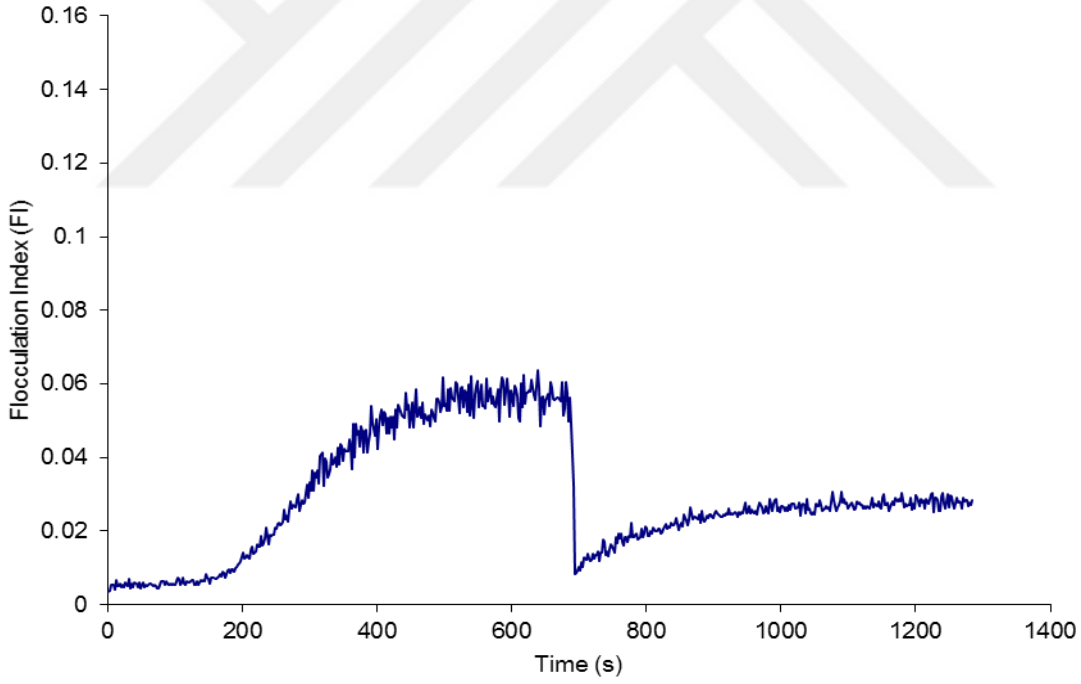

Figure 3.38. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

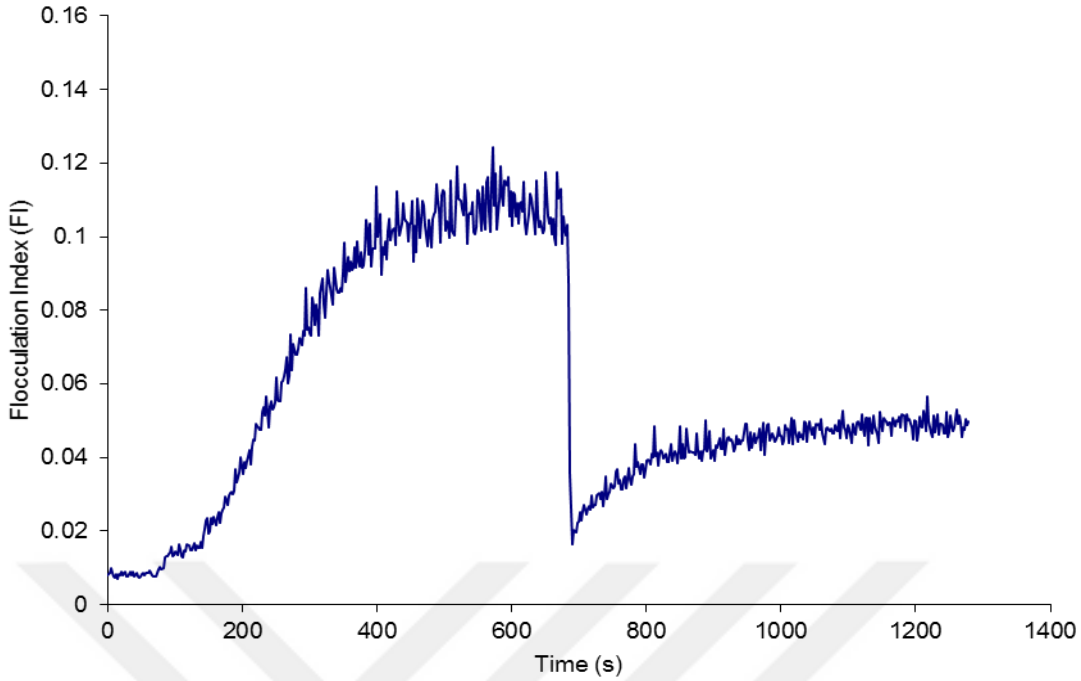

Figure 3.39. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

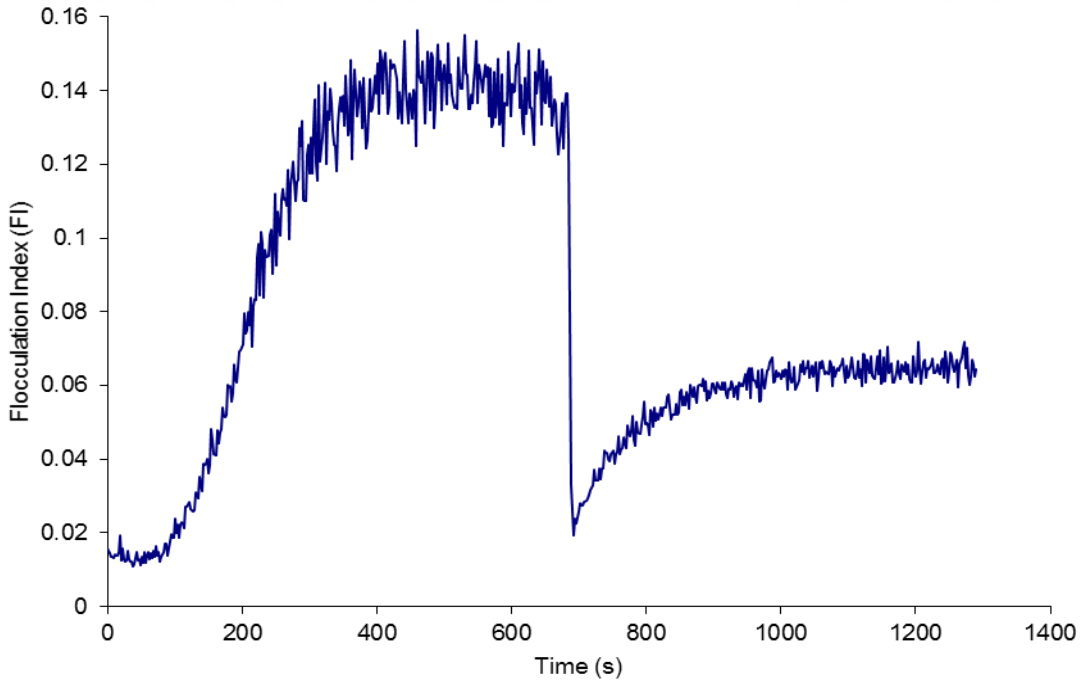

Figure 3.40. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

Similar to flocculation with alum, with PACl larger flocs were formed with increasing humic acid concentration. PACl showed better performance compared to alum in terms of floc size, which is attributed to the higher cationic Al species content of polymeric Al coagulants.

In jar tests with 2.5 mg/L pre-ozonated synthetic raw waters, another feature attracting attention is that the onset of flocculation was delayed as the concentration of humic acid was reduced. In other words, as the humic acid concentration was increased, aggregation started earlier. This is another finding to show that it could be attributed to higher collision efficiency with increasing humic acid concentration.

3.2.2.3. Comparison of floc sizes

Dynamics of flocculation with alum and PACl exhibited a similar pattern; larger flocs were formed with increasing humic acid concentration, which can be attributed to higher collision efficiency.

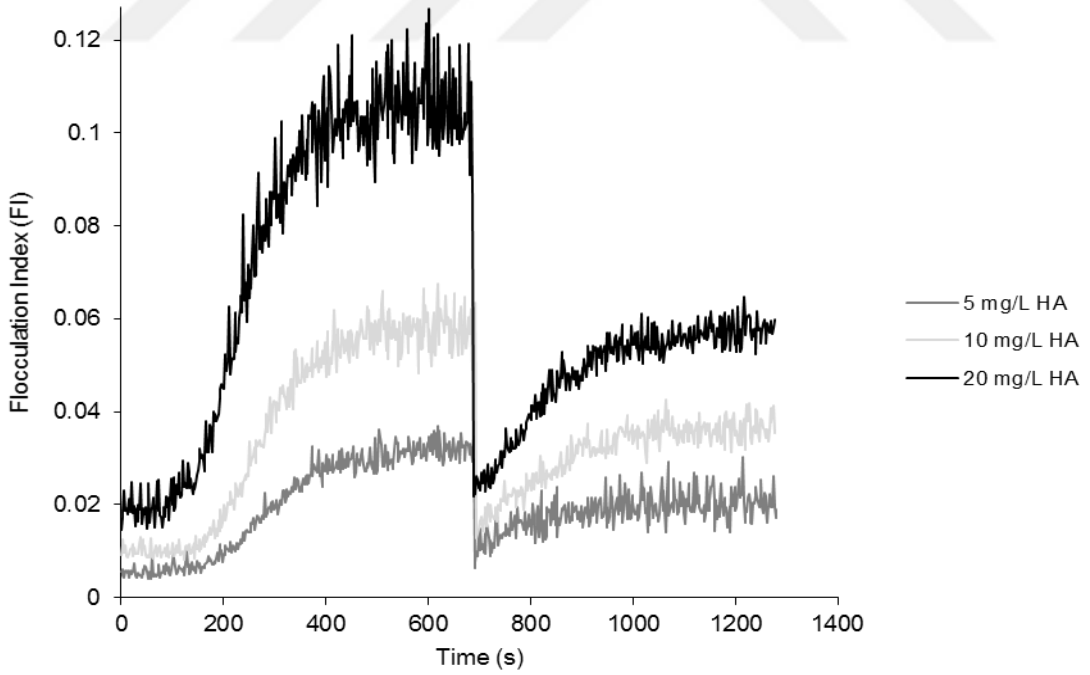

Figure 3.41. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

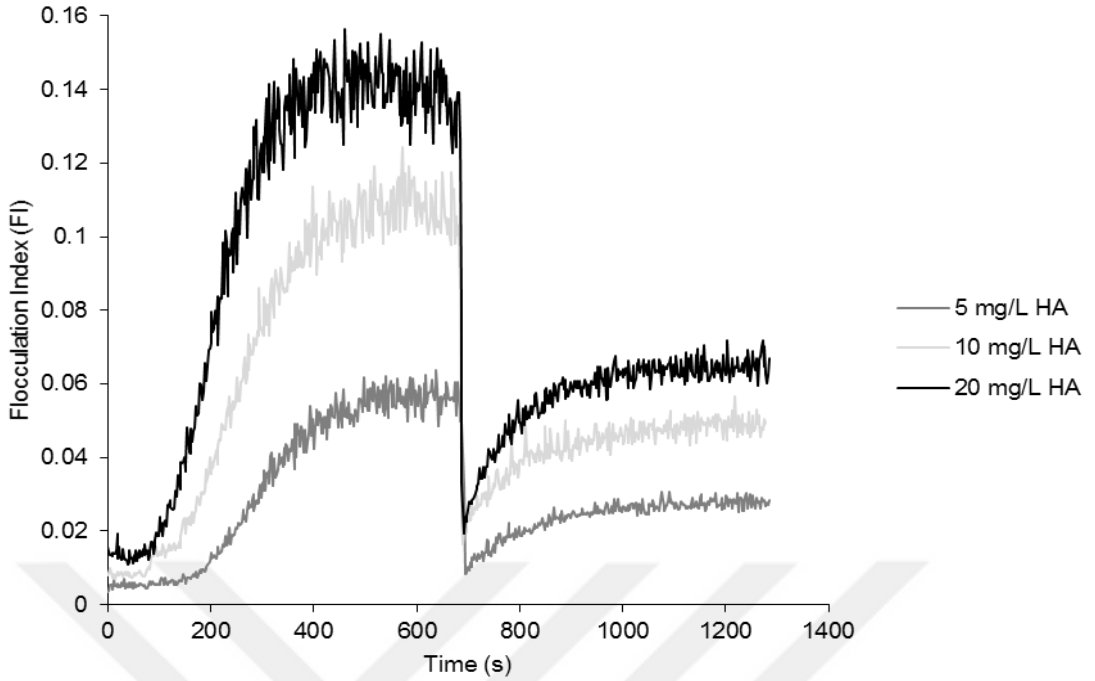

Figure 3.42. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

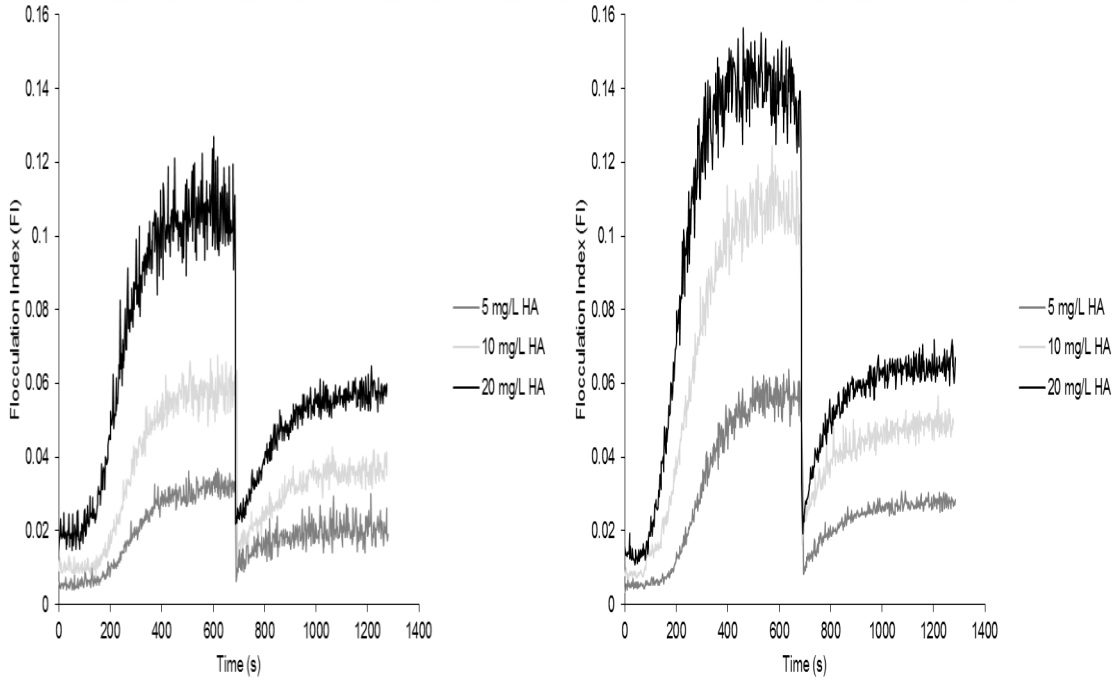

Figure 3.43. Floc growth and regrowth with alum (left) and PACl (right) in 2.5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

When there are more particles in suspension there is more opportunity for more number of collisions, thus aggregation of those particles which come to contact with is more possible. This correlates with the finding that the beginning of floc growth got earlier as the concentration of humic acid was increased.

Compared to alum, larger flocs were obtained with PACl, which is attributed to higher positively charged Al species included in PACl, since it is a pre-hydrolysed coagulant (Figures 3.41-3.43).

With increasing humic acid concentration flocculation with both coagulants showed similar characteristics; earlier onset of flocculation and larger floc formation. Aggregation started relatively earlier with PACl in all humic acid concentrations studied, which was probably because of pre-hydrolysed Al species in PACl.

Hindered floc growth by pre-ozonation can clearly be seen when the FI values obtained in the experiments with unozonated and pre-ozonated synthetic raw waters are examined (Figure 3.19 and Figure 3.43). This is evaluated comprehensively in Section 3.3.

3.2.2.4. Organic carbon removal with $Al_2(SO_4)_3$

With increasing humic acid concentration, floc size also increased with alum. This likely owes to the higher collision efficiency with increasing humic acid concentration. However, with increasing humic acid concentration, residual total organic carbon and dissolved organic carbon concentrations (Figures 3.44 and 3.45) increased. This, at first, might sound contradictory with the observed floc size increase with increasing humic acid concentration though it is not; as expected, residual organic carbon concentration increases when the concentration of humic acid to be treated with the same dose of coagulant is increased. Residual absorbance at 254 nm also correlates with this. On the other hand, organic carbon removal efficiency (Appendix Figures 7 and 8) increased as humic acid concentration was increased, well correlating with floc size data whilst UV_{254} absorbance removal efficiency (Appendix Figure 9) decreased.

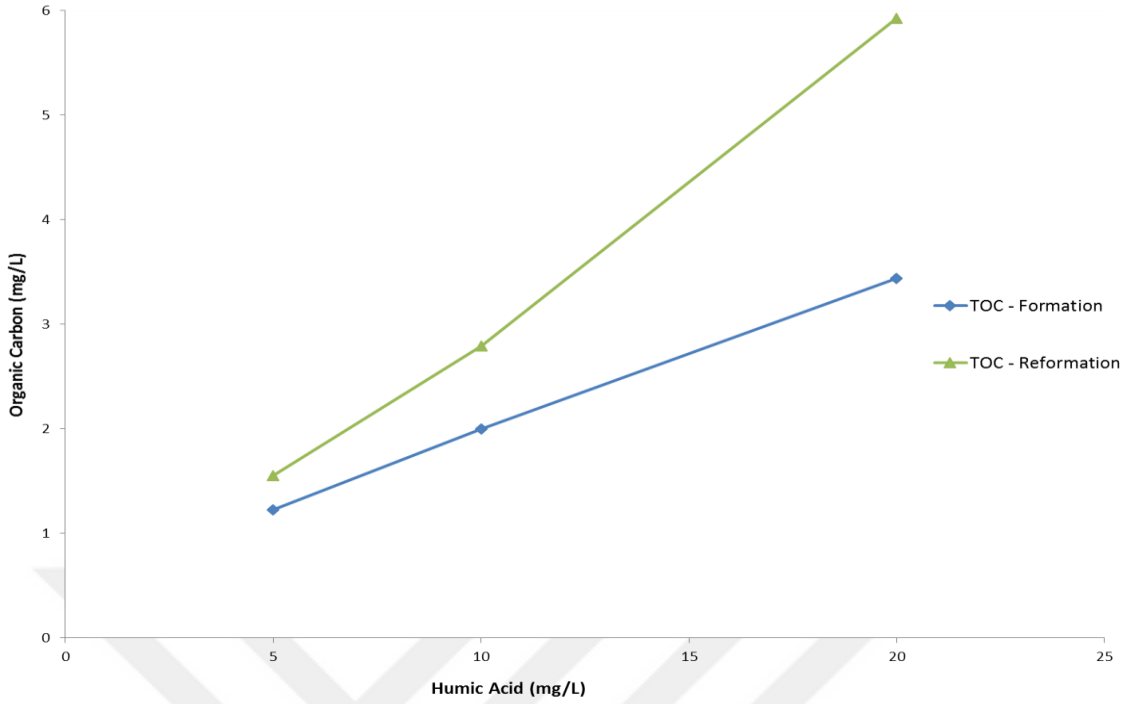

Figure 3.44. Residual TOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

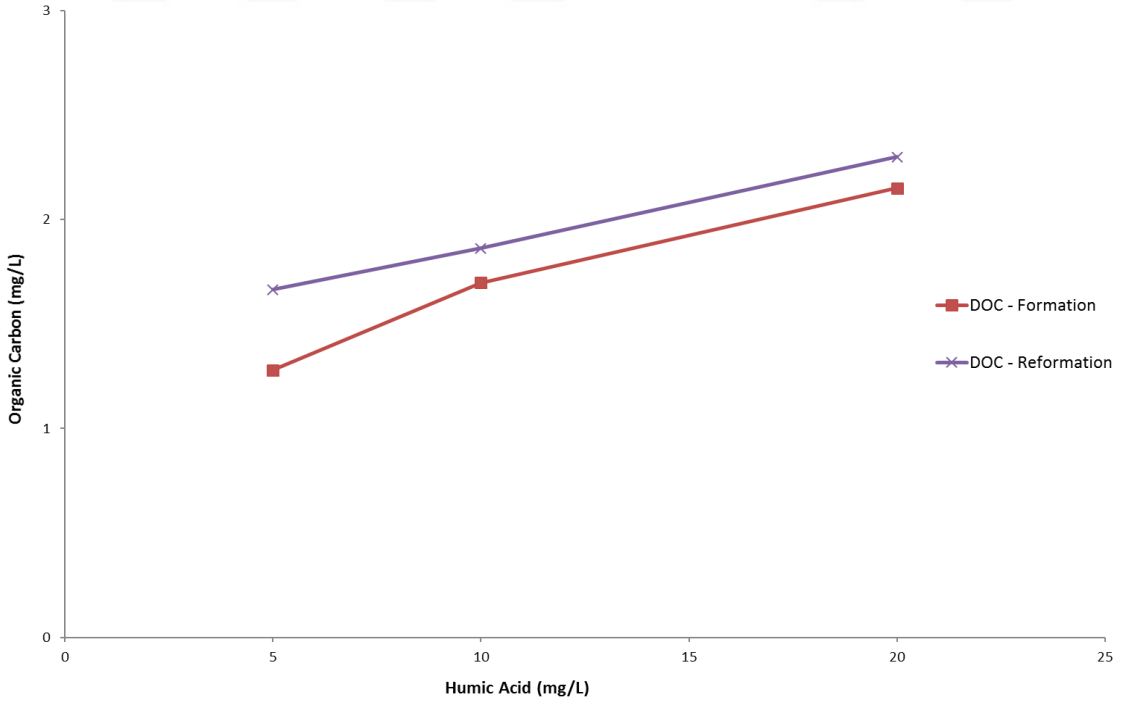

Figure 3.45. Residual DOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

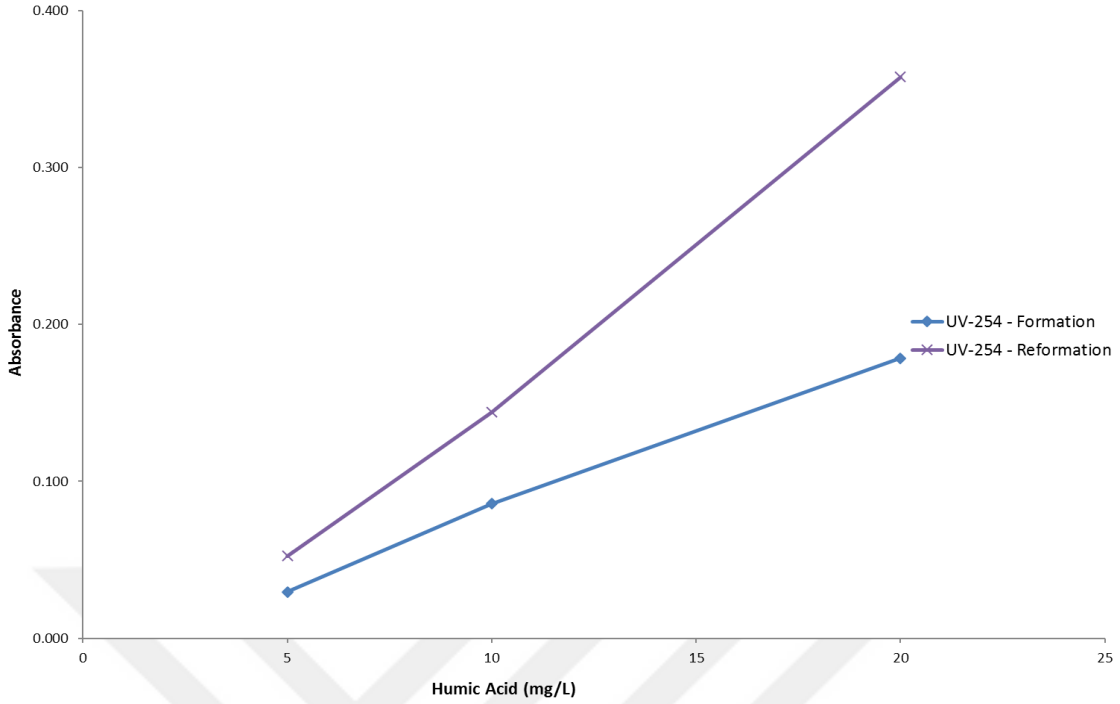

Figure 3.46. Residual absorbance at 254 nm after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

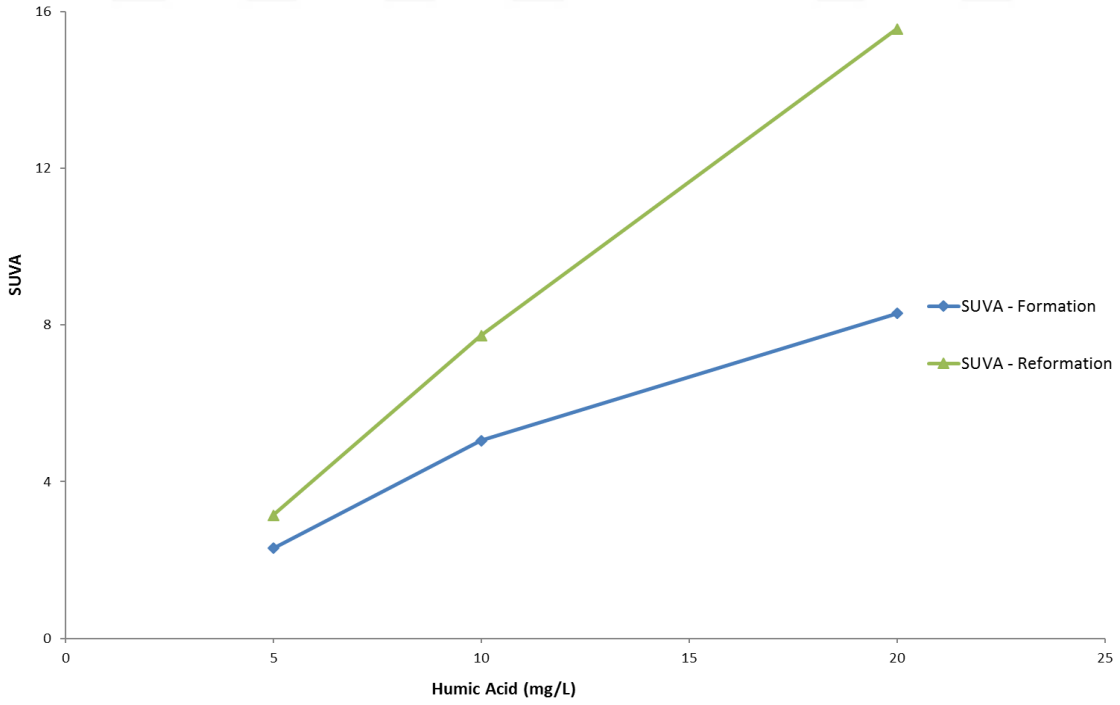

Figure 3.47. Specific UV absorbance (SUVA) after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

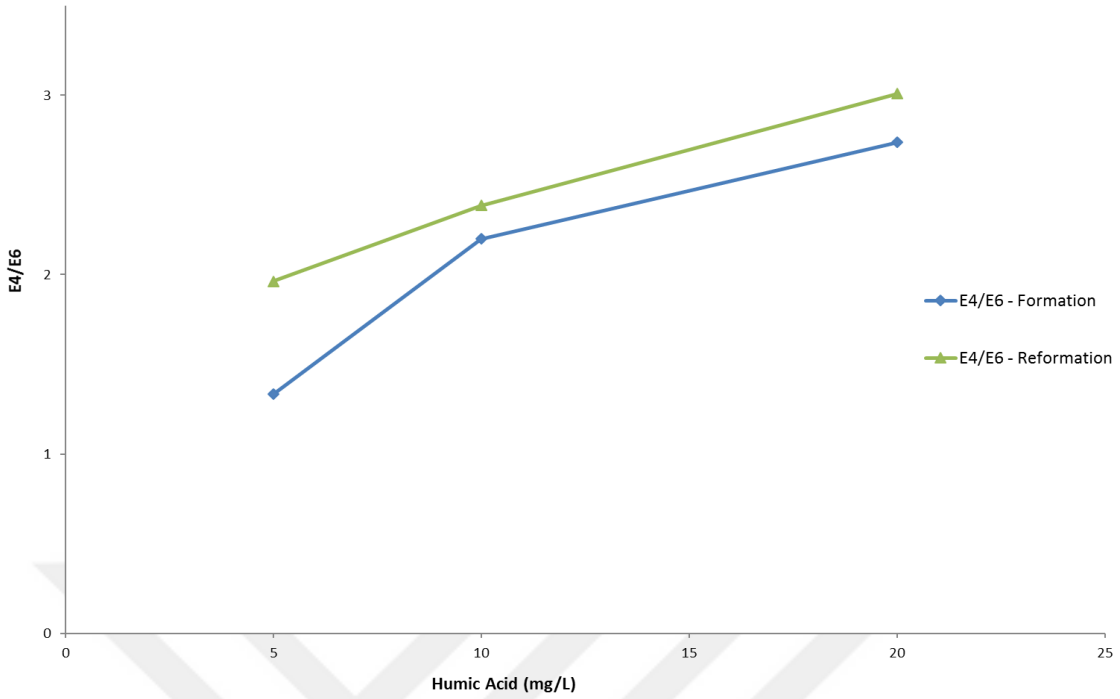

Figure 3.48. E_4/E_6 ratio after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

In Figure 3.47, it is seen that for fully grown flocs SUVA increased over 4 when the humic acid concentration was increased further over 5 mg/L, which indicates that more aromatic fractions were prevailing in suspension. This is correlated with hindered removal efficiency of UV_{254} absorbance with increasing humic acid concentration. Increasing trend in E_4/E_6 ratio when the humic acid concentration was increased suggests that smaller molecules were dominant in the supernate. It can be said that more and more hydrophobic and aromatic parts of humic acid were found in the supernate as the humic acid concentration was increased and coagulant dose became insufficient to efficiently remove smaller molecules.

3.2.2.5. Organic carbon removal with polyaluminium chloride (PACl)

As the concentration of humic acid was increased, floc size also increased in flocculation with PACl, which could be attributed to increasing collision efficiency with increasing humic acid concentration. Residual total organic carbon and dissolved organic carbon concentrations (Figures 3.49 and 3.50) increased with increasing humic

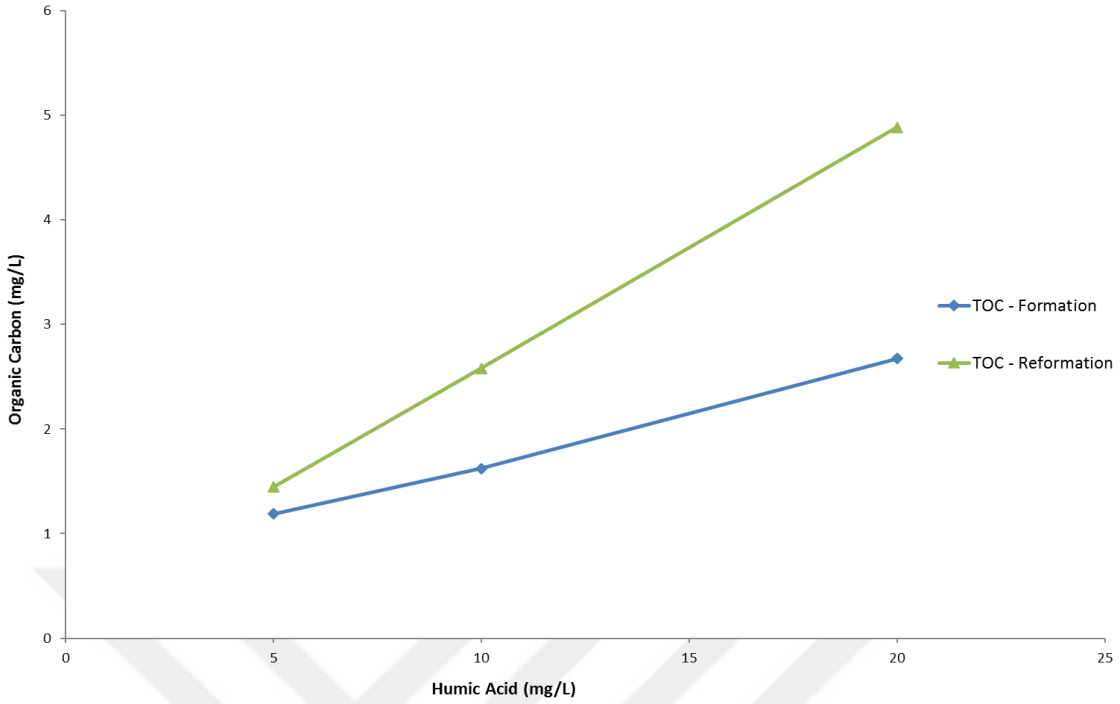

Figure 3.49. Residual TOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

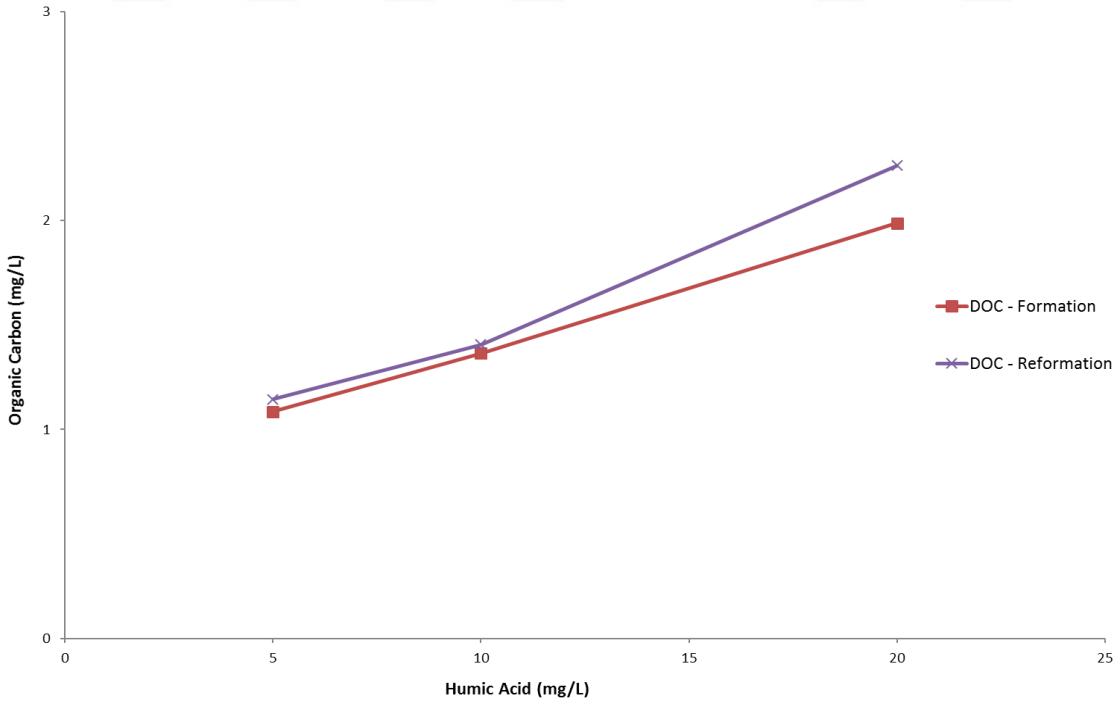

Figure 3.50. Residual DOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

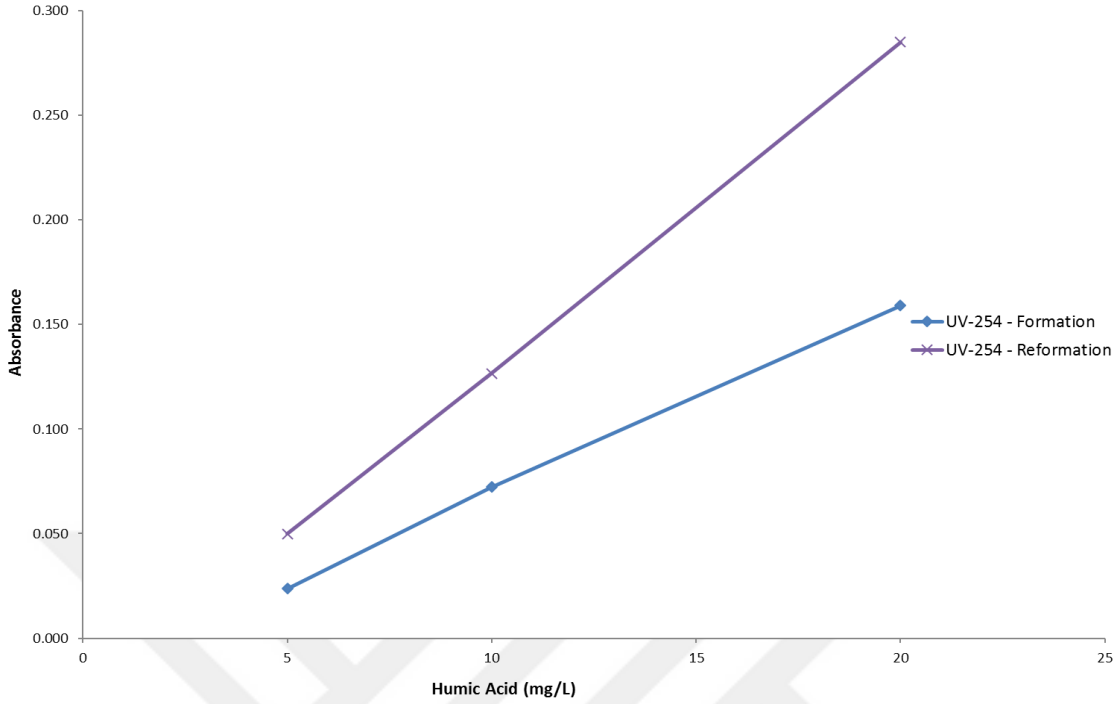

Figure 3.51. Residual absorbance at 254 nm after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

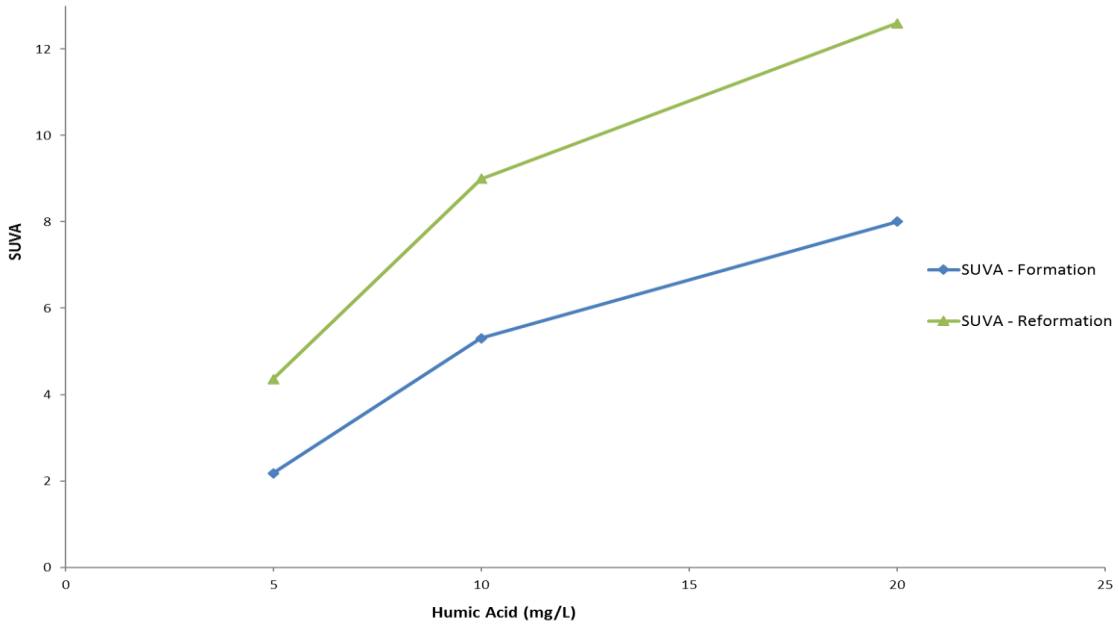

Figure 3.52. Specific UV absorbance (SUVA) after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

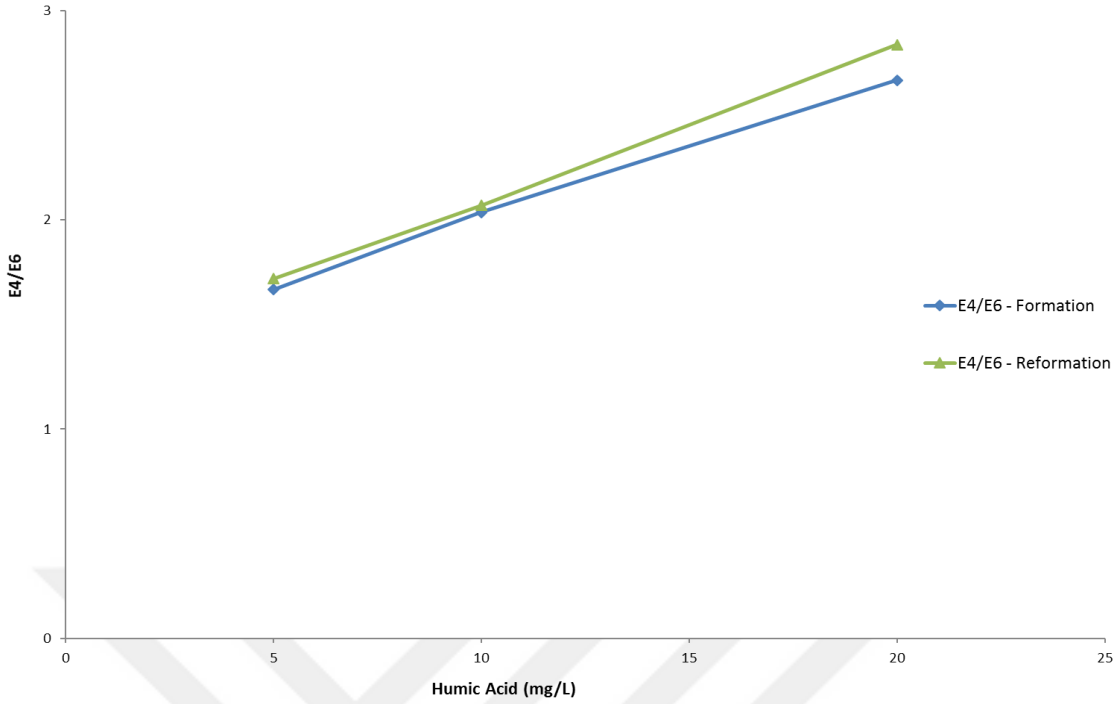

Figure 3.53. E_4/E_6 ratio after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

acid concentration. This might be because residual organic carbon concentration increased when the concentration of humic acid to be treated with the same dose of coagulant was increased. When removal performance is considered, it is seen that organic carbon removal efficiency (Appendix Figure 10 and Figure 11) increased as the humic acid concentration was increased, which is well correlating with floc size data. Correlating with residual organic carbon data, residual UV absorbances at 254 nm also increased with increasing humic acid concentration (Figure 3.51) whilst UV_{254} absorbance removal efficiency diminished (Appendix Figure 12) when the initial humic acid concentration was gradually increased, indicating that pre-ozonation caused release of smaller organics which might have affected flocculation of larger or more readily removable part of organic matter negatively by increasing the net negative charge of the suspension. This is correlated when residual SUVA data (Figure 3.52) are examined; it can be said that as the humic acid concentration was increased further from 5 mg/L removal of hydrophobic or more readily removable part of organic matter by PACl de-

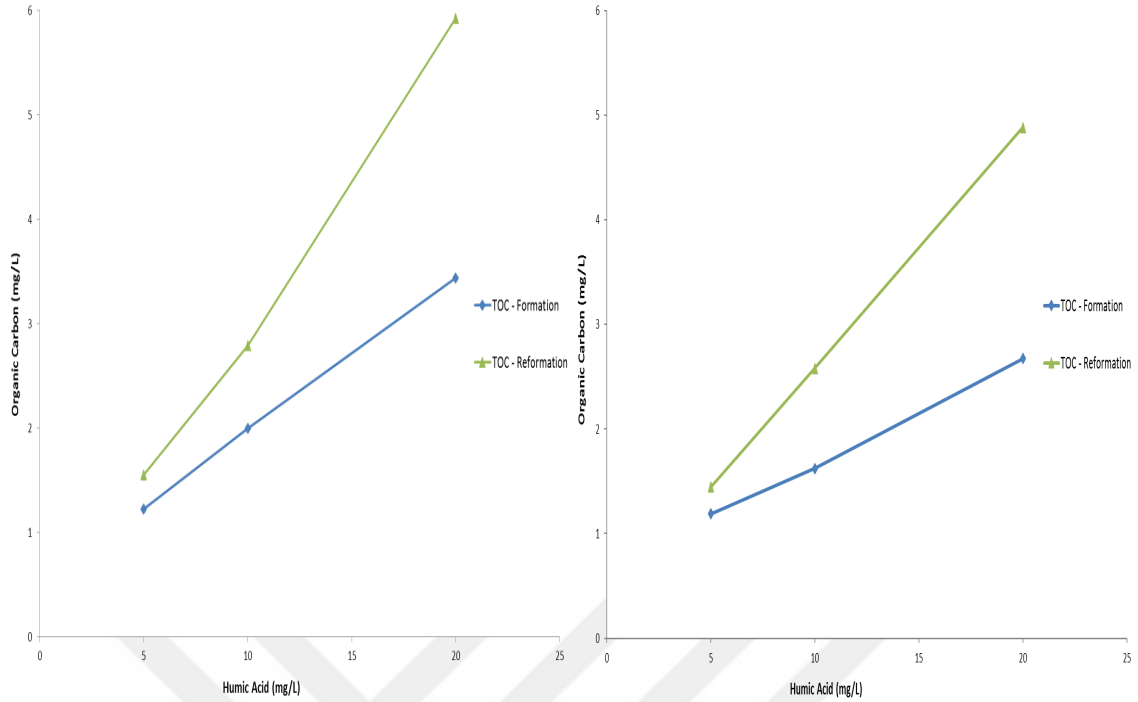

Figure 3.54. Residual TOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

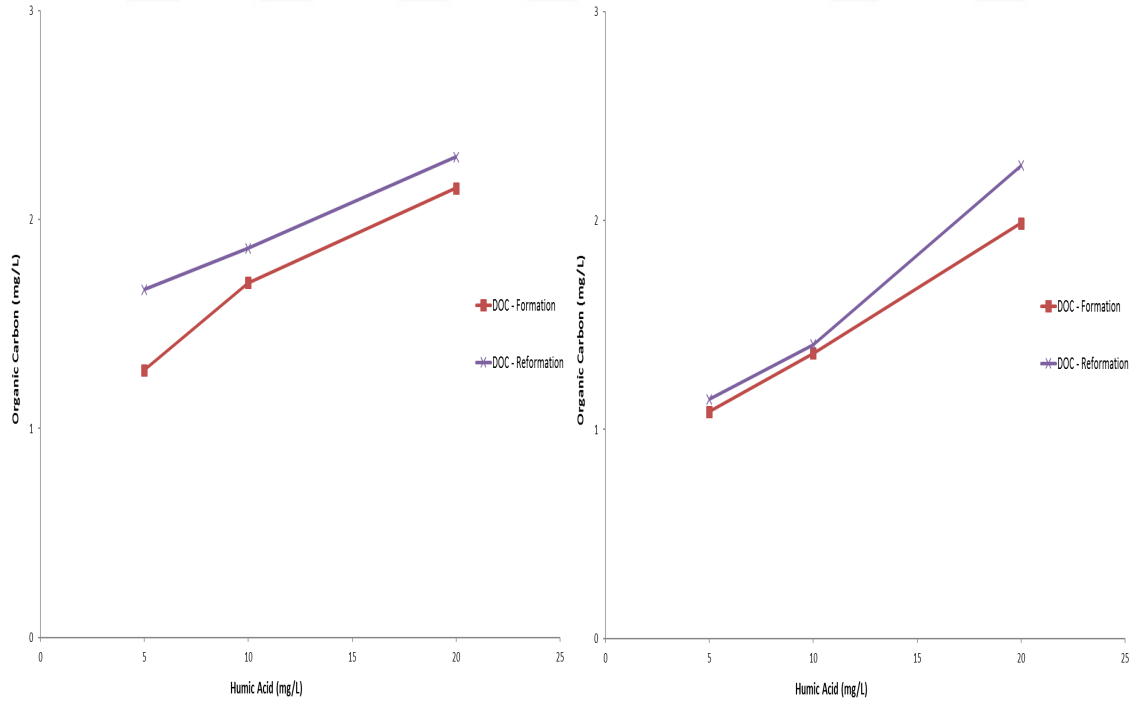

Figure 3.55. Residual DOC after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

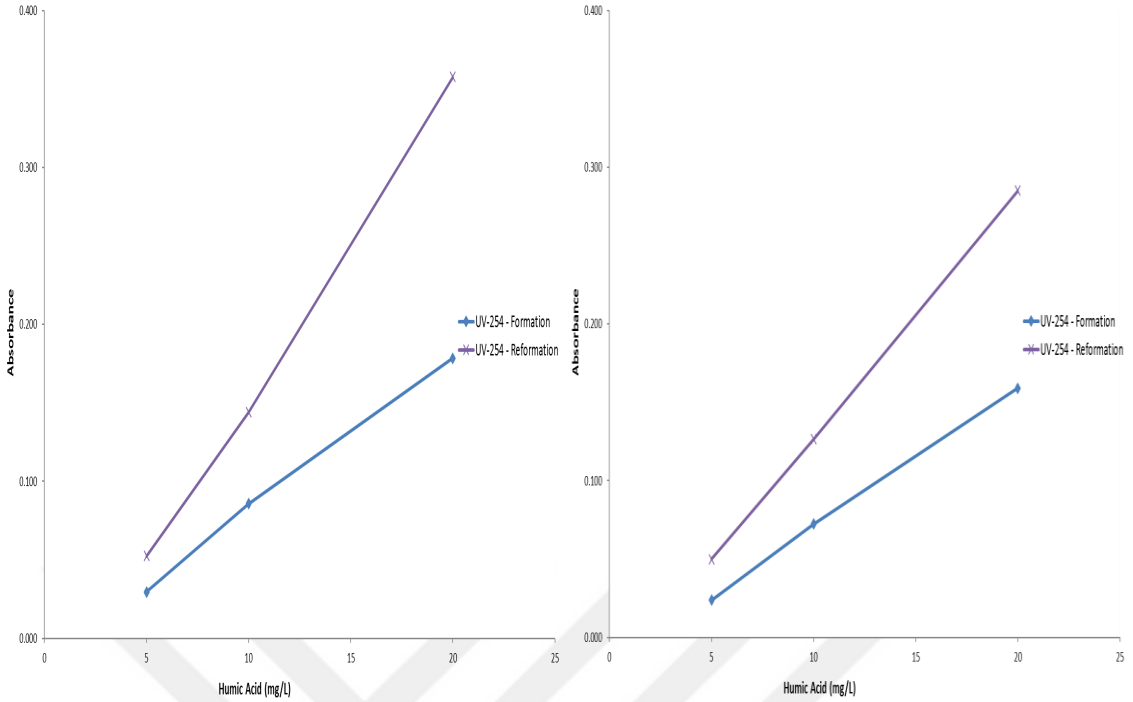

Figure 3.56. Residual abs. at 254 nm after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

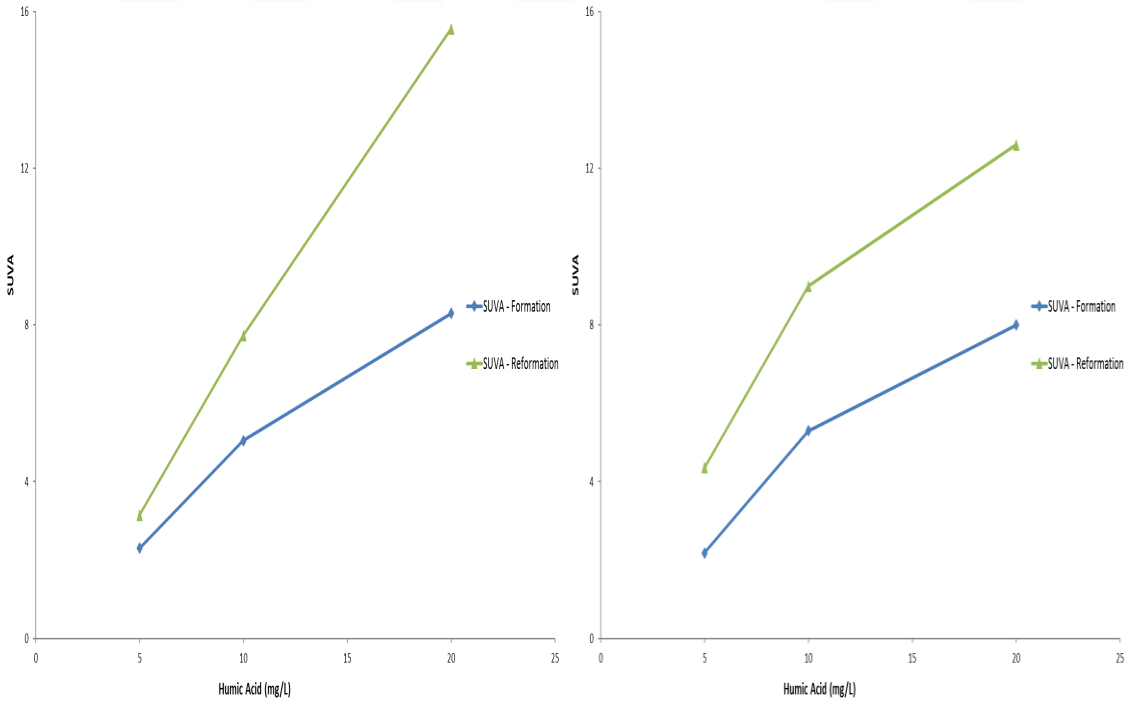

Figure 3.57. Specific UV abs. (SUVA) after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

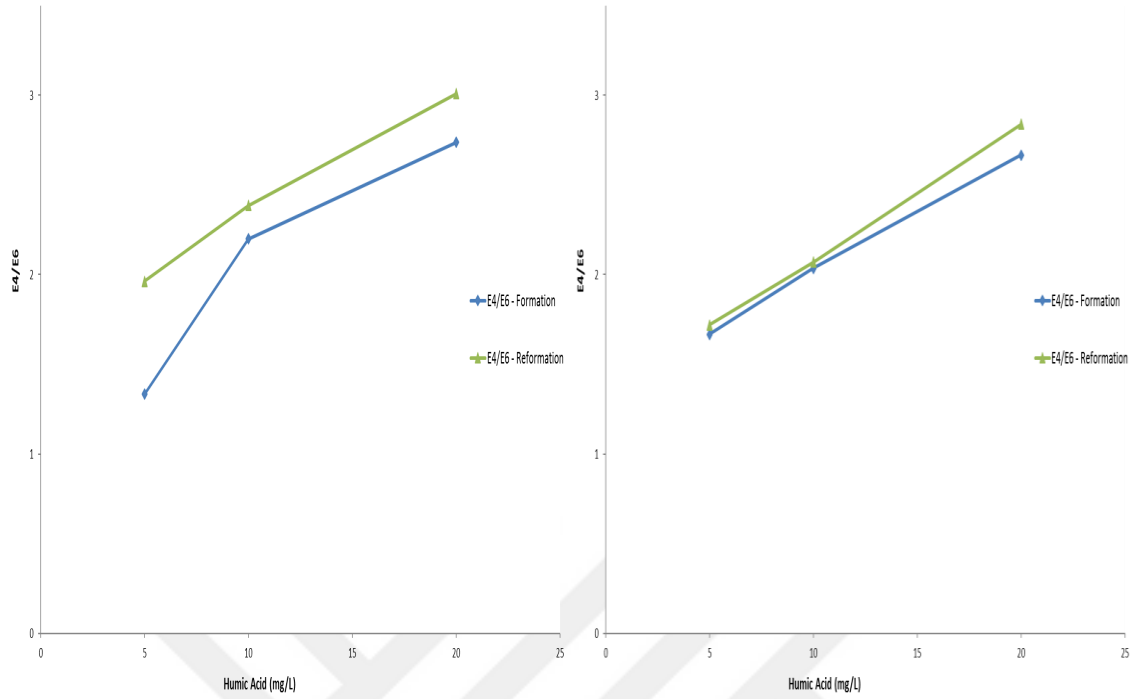

Figure 3.58. E_4/E_6 ratio after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

creased. In correlation with that, E_4/E_6 ratio (Figure 3.53) suggests that smaller molecules left unremoved in suspension as the humic acid concentration was increased.

Compared to alum, larger flocs were formed with PACl, which is attributed to its highly positively charged Al species content, thus residual TOC and DOC concentrations were lower with PACl (Figures 3.54 and 3.55). Consistent with relative floc size data (Figure 3.43), TOC and DOC removals with regrown flocs of PACl were also better. Residual UV absorbance at 254 nm measurements correlate with these findings. SUVA data and E_4/E_6 ratio (Figures 3.126 and 3.127) suggest that flocculation with both coagulants exhibited similarity in terms of hindered removal of more readily removable part and smaller molecules of organic matter with increasing humic acid concentration.

3.2.3. Experiments with 5 mg/L pre-ozonated synthetic raw waters

3.2.3.1. Experiments with $Al_2(SO_4)_3$

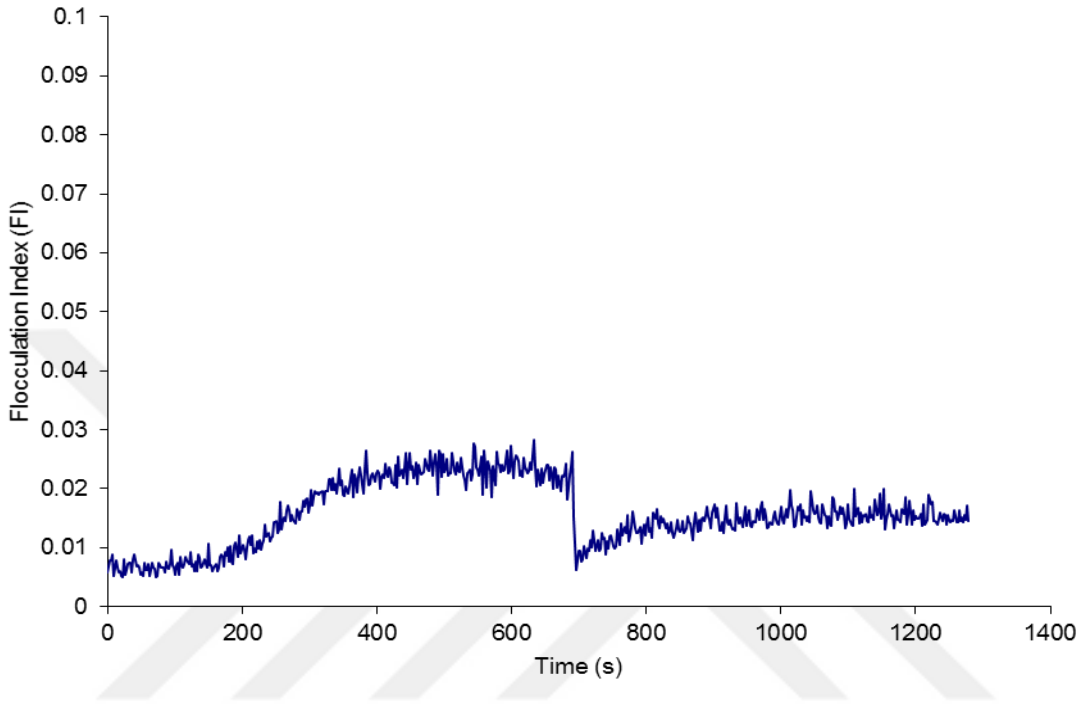

Figure 3.59. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

The same observation is also valid for flocculation tests with 5 mg/L pre-ozonated synthetic raw waters: larger flocs were formed with increasing humic acid concentration, which can be attributed to higher collision efficiency. This observation was also the same for flocs regrown after breakage.

Same as in the jar tests performed with unozonated and 2.5 mg/L pre-ozonated synthetic raw waters, flocculation started earlier as the concentration of humic acid was increased. This could also be attributed to higher collision efficiency with increasing humic acid concentration.

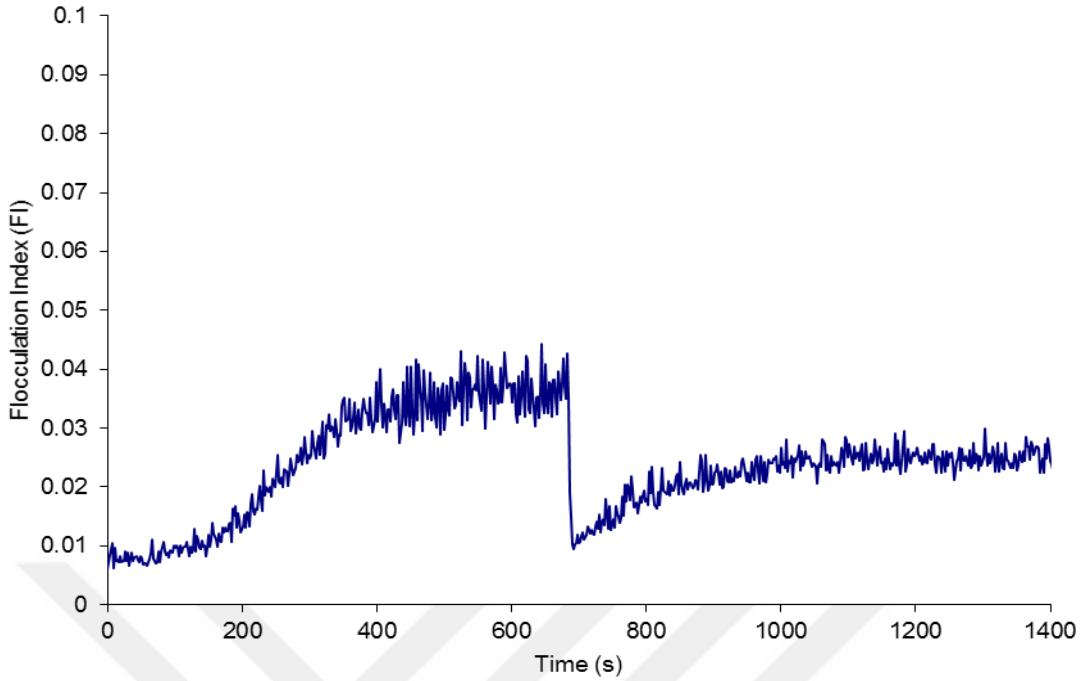

Figure 3.60. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

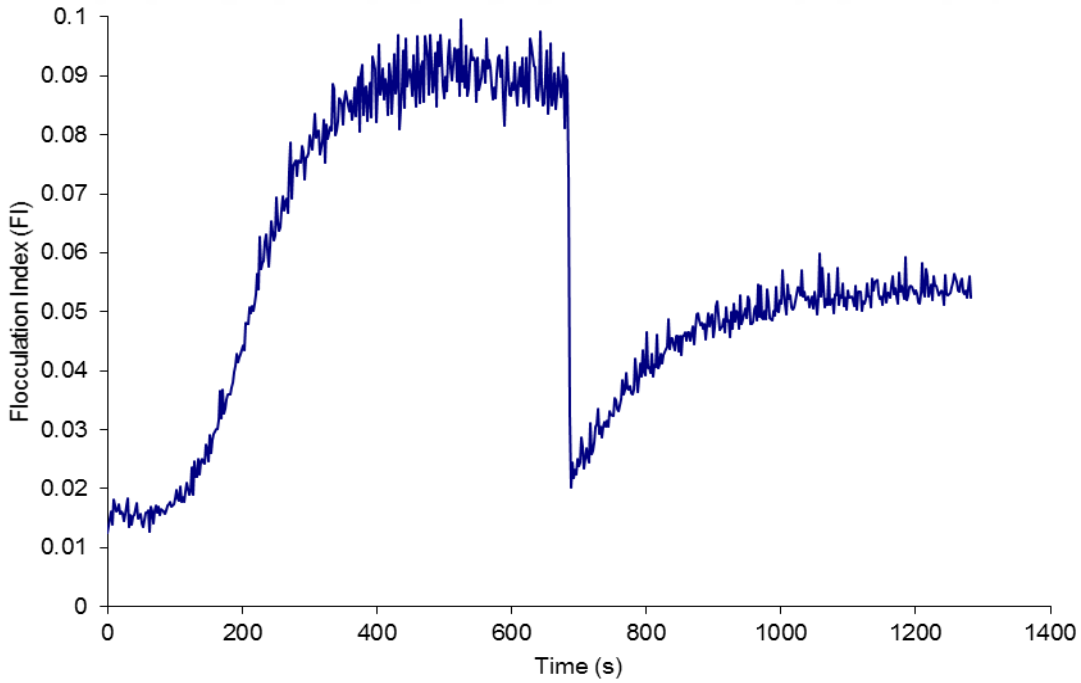

Figure 3.61. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

3.2.3.2. Experiments with polyaluminium chloride (PACl)

Flocculation with PACl was akin to alum. Relative floc size increased with increasing humic acid concentration. It can be attributed to higher collision efficiency. Larger flocs were formed with PACl than with alum, which is attributed to the higher cationic Al species included in polymeric Al coagulants.

Previously performed jar tests with unozonated and 2.5 mg/L pre-ozonated synthetic raw waters showed that the onset of flocculation was delayed as the concentration of humic acid was decreased. This observation is also valid for 5 mg/L pre-ozonated synthetic raw waters flocculated by using PACl; as the humic acid concentration was increased aggregation started earlier, which is another finding to show that it could be attributed to higher collision efficiency with increasing humic acid concentration.

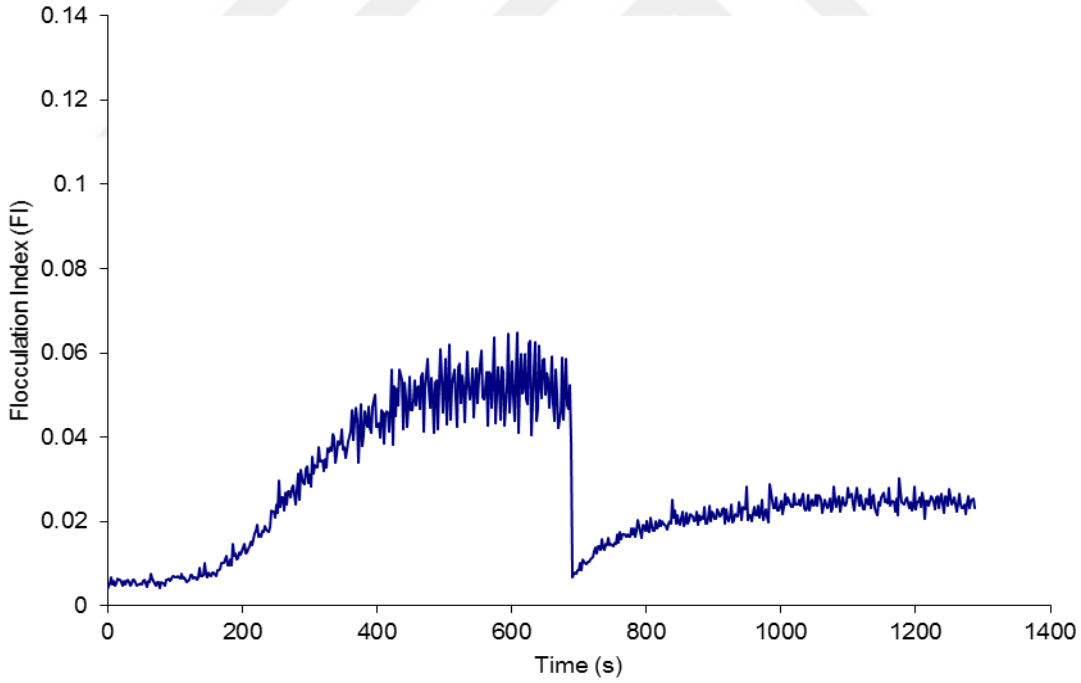

Figure 3.62. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

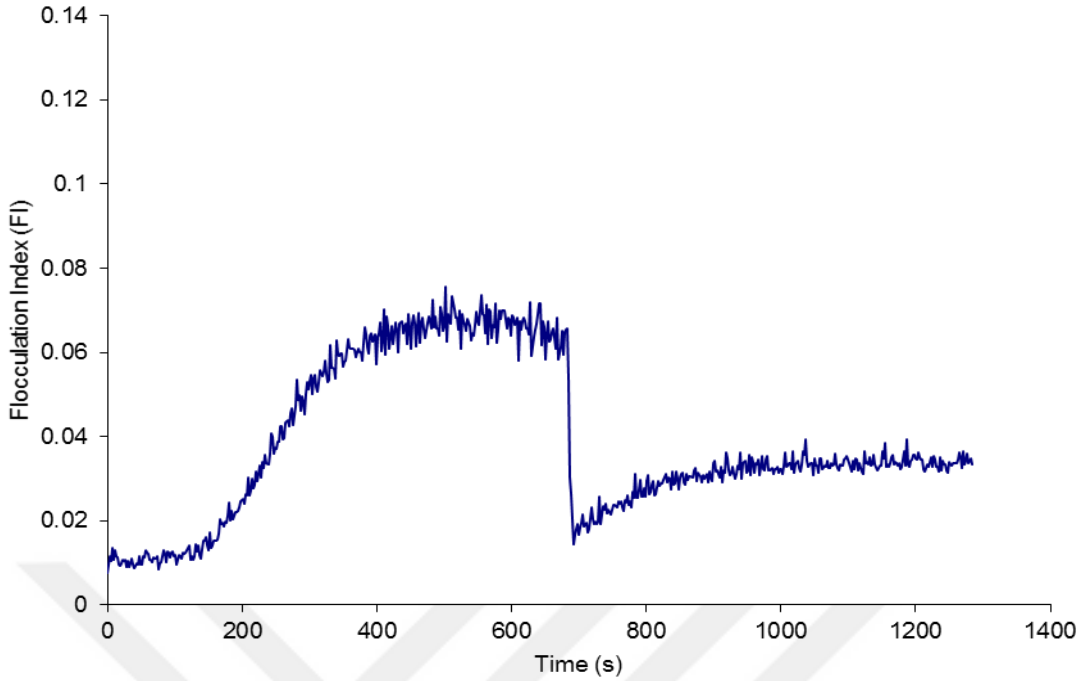

Figure 3.63. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

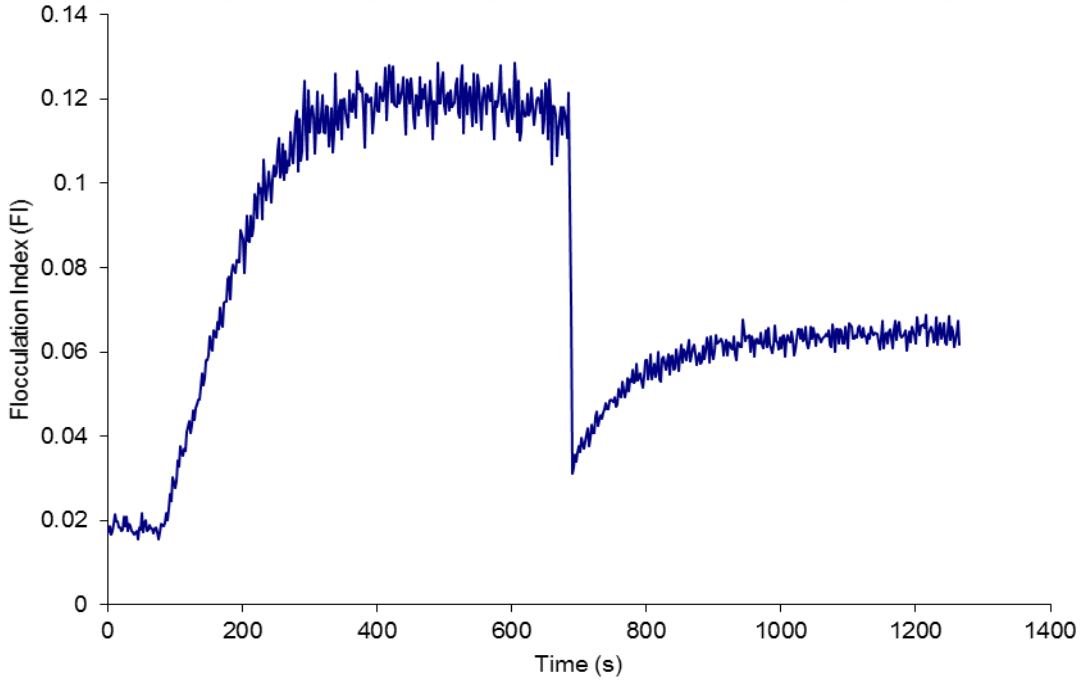

Figure 3.64. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

3.2.3.3. Comparison of floc sizes

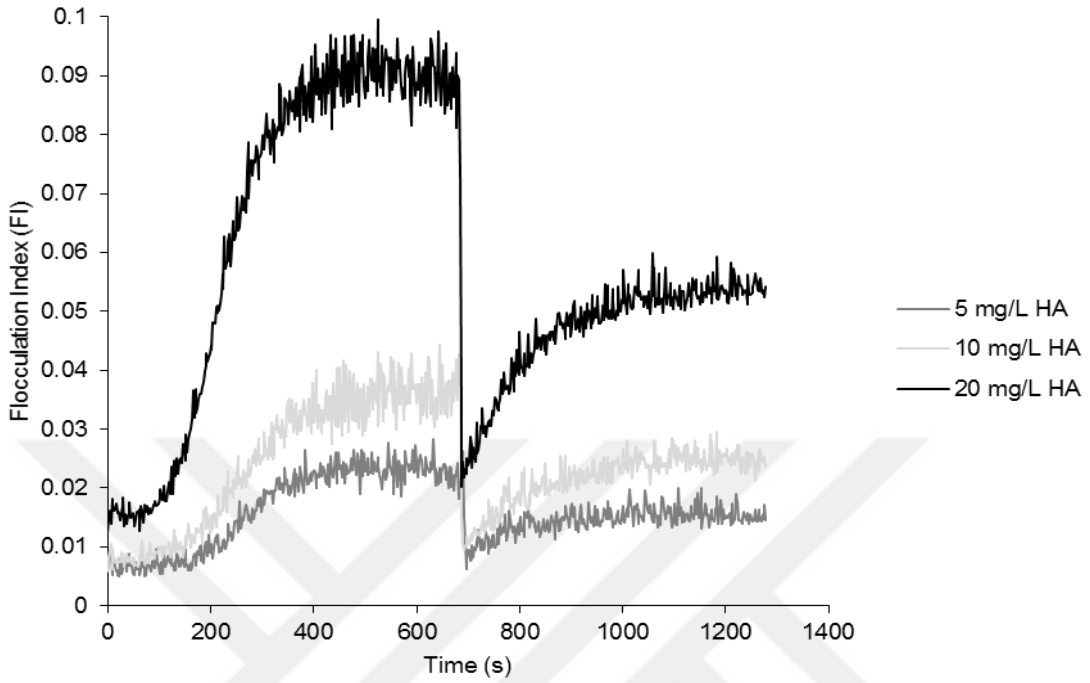

Figure 3.65. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

As in previous experiments performed with unozonated and 2.5 mg/L ozonated synthetic raw waters alum and PACl exhibited a similar pattern in flocculation of 5 mg/L pre-ozonated synthetic raw waters; larger flocs were formed with increasing humic acid concentration. Increase in floc size with increasing concentration of particulates to be flocculated can be attributed to higher collision efficiency. Another feature correlating this suggestion is that the beginning of floc growth was earlier as the concentration of humic acid was increased. It is known that when enough coagulant dose is used, aggregation starts earlier in waters with higher particulate concentration because of higher collision efficiency (Şam and Yükselen, 2006; Sam et al., 2010).

Furthermore, larger floc formation was observed with PACl compared to alum, which is attributed to higher positively charged Al species contributed by PACl, since it is a pre-hydrolysed coagulant.

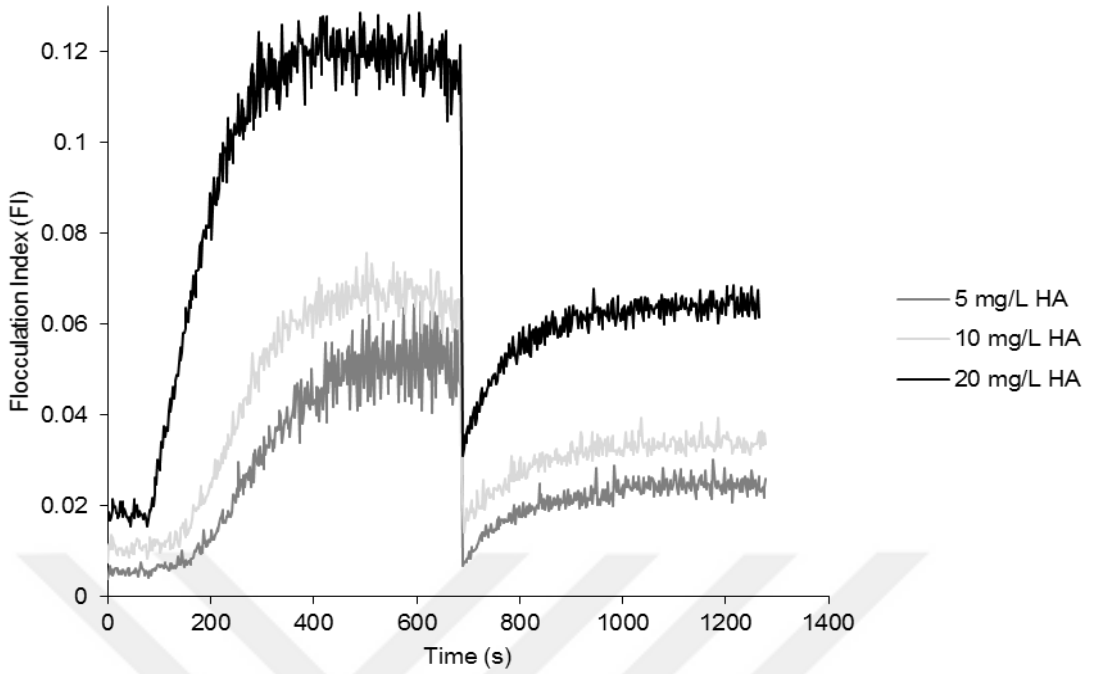

Figure 3.66. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

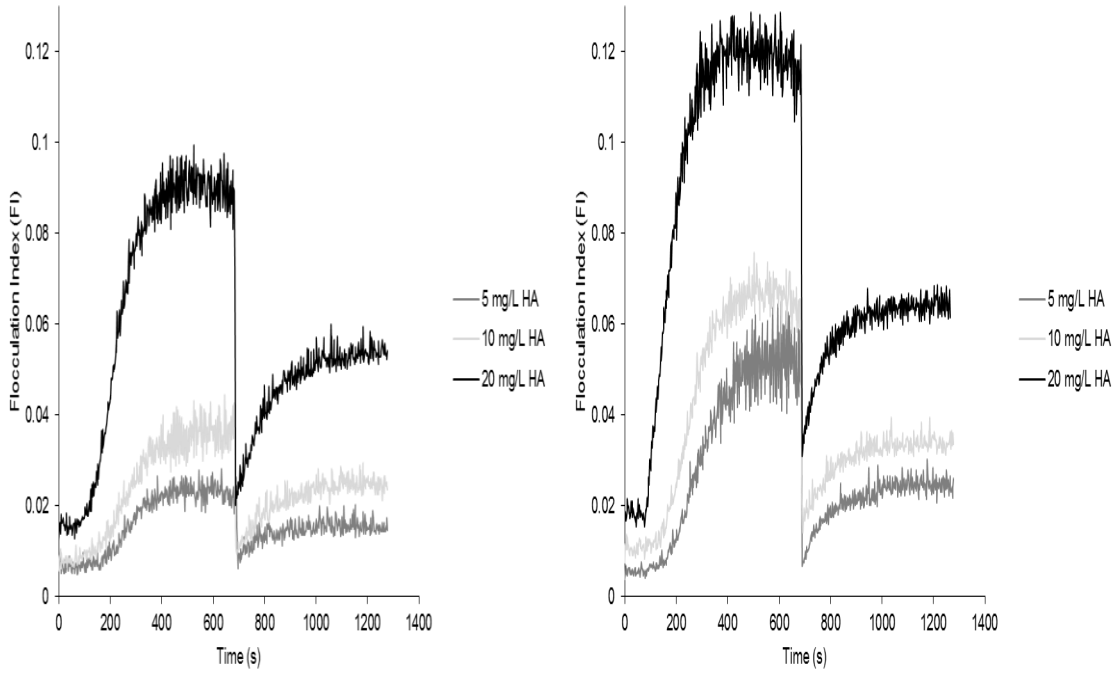

Figure 3.67. Floc growth and regrowth with alum (left) and PACl (right) in 5 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

3.2.3.4. Organic Carbon Removal with $Al_2(SO_4)_3$

Floc size increased in alum flocculation as the concentration of humic acid was increased, very likely due to increasing collision efficiency. Residual total organic carbon and dissolved organic carbon concentrations (Figures 3.68 and 3.69) increased with increasing humic acid concentration because as expected residual organic carbon concentration increases when the concentration of humic acid to be treated with the same dose of coagulant is increased. When the removal performances are examined, it is seen that dissolved organic carbon removal efficiency increased with increasing humic acid concentration (Appendix Figure 14) whereas total organic carbon removal efficiency slightly decreased when the humic acid concentration was increased from 10 mg/L to 20 mg/L (Appendix Figure 13). Residual UV_{254} concentration got worse (increased) with increasing humic acid concentration, interesting enough, UV_{254} removal efficiency also worsened. SUVA increased over 4 when the humic acid concentration was increased from 5 mg/L to 10 mg/L, which indicates that more hydrophobic and aromatic fractions were prevailing in the supernate. E_4/E_6 ratio also in-

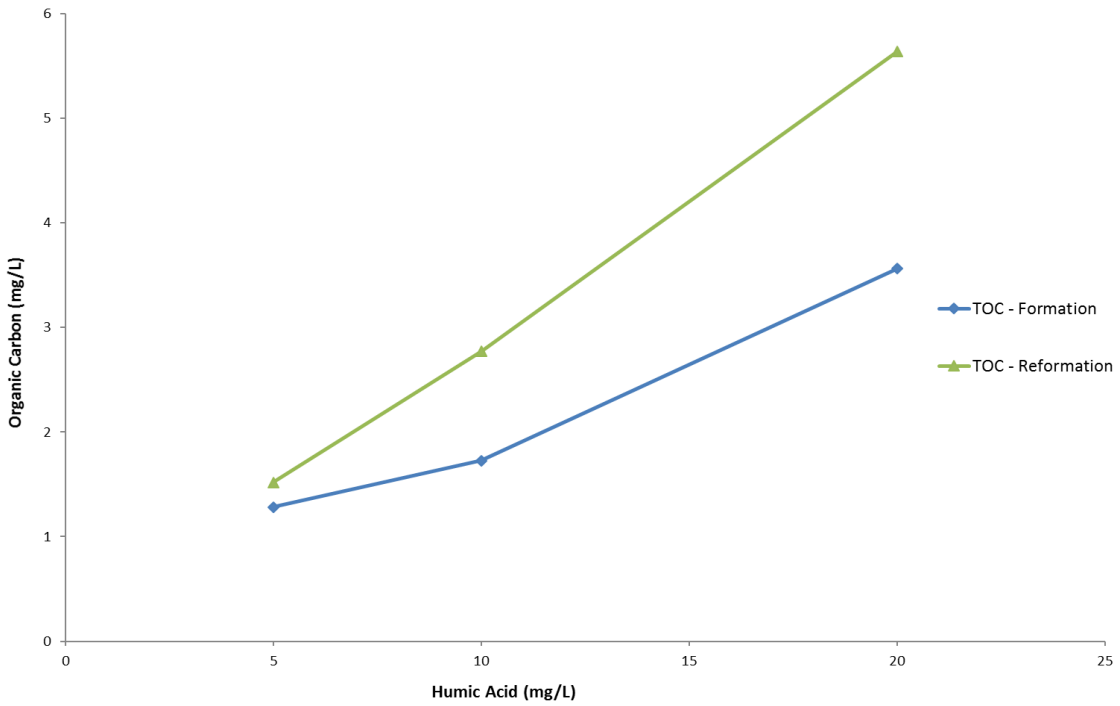

Figure 3.68. Residual TOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

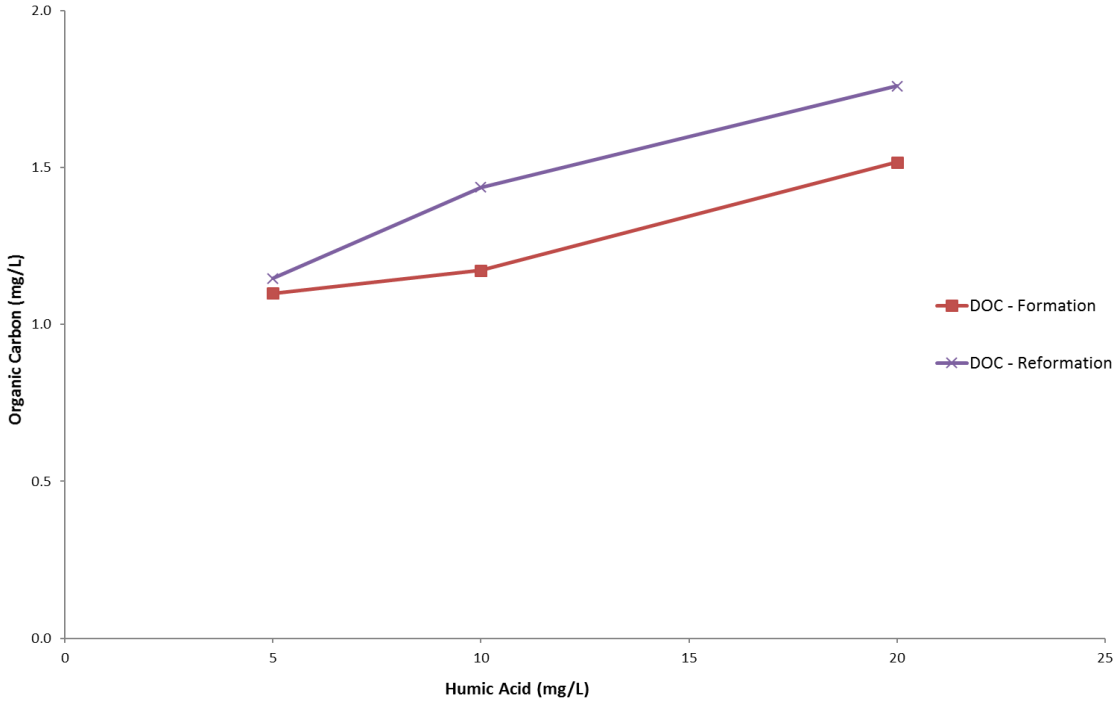

Figure 3.69. Residual DOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

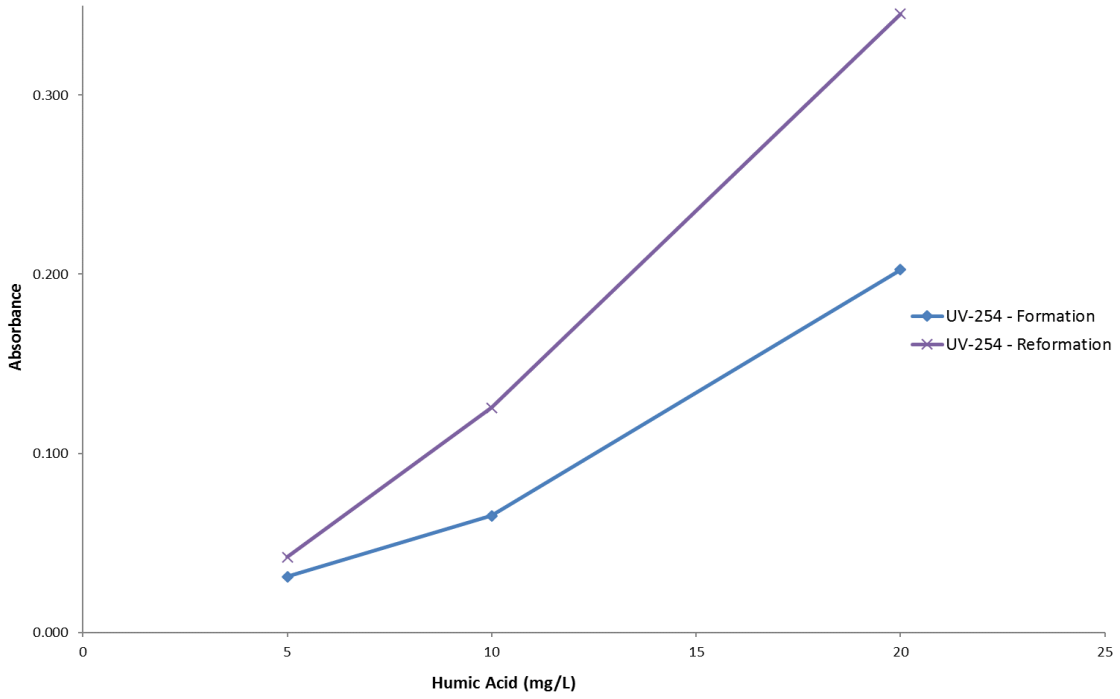

Figure 3.70. Residual absorbance at 254 nm after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

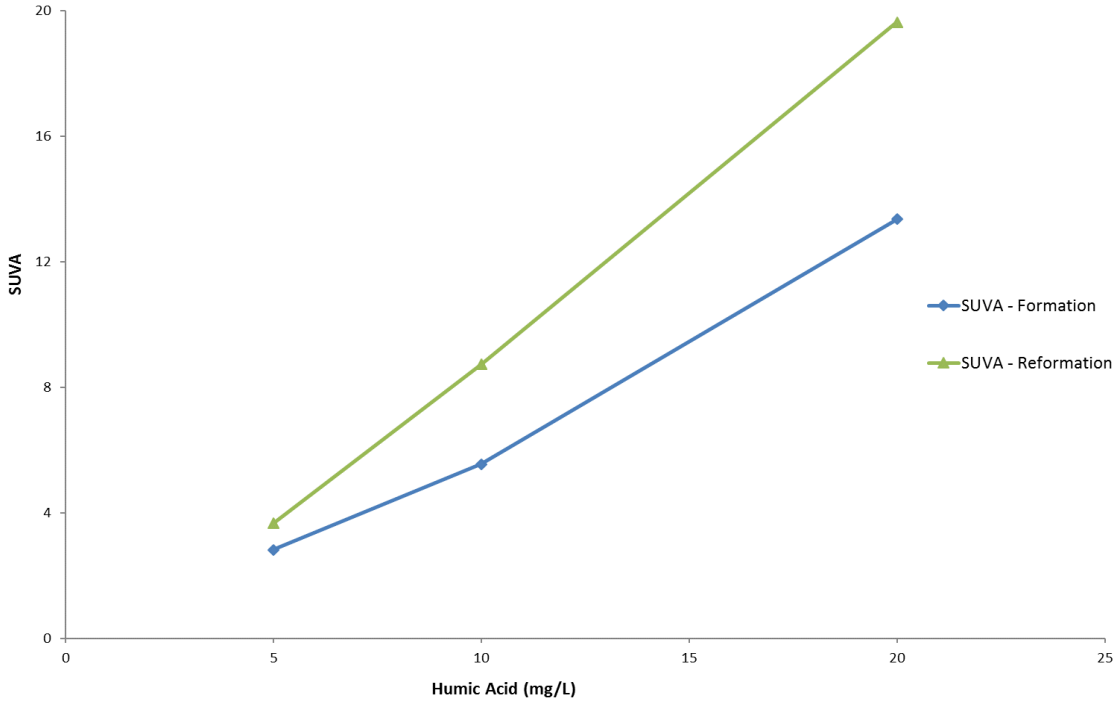

Figure 3.71. Specific UV absorbance (SUVA) after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

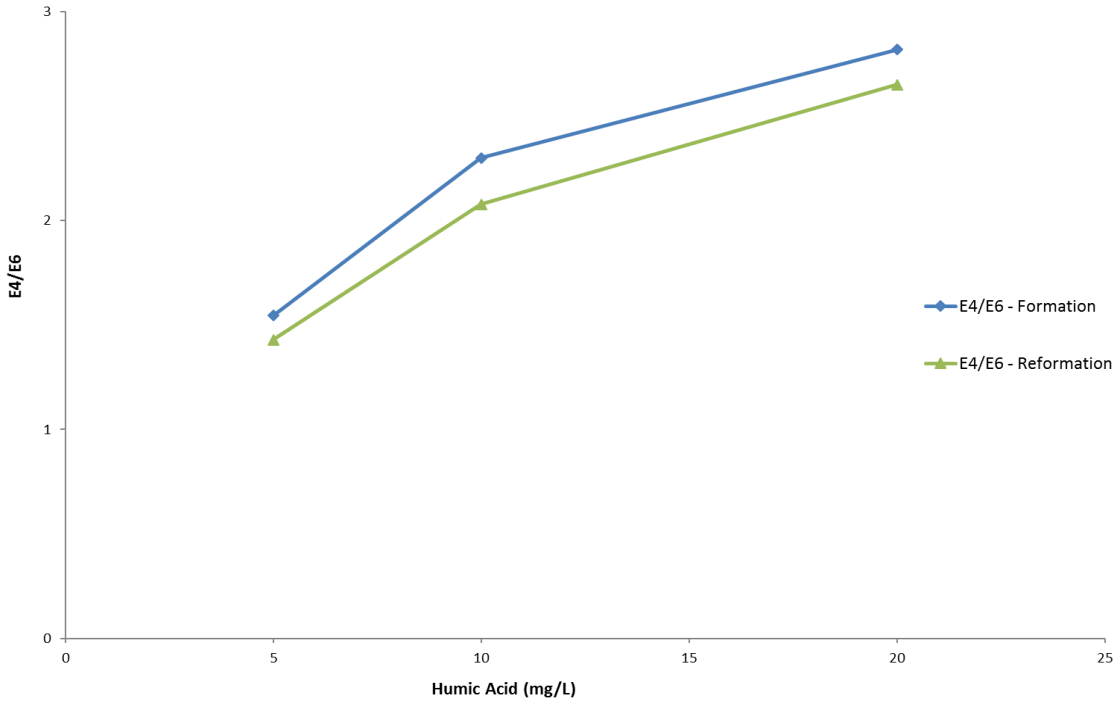

Figure 3.72. E_4/E_6 ratio after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

creased with increasing humic acid concentration, implicating that smaller molecules were dominant in the suspension. When residual UV_{254} absorbance, SUVA and E_4/E_6 ratio are interpreted together it can be said that as the humic acid concentration was increased coagulant dose became insufficient possibly because ozonation of humic acid led to release of smaller organic molecules.

3.2.3.5. Organic carbon removal with polyaluminium chloride (PACl)

Similar to alum flocculation, floc size also increased with increasing humic acid concentration in flocculation with PACl, which could be attributed to increasing collision efficiency with increasing humic acid concentration. Residual total organic carbon (Figure 3.73) and dissolved organic carbon (Figures 3.74) concentrations increased when the humic acid concentration was increased. This might seem contradicting with floc size data, however removal efficiencies increased (Appendix Figure 16 and Figure 17) as the humic acid concentration was increased, which is in good correlation with floc size data. In correlation with residual organic carbon data, re-

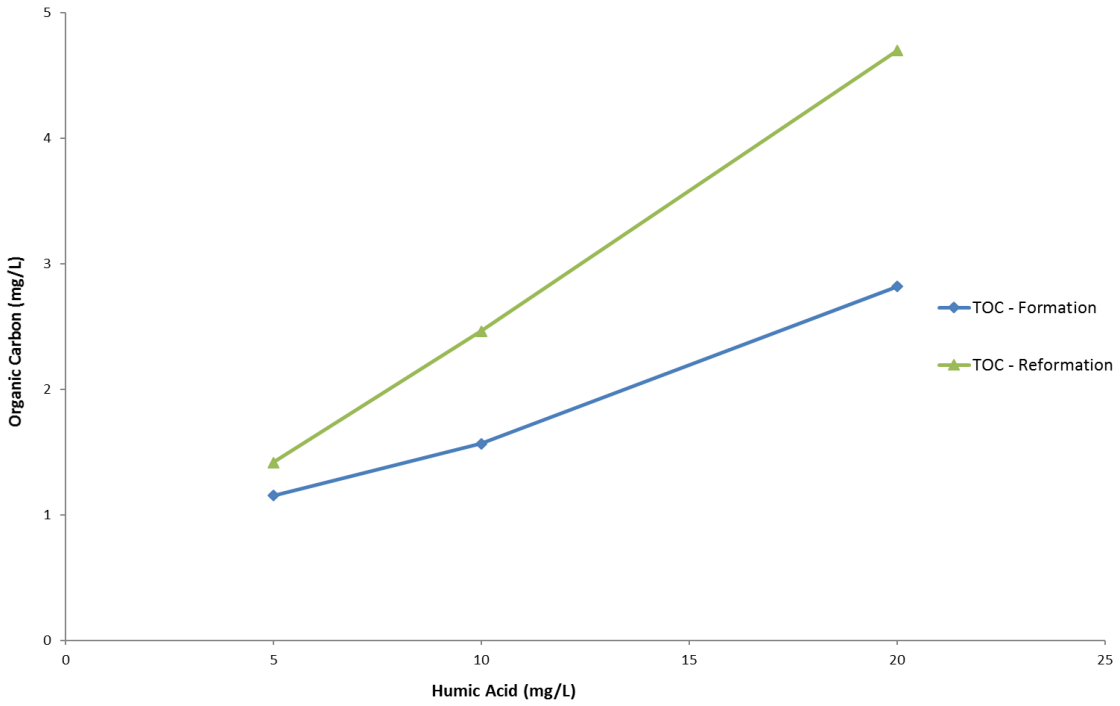

Figure 3.73. Residual TOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

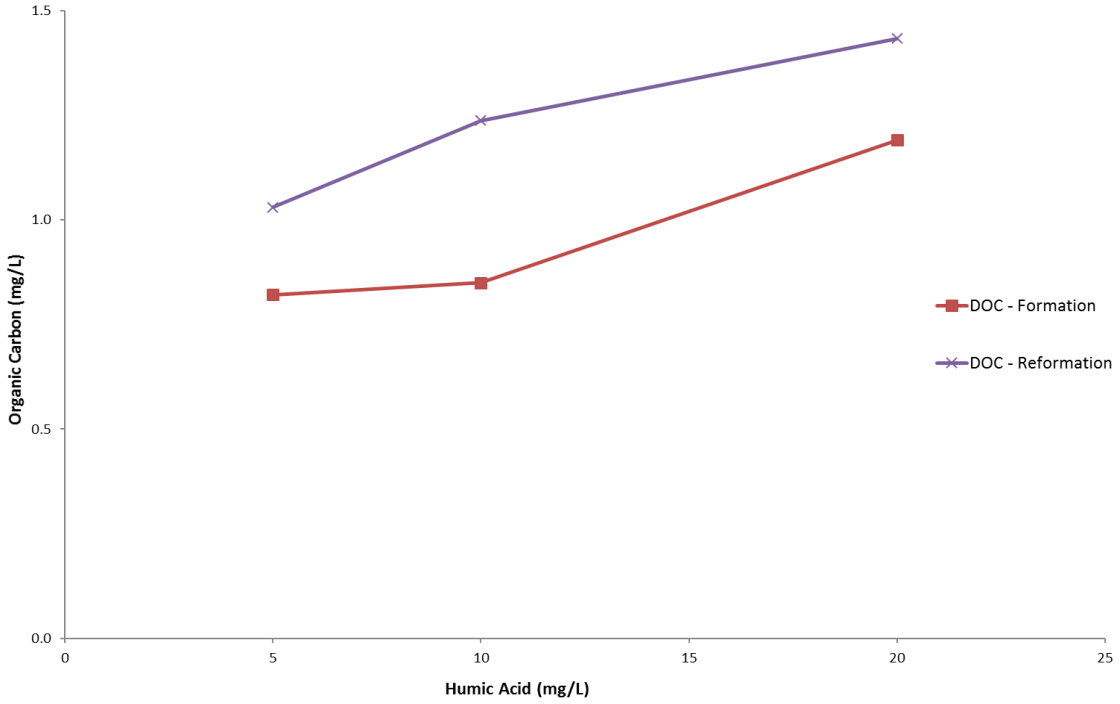

Figure 3.74. Residual DOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

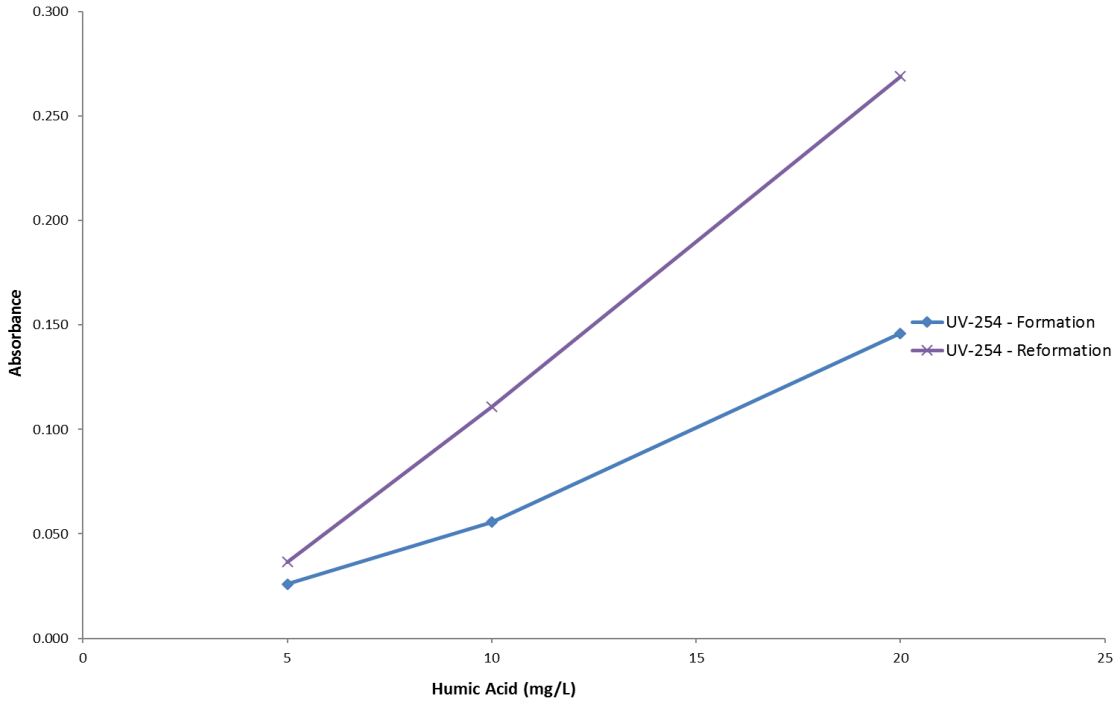

Figure 3.75. Residual absorbance at 254 nm after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

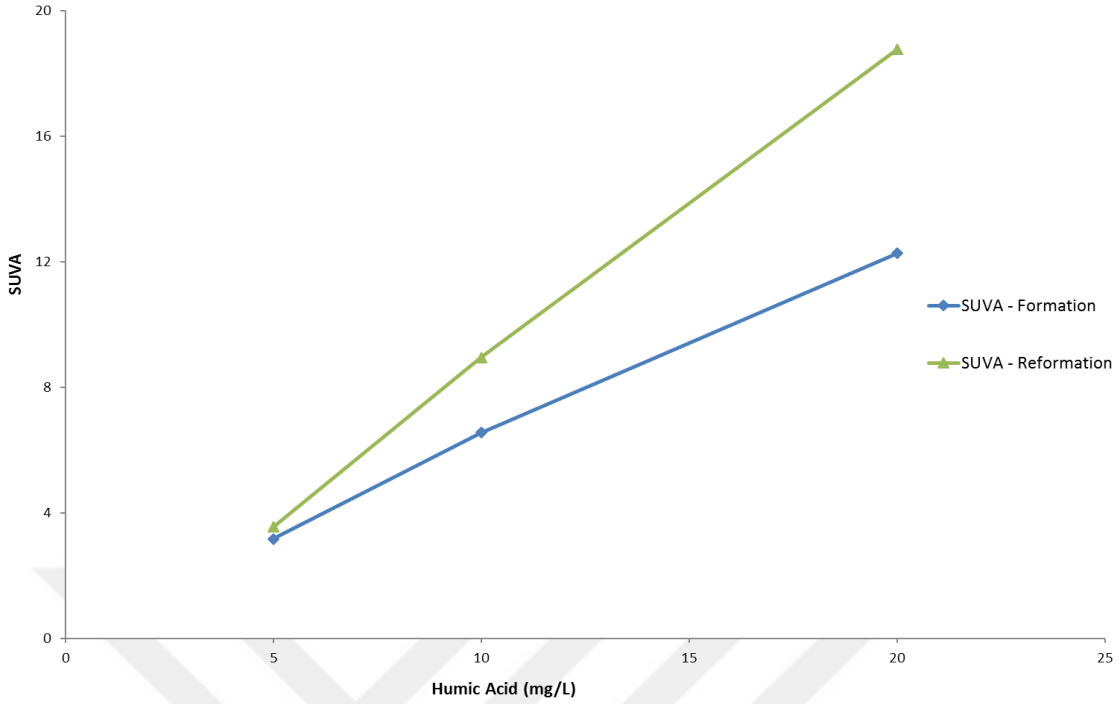

Figure 3.76. Specific UV absorbance (SUVA) after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

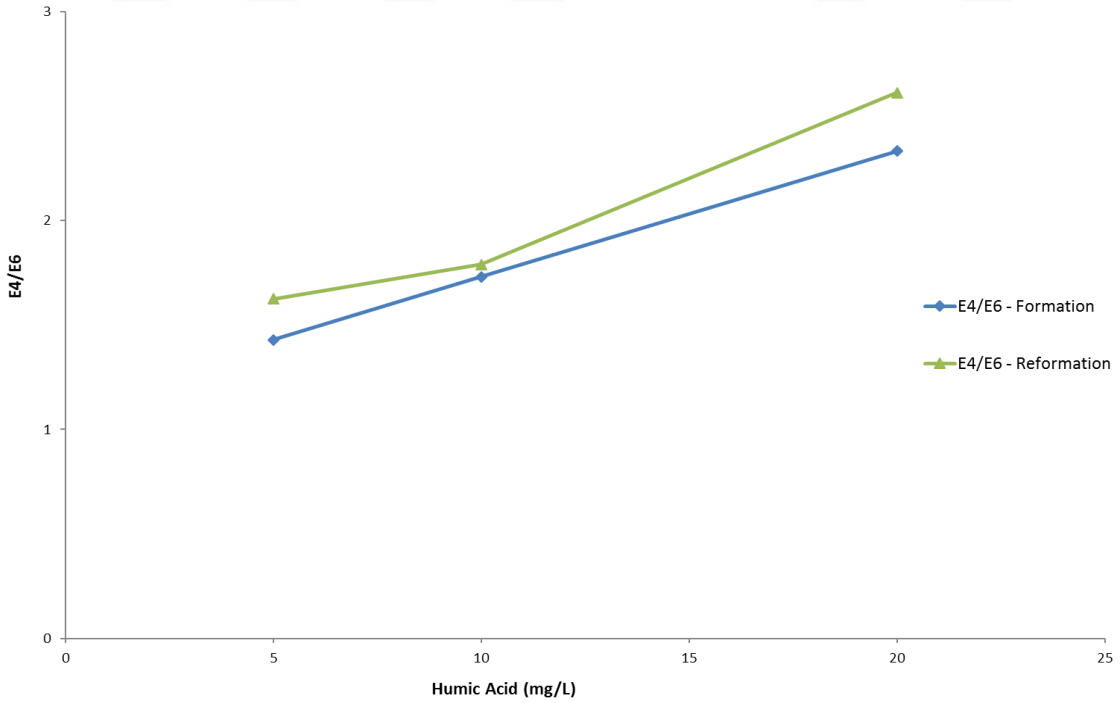

Figure 3.77. E_4/E_6 ratio after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

sidual UV absorbances at 254 nm also increased with increasing humic acid concentration. When UV_{254} absorbance removal efficiency is considered, it becomes evident that performance declined as the humic acid concentration was gradually increased. Examination of Figure 3.76 (SUVA data) shows that removal of hydrophobic or more readily removable part of organic matter by PACl decreased when the humic acid concentration was increased over 5 mg/L. Correlatingly, with increasing humic acid concentration removal of smaller organic molecules was hindered (E_4/E_6 ratio depicted in Figure 3.77).

Owing to its higher positively charged Al species content, PACl showed larger floc formation and thus better organic matter removal (Figures 3.78 and 3.79). Residual parameter curves are similar with both coagulants, indicating alum and PACl showed similar flocculation characteristics. UV data (Figure 3.80) are also in good correlation with these findings; with both coagulants residual UV absorbance at 254 nm curves and residual TOC curves look alike. Examinations of SUVA data and E_4/E_6 ratio suggest that with increasing humic acid concentration flocculation with both coagulants

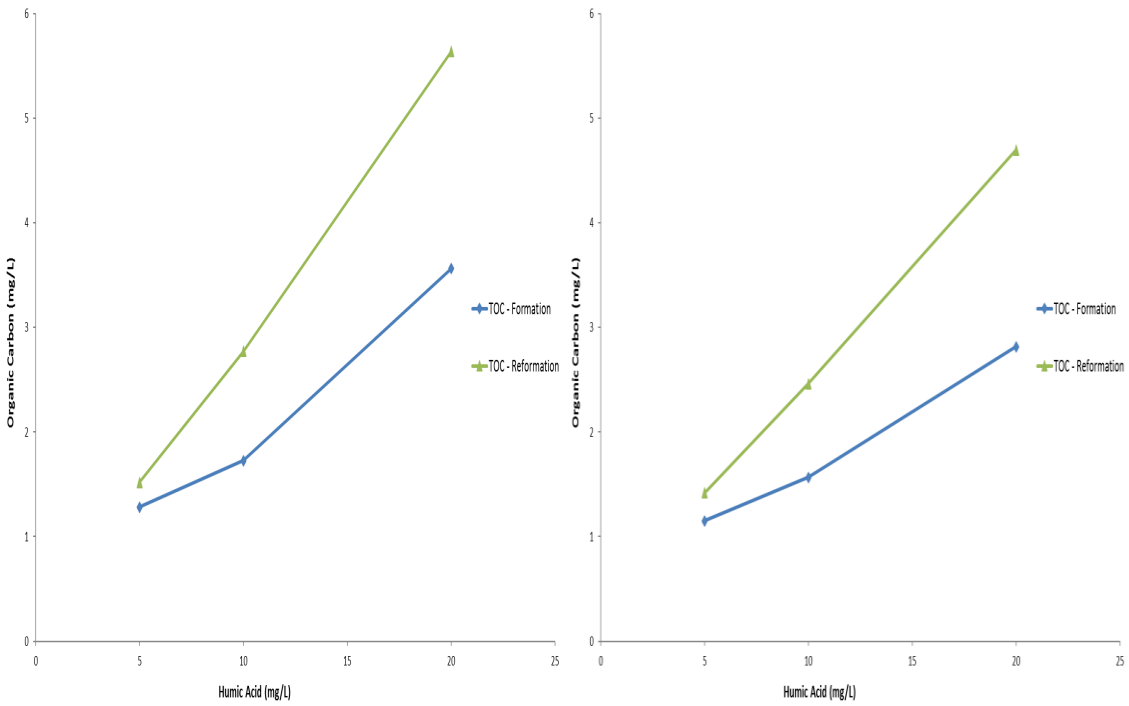

Figure 3.78. Residual TOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

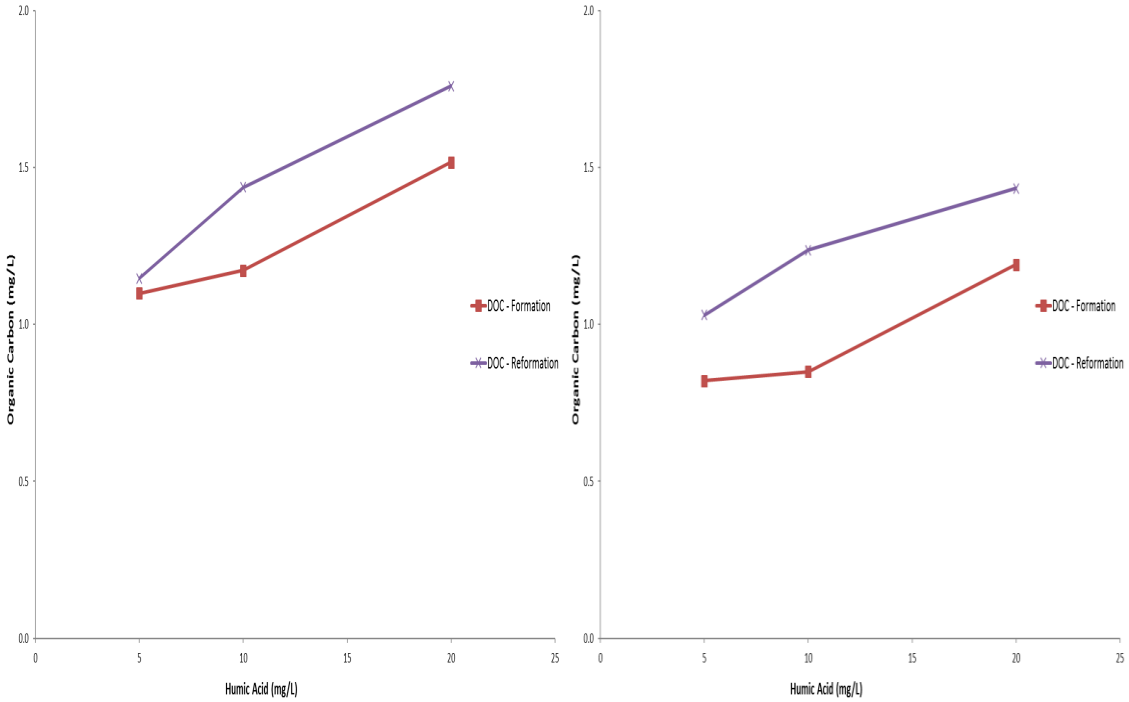

Figure 3.79. Residual DOC after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

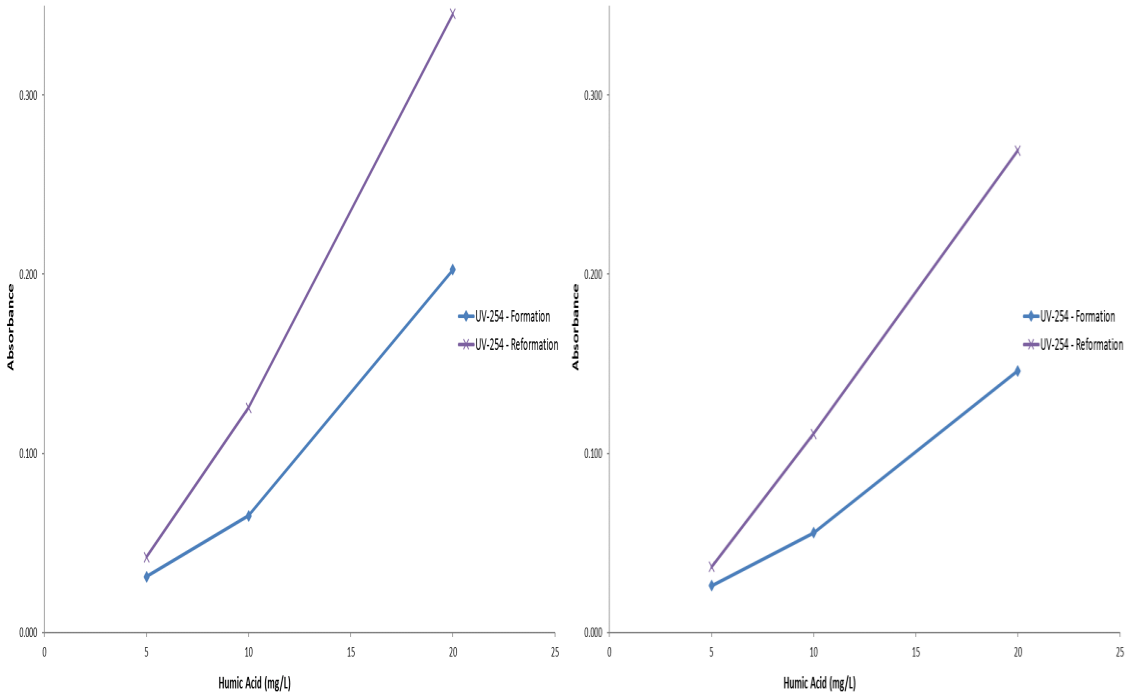

Figure 3.80. Residual absorbance at 254 nm after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

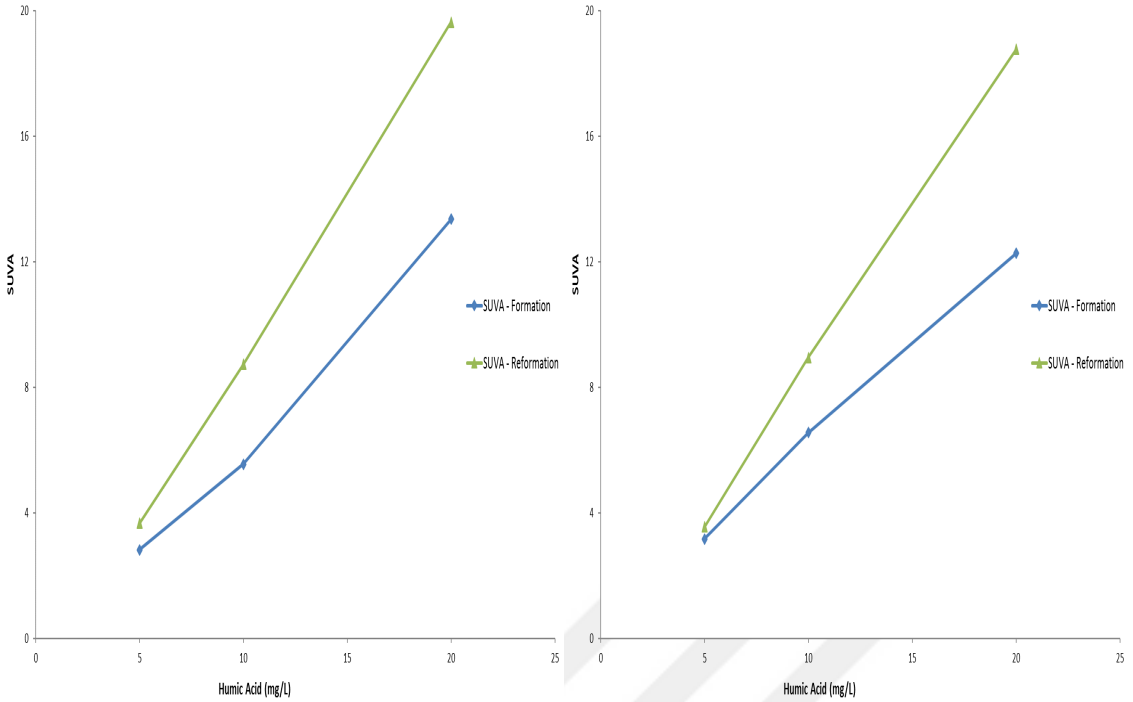

Figure 3.81. Specific UV abs. (SUVA) after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

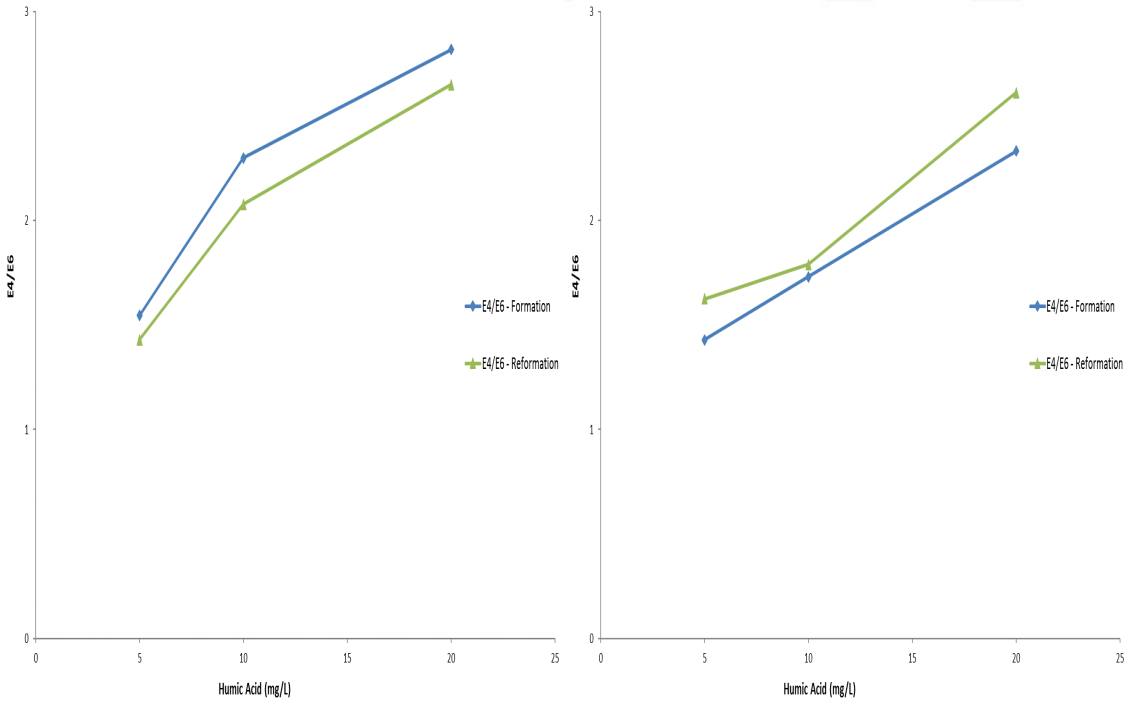

Figure 3.82. E_4/E_6 ratio after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

exhibited similarity in terms of hindered removal of more readily removable part and smaller molecules of organic matter.

3.2.4. Experiments with 10 mg/L pre-ozonated synthetic raw waters

10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid were flocculated using aluminium sulphate and polyaluminium chloride:

3.2.4.1. Experiments with $Al_2(SO_4)_3$

As in previous pre-ozonation doses relative floc size was observed to increase with increasing humic acid concentration. Increase in collision efficiency with increasing humic acid concentration might be the probable reason. Also, relative size of flocs reformed after breakage increased with increasing humic acid concentration but flocs never recovered to their sizes before breakage. As observed with previous pre-ozonation doses, flocculation initiated earlier and steady-state floc size distribution was reached in shorter time as the humic acid concentration was increased, which together

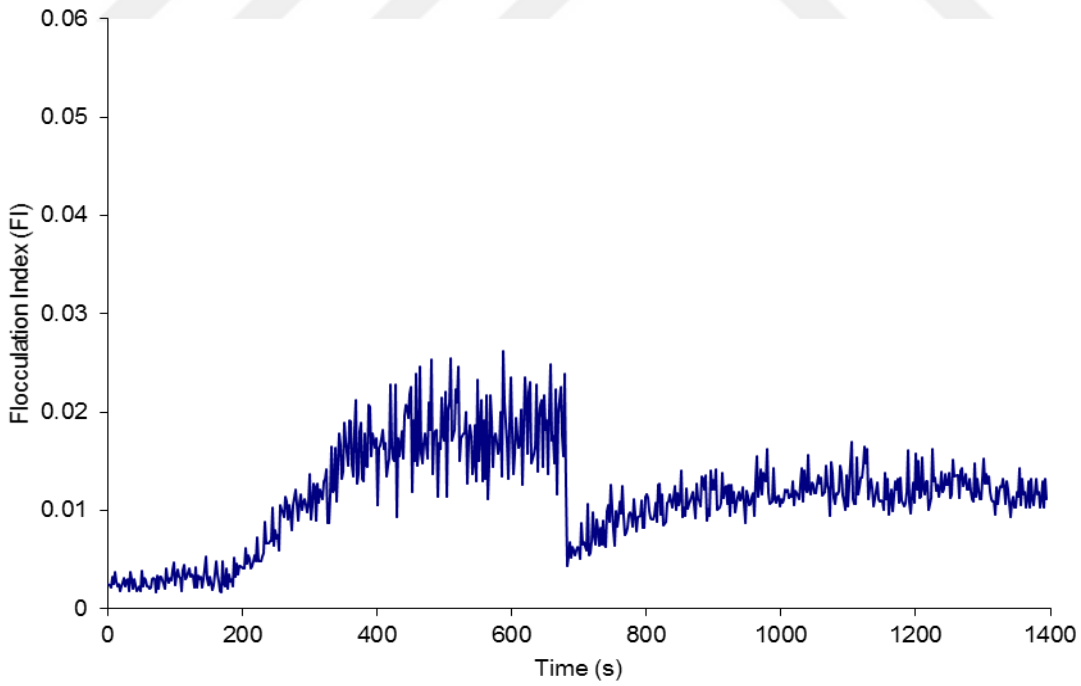

Figure 3.83. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

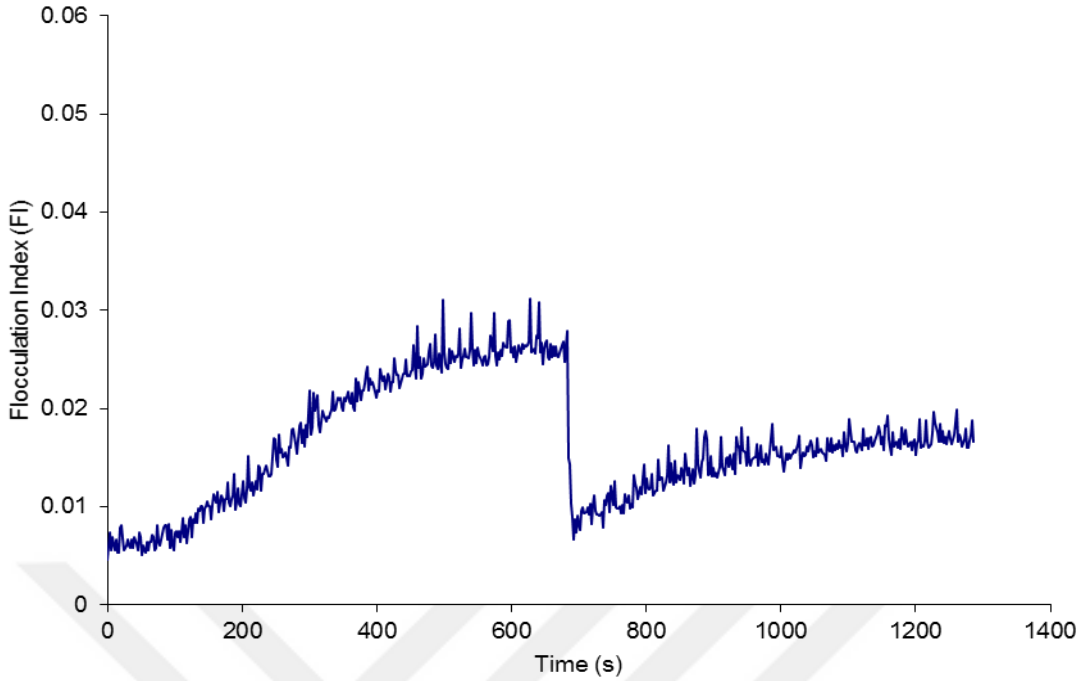

Figure 3.84. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

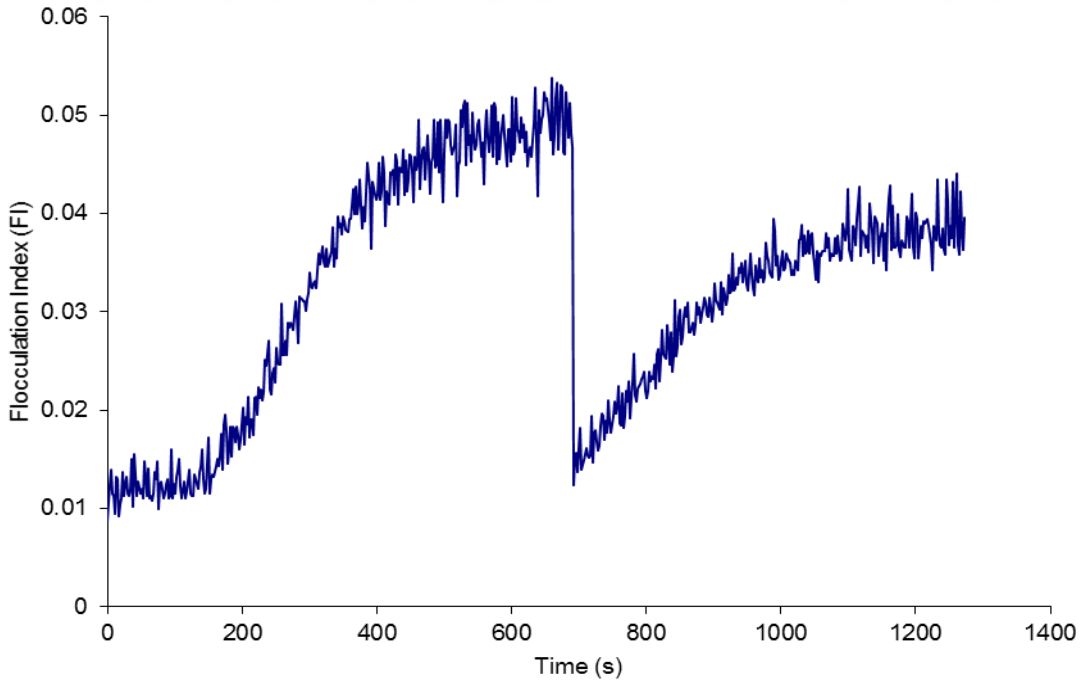

Figure 3.85. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

makes the floc growth curve steeper with increasing humic acid concentration.

3.2.4.2. Experiments with polyaluminium chloride (PACl)

PACl exhibited similar character in flocculation of 10 mg/L pre-ozonated synthetic raw waters: larger flocs were formed with increasing humic acid concentration, which can be attributed to increasing collision efficiency. PACl showed better performance compared to alum in terms of forming larger flocs. This is attributed to the higher cationic Al species included in polymeric aluminium coagulants. Similar to alum the onset of aggregation started earlier as the humic acid concentration was increased, which was also observed as characteristic to both coagulants in previously presented flocculation experiments with with unozonated, 2.5 mg/L and 5 mg/L pre-ozonated synthetic raw waters.

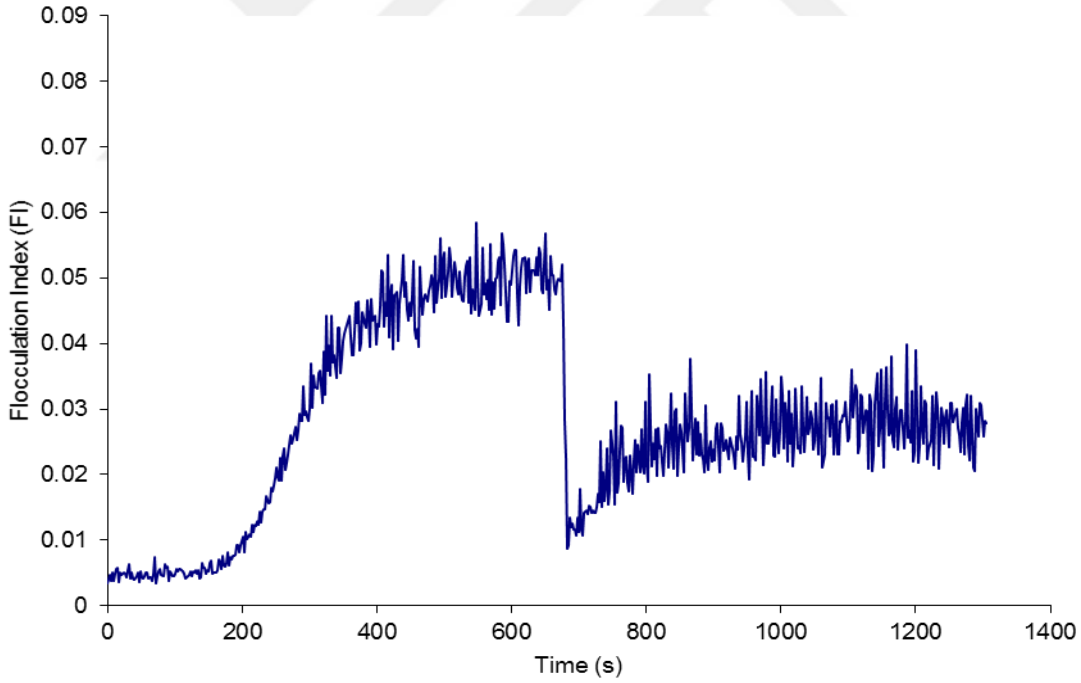

Figure 3.86. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

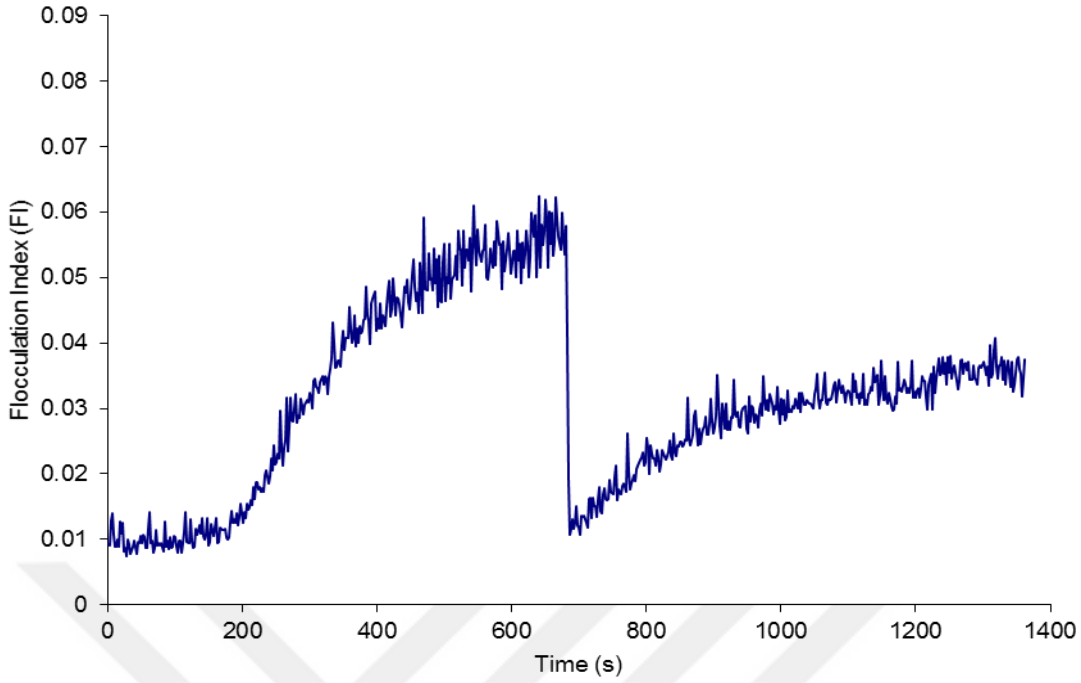

Figure 3.87. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

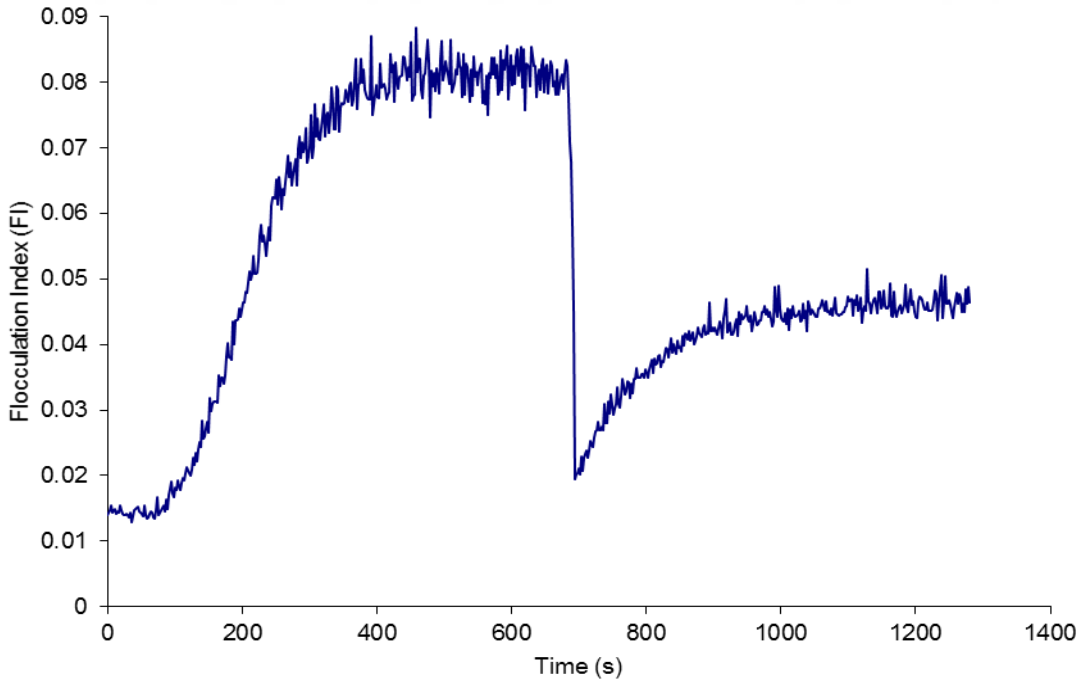

Figure 3.88. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

3.2.4.3. Comparison of floc sizes

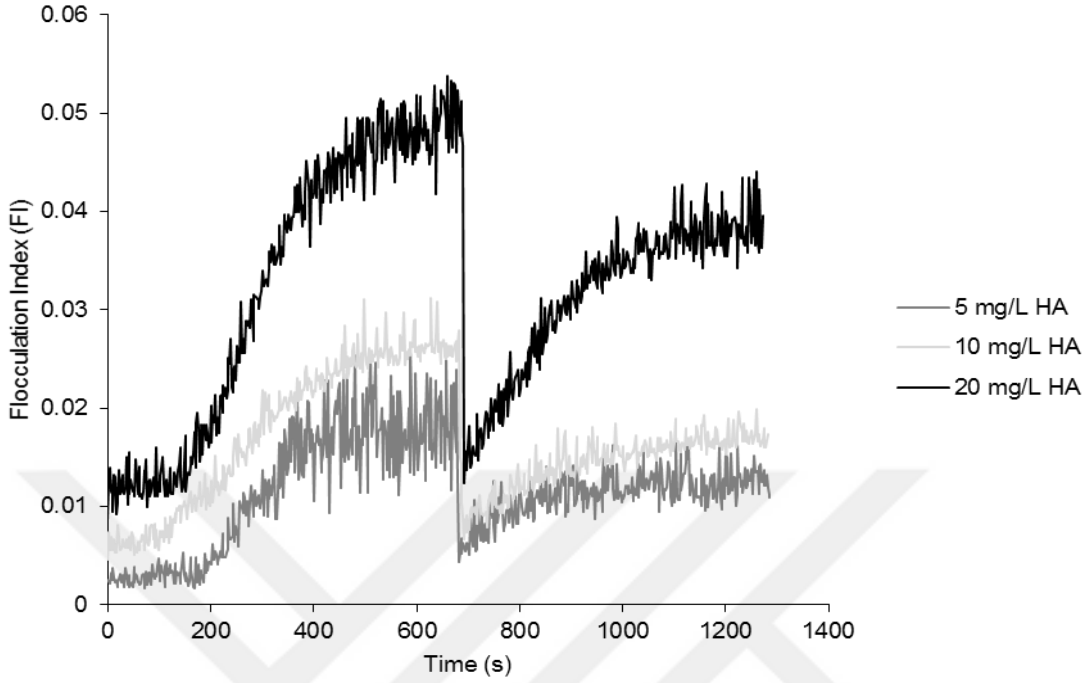

Figure 3.89. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

It can be seen from Figures 3.89-3.91 that alum and PACl showed a similar flocculation pattern; floc formation started earlier with increasing humic acid concentration. Aggregation started relatively earlier with PACl in all humic acid concentrations studied, which is thought to be because of pre-hydrolysed Al species in PACl. Also, as the concentration of humic acid was increased, larger flocs formed. Increase in floc size can be attributed to increasing collision efficiency with increasing concentration of particulates. Like the observations in previous flocculation experiments with unozonated, 2.5 mg/L and 5 mg/L ozonated synthetic raw waters, larger flocs formed with PACl compared to alum, which is attributed to higher positive charge Al species included in PACl since it is a pre-hydrolysed coagulant. Similarity in flocculation character with both coagulants may be expected for they are both derivatives of aluminium salts, the difference is that one was pre-hydrolysed, hence it contains higher valence Al species, which led to better flocculation performance.

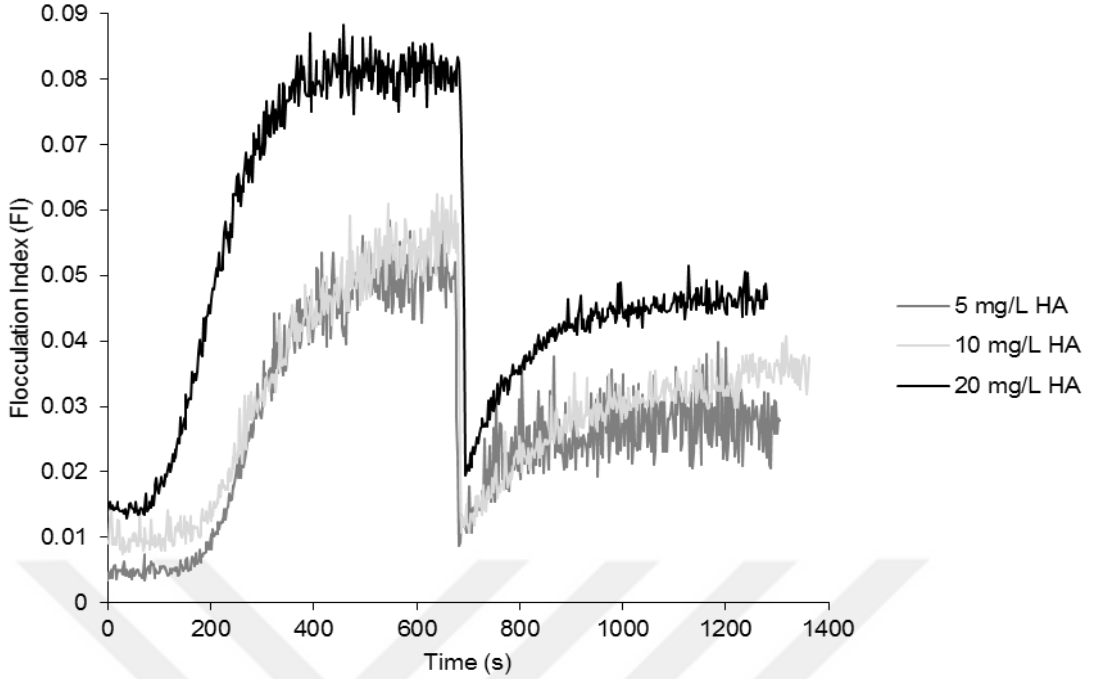

Figure 3.90. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

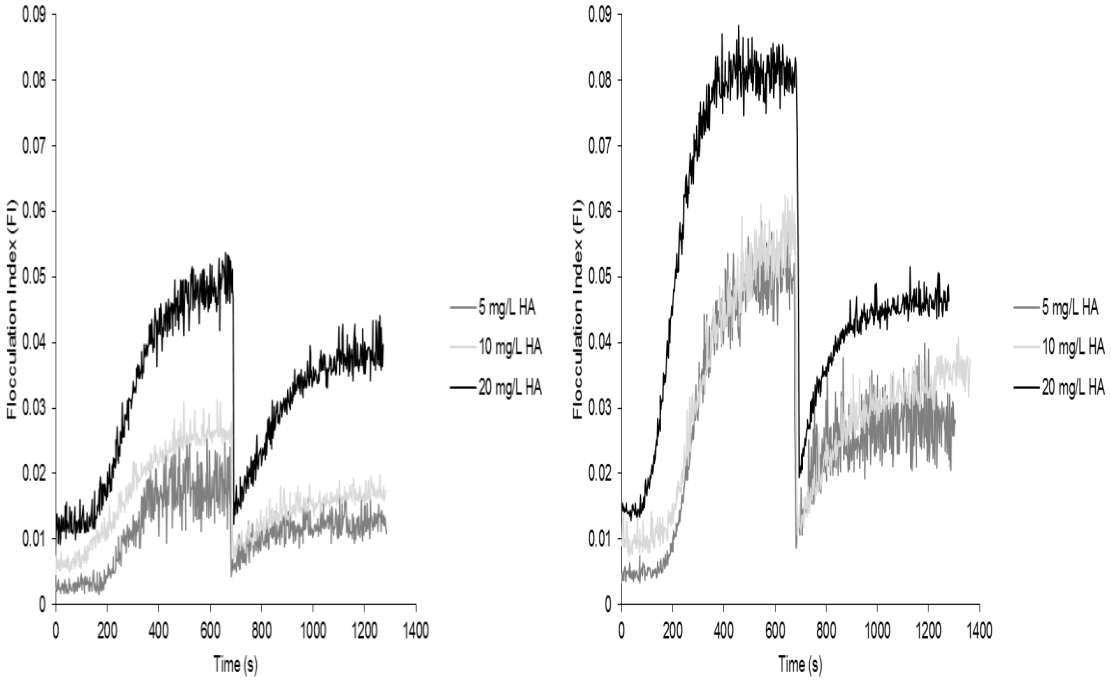

Figure 3.91. Floc growth and regrowth with alum (left) and PACl (right) in 10 mg/L pre-ozonated synthetic raw waters containing 5, 10 and 20 mg/L humic acid

3.2.4.4. Organic carbon removal with $Al_2(SO_4)_3$

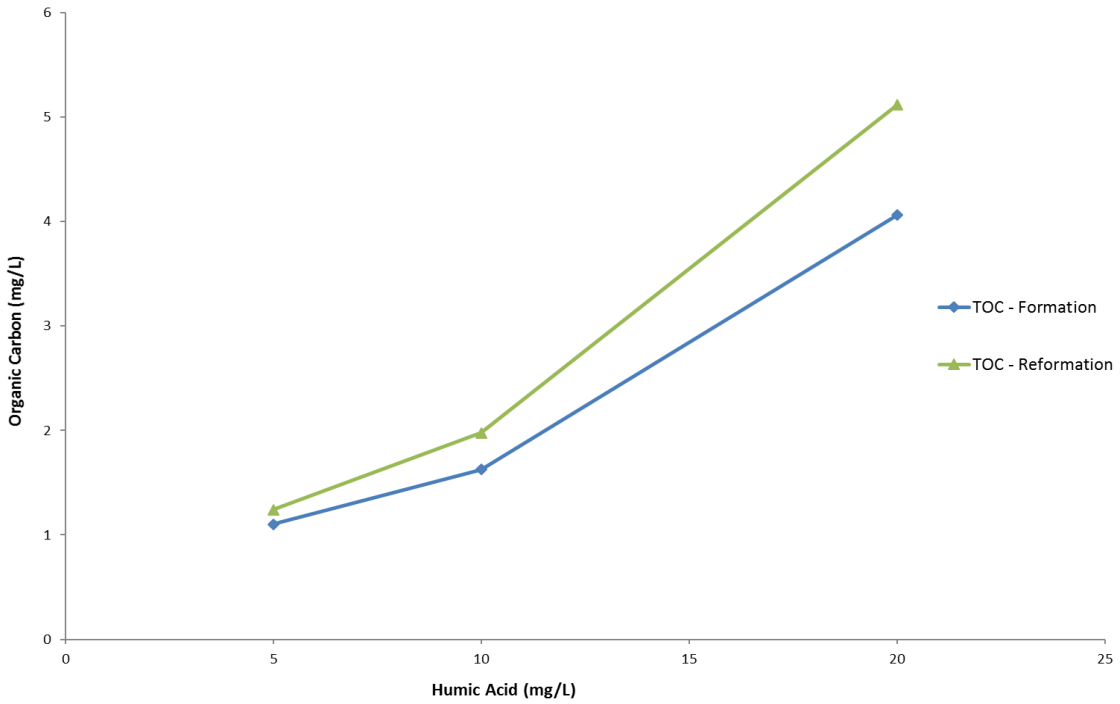

Figure 3.92. Residual TOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

Residual total organic carbon and dissolved organic carbon concentrations (Figures 3.92 and 3.93) increased with increasing humic acid concentration. As contradicting to floc size data as that might sound, it is actually in correlation with them because residual organic carbon concentration increases when the concentration of humic acid to be treated with the same dose of coagulant is increased. DOC removal efficiency increased with increasing humic acid concentration (Appendix Figure 20), however when the humic acid concentration was increased to 20 mg/L TOC removal efficiency was found to decrease (Appendix Figure 19). Residual UV_{254} absorption increased with increasing humic acid concentration, which correlates well with these findings (Figure 3.94). UV_{254} removal efficiency was found to decrease when the humic acid concentration was increased (Appendix Figure 21). The increase in SUVA when the humic acid concentration was increased (Figure 3.95) indicates that increasing concentrations of hydrophobic/aromatic fractions were prevailing in the supernate. E_4/E_6

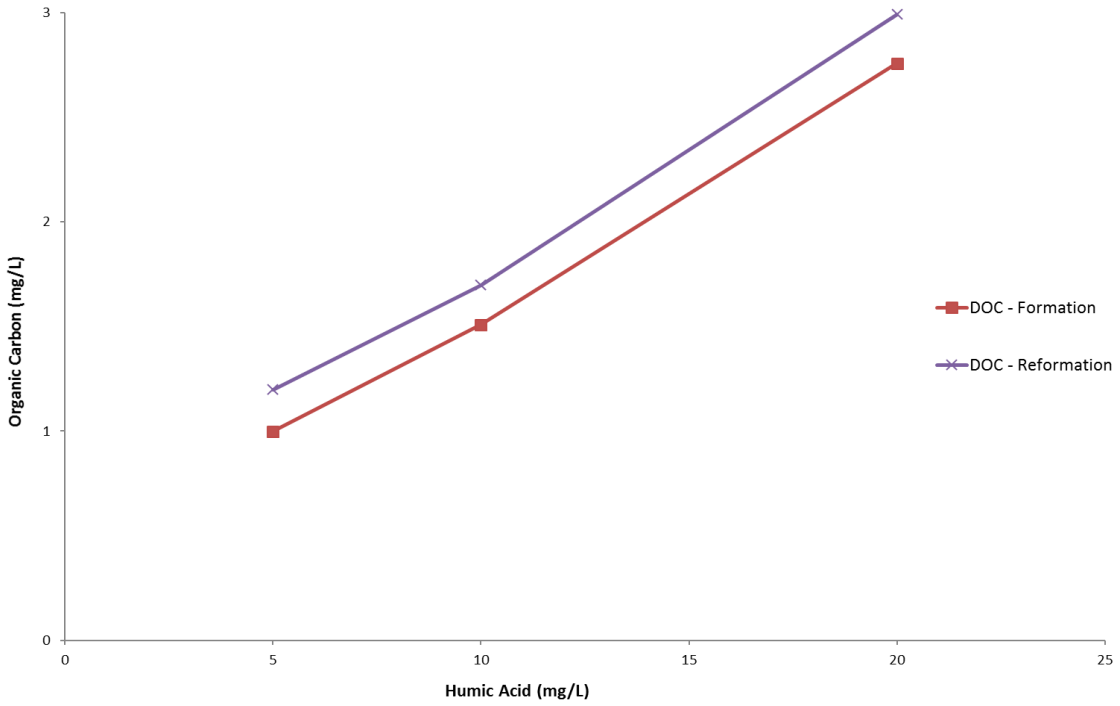

Figure 3.93. Residual DOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

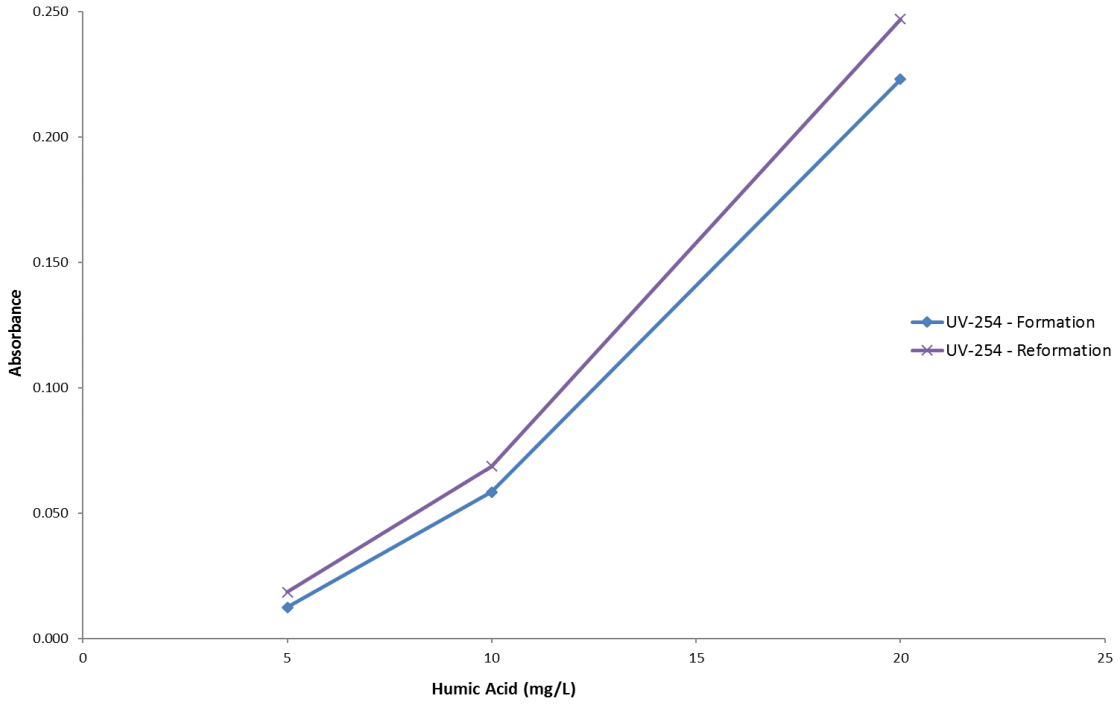

Figure 3.94. Residual absorbance at 254 nm after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

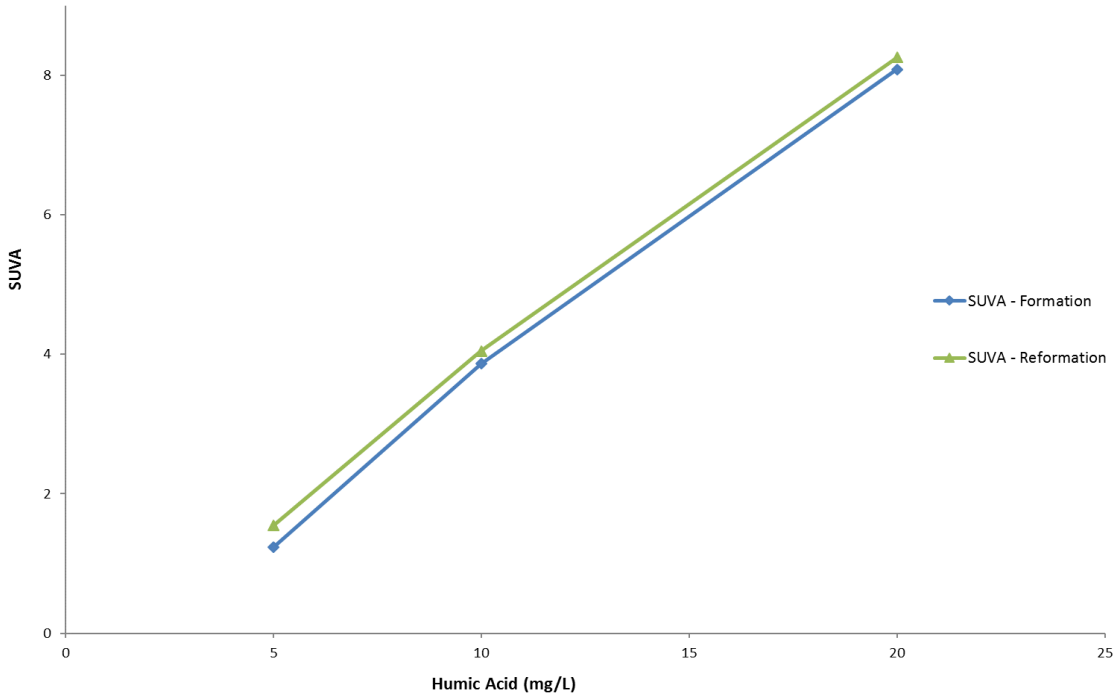

Figure 3.95. Specific UV absorbance (SUVA) after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

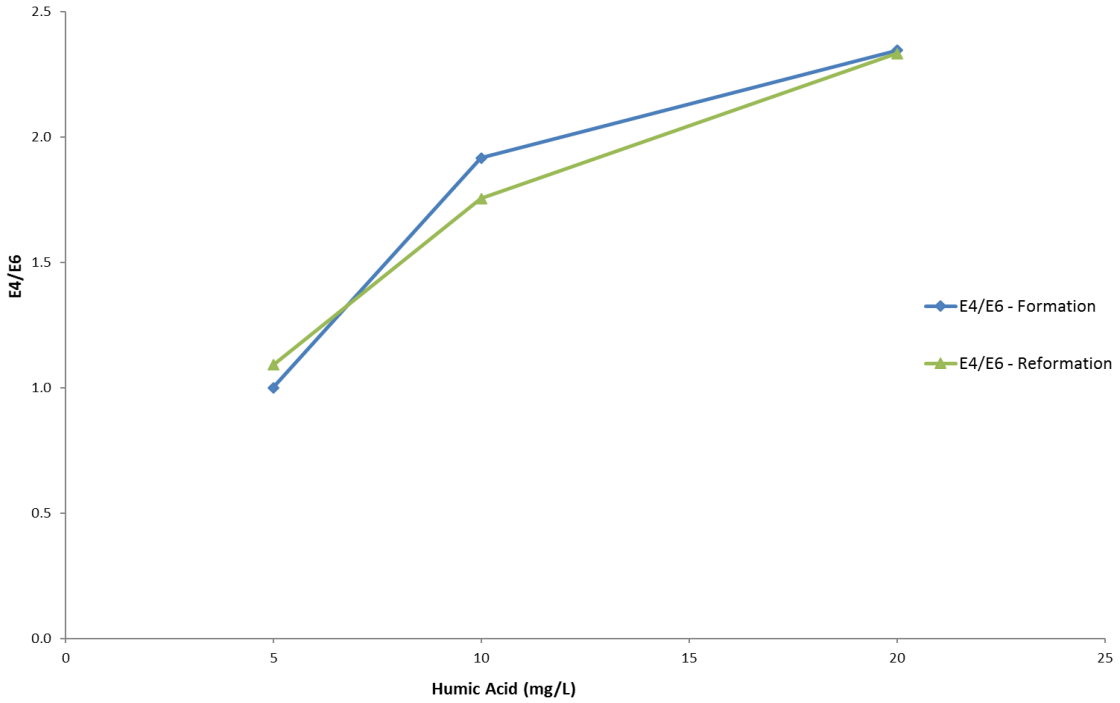

Figure 3.96. E_4/E_6 ratio after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

ratio increased as well, with increasing humic acid concentration (Figures 3.96), which implicates that smaller molecules were becoming dominant in the suspension as the humic acid concentration was increased. By examining SUVA data and E_4/E_6 ratio together, it can be said as the humic acid concentration was increased hydrophobic/aromatic fractions and smaller molecules became harder to remove by the same dose of coagulant.

3.2.4.5. Organic carbon removal with polyaluminium chloride (PACl)

Flocculation with PACl exhibited similar pattern to alum. Residual total organic carbon (Figure 3.97) and dissolved organic carbon (Figure 3.97) concentrations increased as the concentration of humic acid was increased. One might think that as the acid concentration was increased, relative floc size increased but residual organic carbon concentrations increased as well and find that a contradiction; although, residual organic carbon concentration increased for humic acid concentration to be treated with

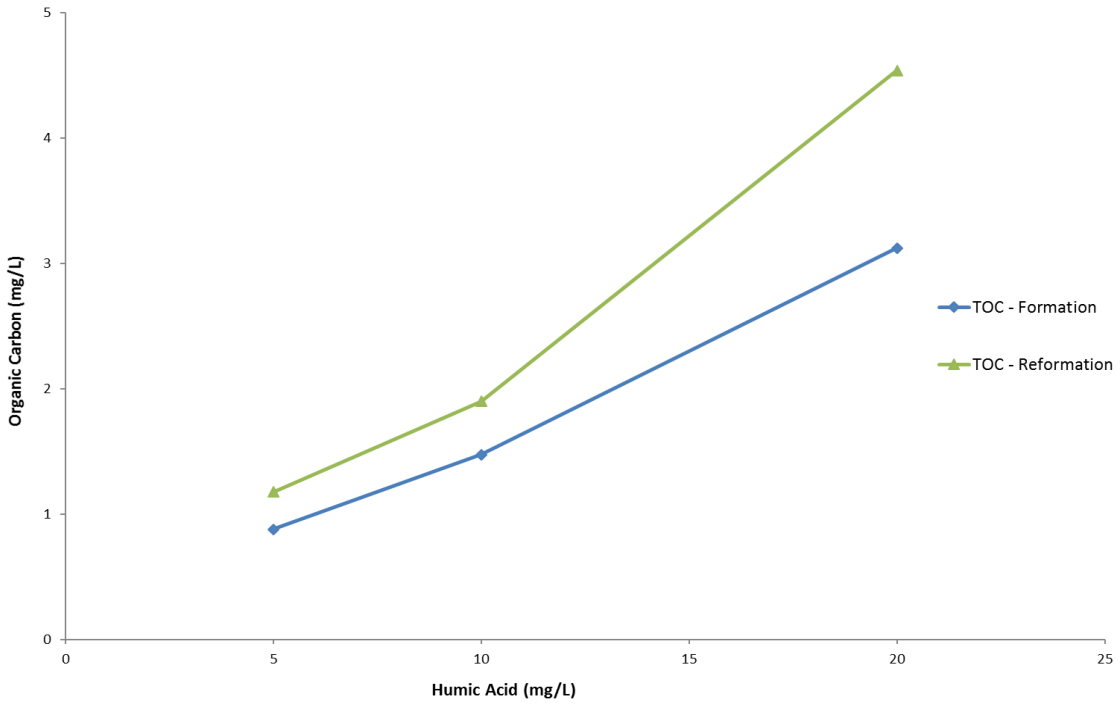

Figure 3.97. Residual TOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

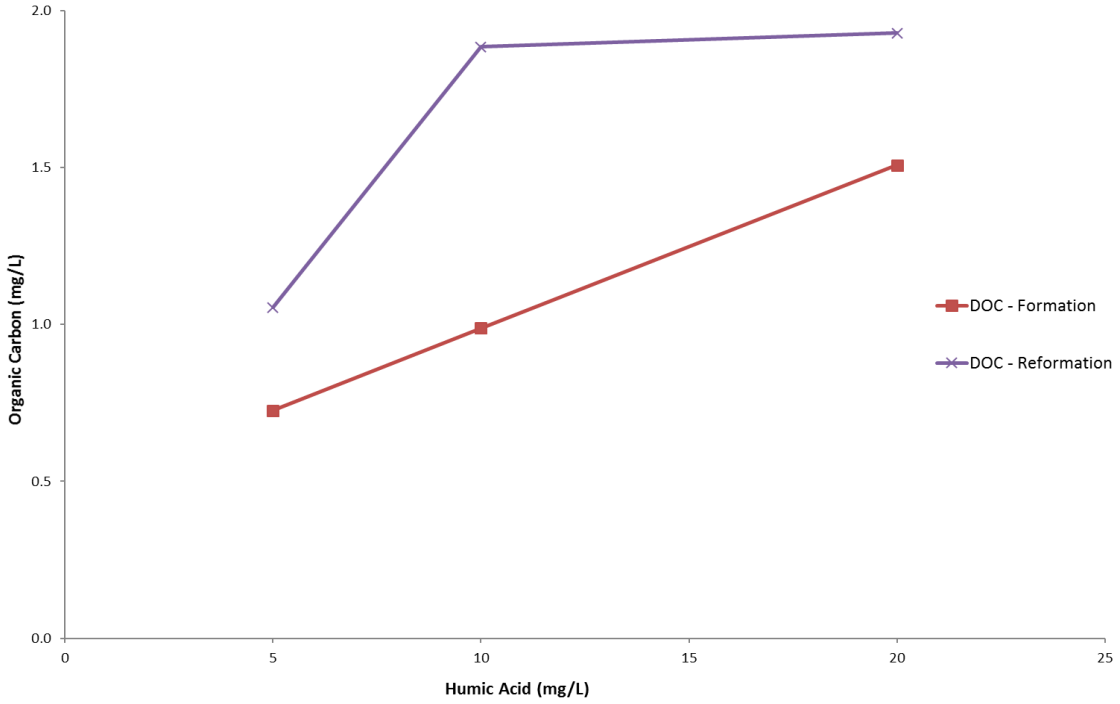

Figure 3.98. Residual DOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

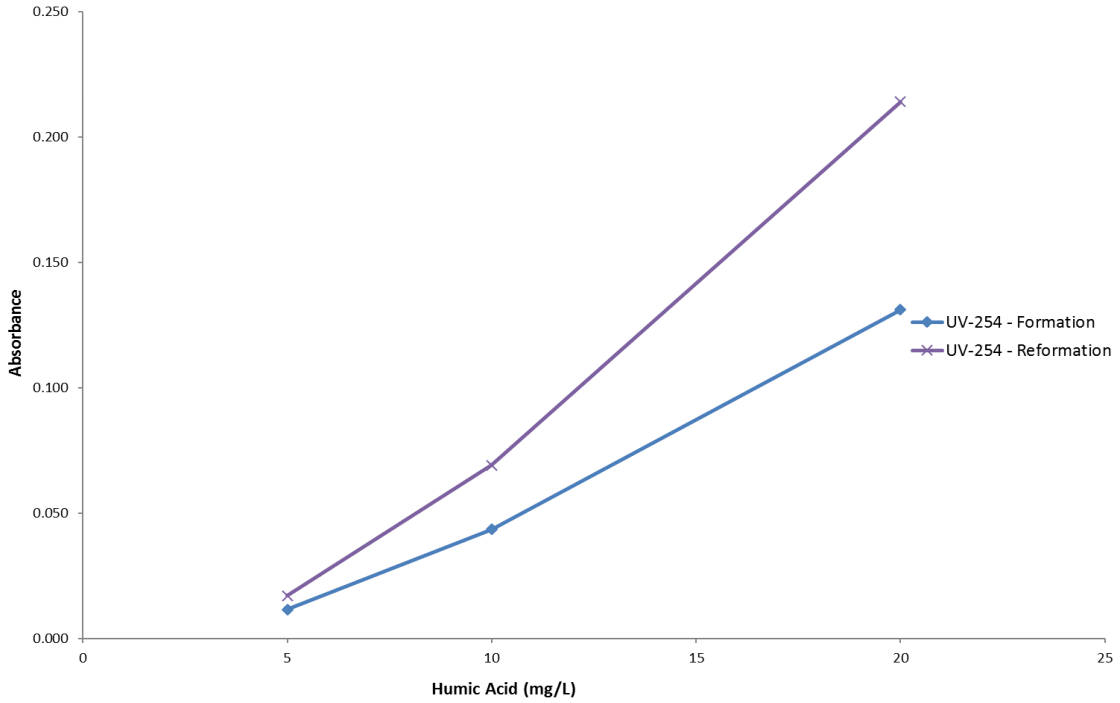

Figure 3.99. Residual absorbance at 254 nm after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

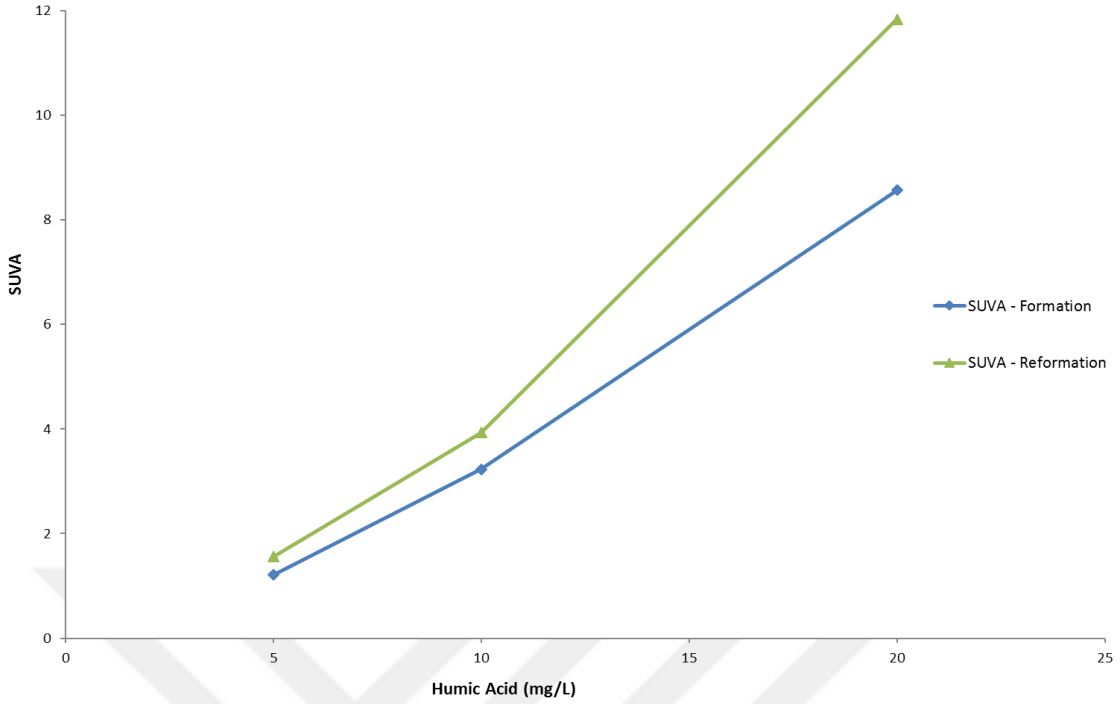

Figure 3.100. Specific UV absorbance (SUVA) after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

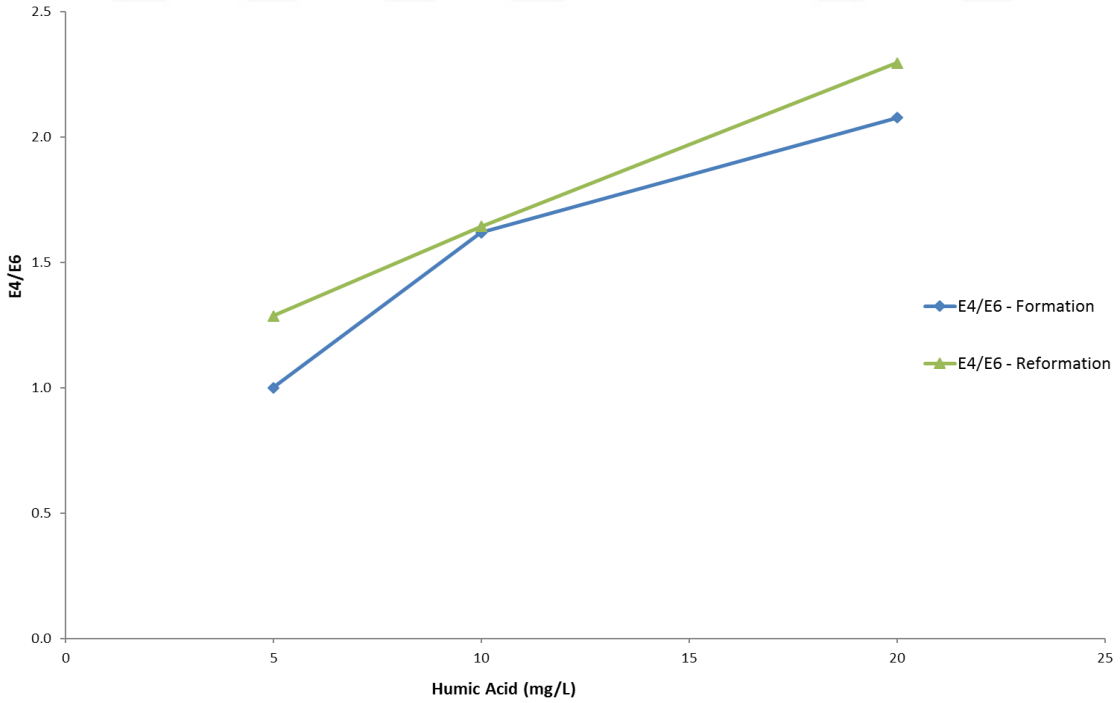

Figure 3.101. E_4/E_6 ratio after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

the same dose of coagulant was increased, which actually correlates with floc size data. Examination of removal performances shows that dissolved organic carbon removal efficiency increased with increasing humic acid concentration (Appendix Figure 23) whereas total organic carbon removal efficiency slightly decreased when the humic acid concentration was increased from 10 mg/L to 20 mg/L (Appendix Figure 22). Residual UV absorbances at 254 nm, in correlation with residual organic carbon data, also increased with increasing humic acid concentration (Figure 3.99), however, UV_{254} removal efficiency was measured to decrease (Appendix Figure 24). Examination of SUVA data exhibits that as the humic acid concentration was increased, more amounts of hydrophobic/aromatic part of organic matter were found in the supernate (Figure 3.100). Higher amounts of smaller organic molecules were measured in the residue with increasing humic acid concentration (Figure 3.101).

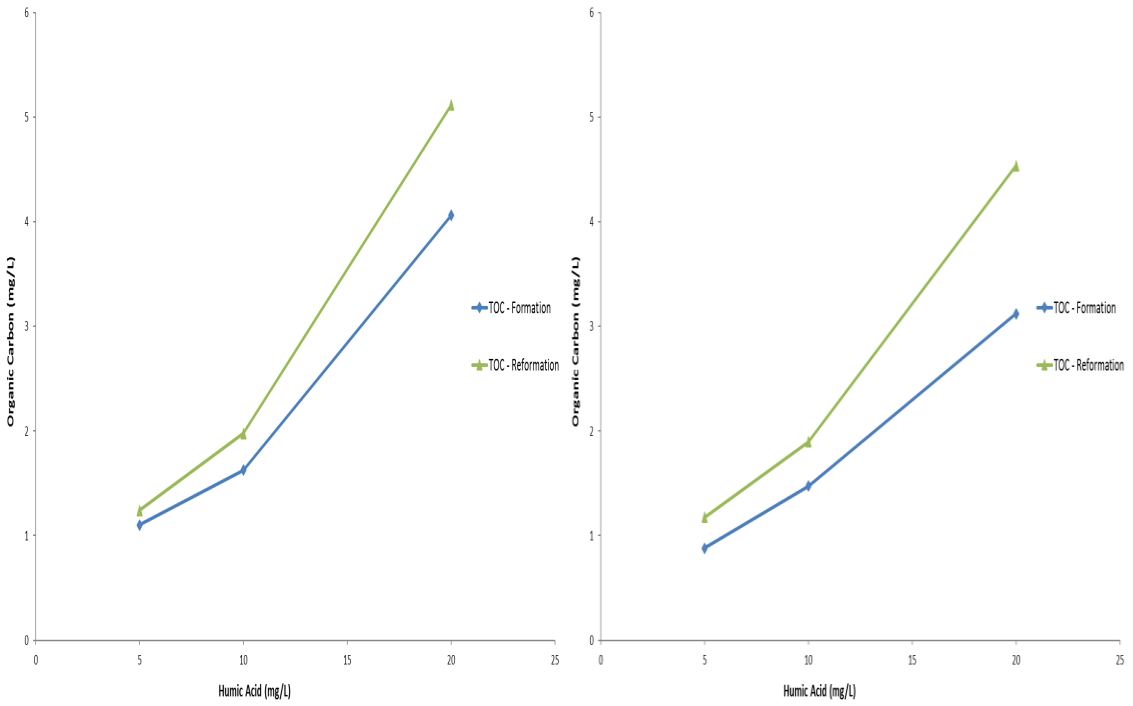

Figure 3.102. Residual TOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

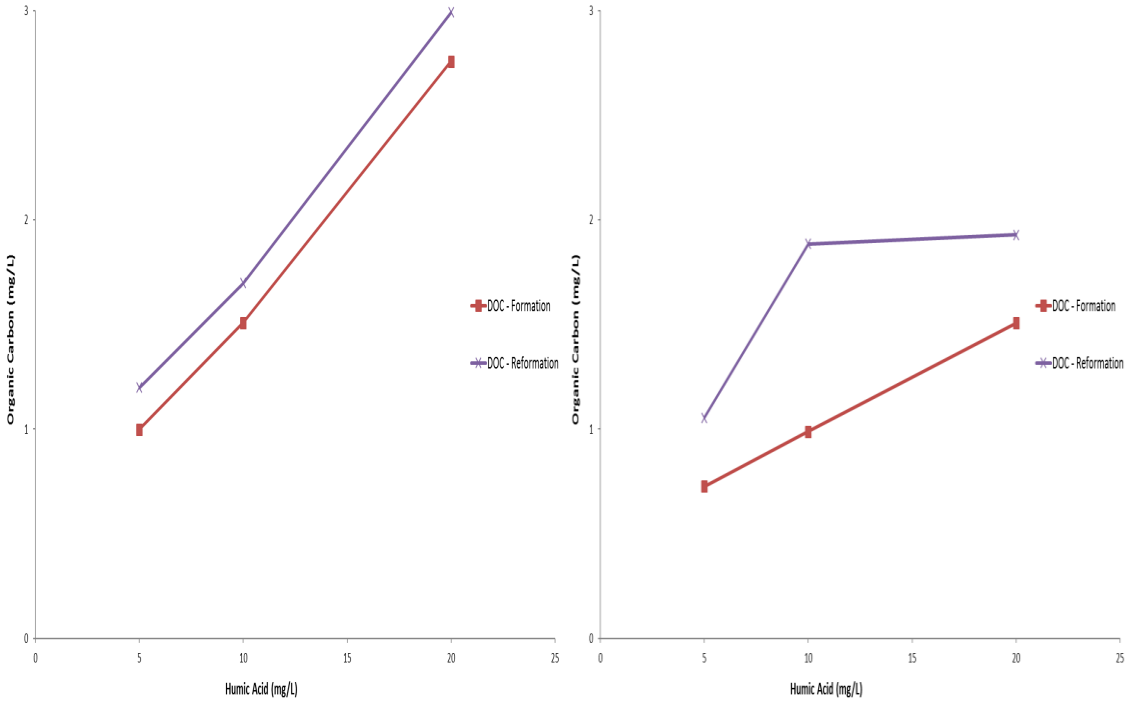

Figure 3.103. Residual DOC after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

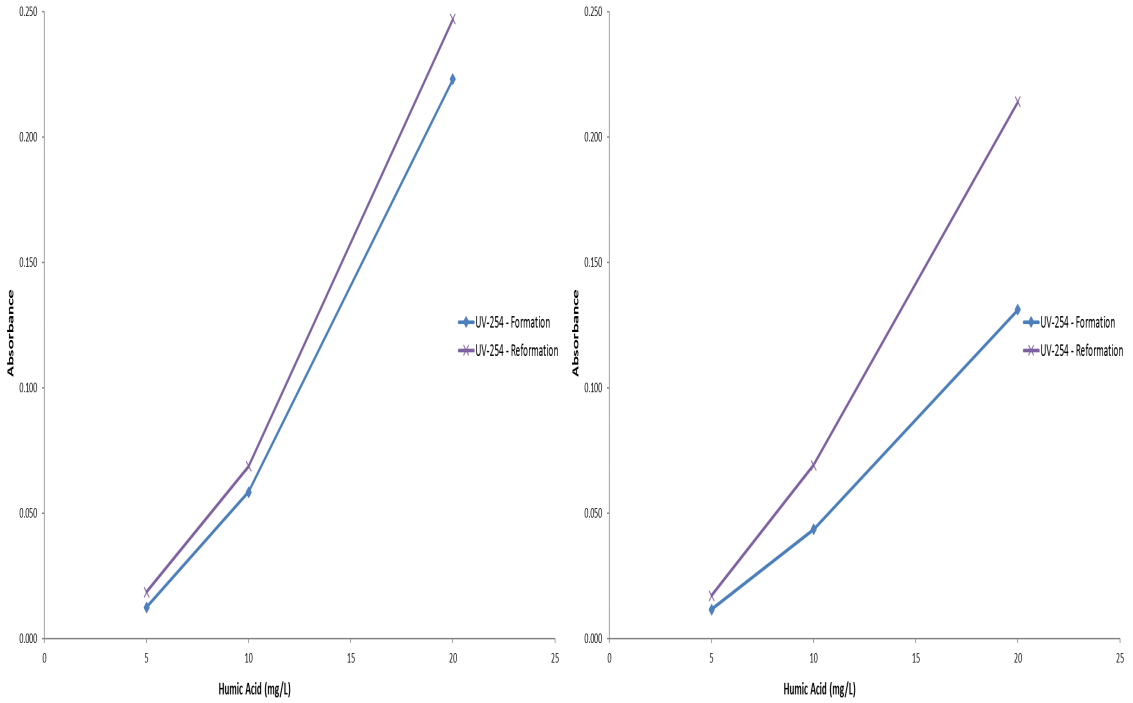

Figure 3.104. Residual abs. at 254 nm after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

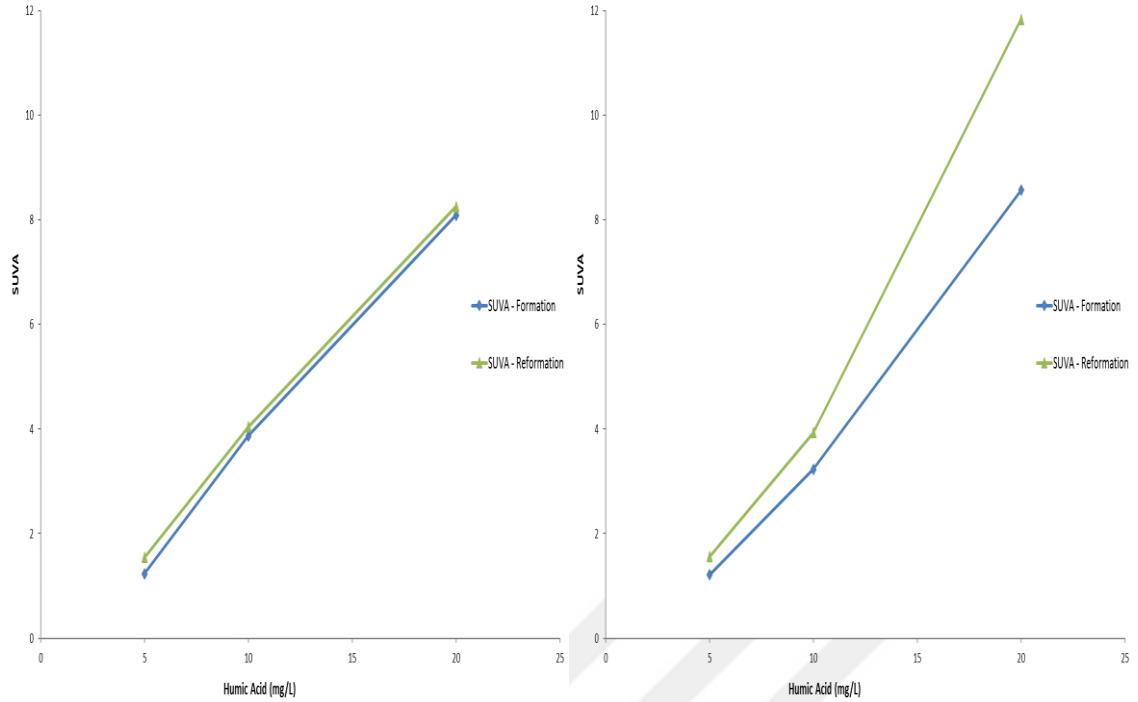

Figure 3.105. Specific UV abs. (SUVA) after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L HA with alum (left) and PACl (right)

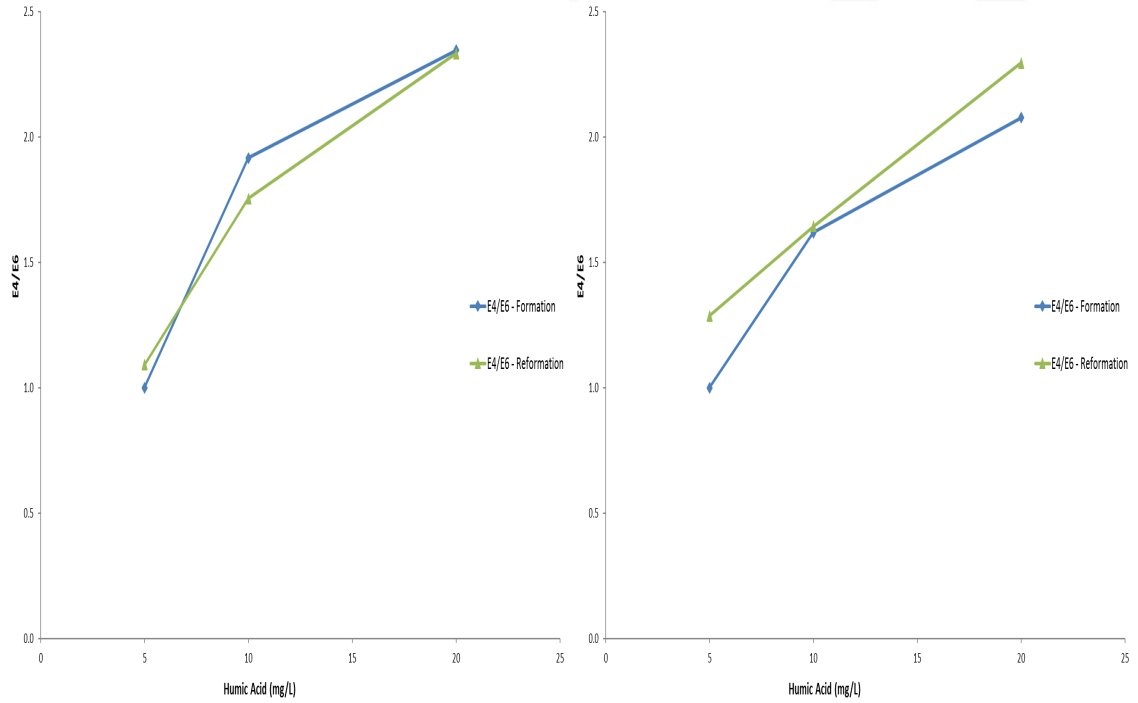

Figure 3.106. E_4/E_6 ratio after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum (left) and PACl (right)

When the flocculation performances of aluminium sulphate and polyaluminium chloride in 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid are compared it is seen that larger flocs were formed with PACl because of its higher positively charged Al species content (Figures 3.89-3.91). Consistently, residual total and dissolved organic carbon concentrations were lower with PACl (Figure 3.102 and Figure 3.103, respectively). At 20 mg/L humic acid concentration the difference between residual organic carbon concentrations was higher because the difference between relative floc sizes at that humic acid concentration was greater in favour of PACl. Residual UV absorbance at 254 nm measurements correlate with residual organic carbon measurements (Figure 3.104) whilst UV_{254} removal efficiencies decreased with increasing humic acid concentration (Appendix Figures 21 and 24). SUVA data and E_4/E_6 ratios showed very similar curves (Figure 3.105 and Figure 3.106, respectively); their examination suggests that as the humic acid concentration was increased, removal of more readily removable part and smaller molecules of organic matter worsened with both coagulants.

SUVA nearly always went over 4 and kept increasing as the humic acid concentration was increased, indicating that there were more amounts of hydrophobic/aromatic fractions in the settled waters' supernate. E_4/E_6 ratio increased with increasing the humic acid concentration, implying that increased amount of smaller organic molecules were present in the supernate. SUVA data and E_4/E_6 ratio together can be interpreted that as the humic acid concentration was increased, coagulant dose flocculated maybe little more and more amounts of hydrophobic/aromatic fractions and smaller organic molecules since the relative floc sizes increased but it became gradually less sufficient to remove them by the same ratio.

To conclude this section, it can be stated that in all pre-ozonation cases, with both of the coagulants residual total and dissolved organic carbon concentrations and residual UV_{254} absorbances increased with increasing humic acid concentration whilst larger flocs were obtained, which can be seen as a contradiction at first, nonetheless when it is thought that the amount of organic matter to be flocculated with the same dose of coagulant increased as the humic acid concentration was increased, it is seen that that is not a contradiction, actually. Improved total and dissolved organic carbon

removal efficiencies with increasing humic acid concentration well correlate with increasing relative floc sizes, which could be attributed to increasing number of collisions as the humic acid concentration was increased. Organic carbon removal efficiency increased with increasing humic acid concentration but in waters containing 20 mg/L initial humic acid concentration, improvement of organic carbon removal lessened when pre-ozonated raw waters were used, organic carbon removal efficiency practically did not improve when the pre-ozonation dose was increased to 5 mg/L and when the pre-ozonation dose was further increased to 10 mg/L, eventually it worsened with alum, did not improve practically with PACl, indicating that PACl is less affected by pre-ozonation. Removal efficiency of UV absorbance at 254 nm improved in unozonated waters as the humic acid concentration was increased but it was reversed when pre-ozonation started. All these point out that pre-oxidation of humic acid with increased doses of ozone changed the chemistry, which is tried to be argued how in the following section.

3.3. The Effect of Pre-ozonation Dose

3.3.1. Experiments with $Al_2(SO_4)_3$

3.3.1.1. Experiments with synthetic raw waters containing 5 mg/L humic acid

When fully grown flocs are exposed to rupture, it has become a common knowledge that in sweep flocculation regime flocs cannot fully recover their sizes (i.e. cannot grow back to their sizes before breakage) as depicted in Figures 3.107-3.110. It is thought that in sweep flocculation, aggregation is in the form of entrapment of particles/adsorption of dissolved organic molecules in growing amorphous metal hydroxide precipitates rather than electrostatic attraction between destabilised particles. It was observed in all the experiments performed where fully grown flocs were exposed to high shear and break-up.

Dynamic monitoring of floc formation (Figures 3.107-3.111) showed that increasing pre-ozone dose led to gradual reduction in floc size. Also, from Figure 3.111 it is seen the onset of flocculation was delayed and the time required to reach a steady-

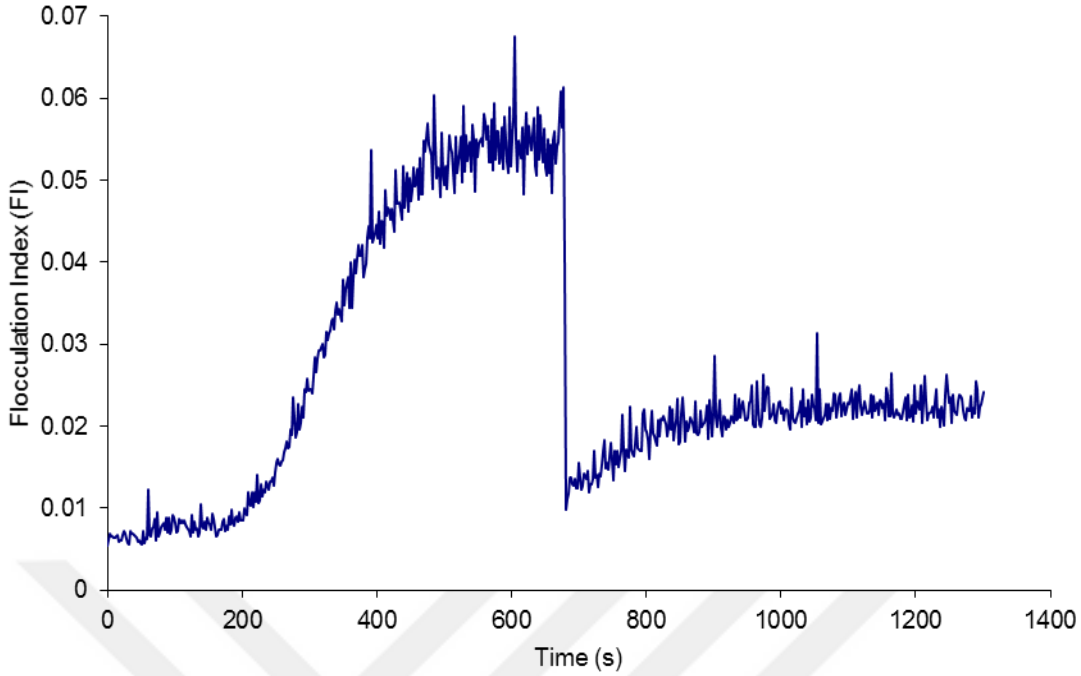

Figure 3.107. Floc growth and regrowth with alum in un-ozonated synthetic raw water containing 5 mg/L humic acid

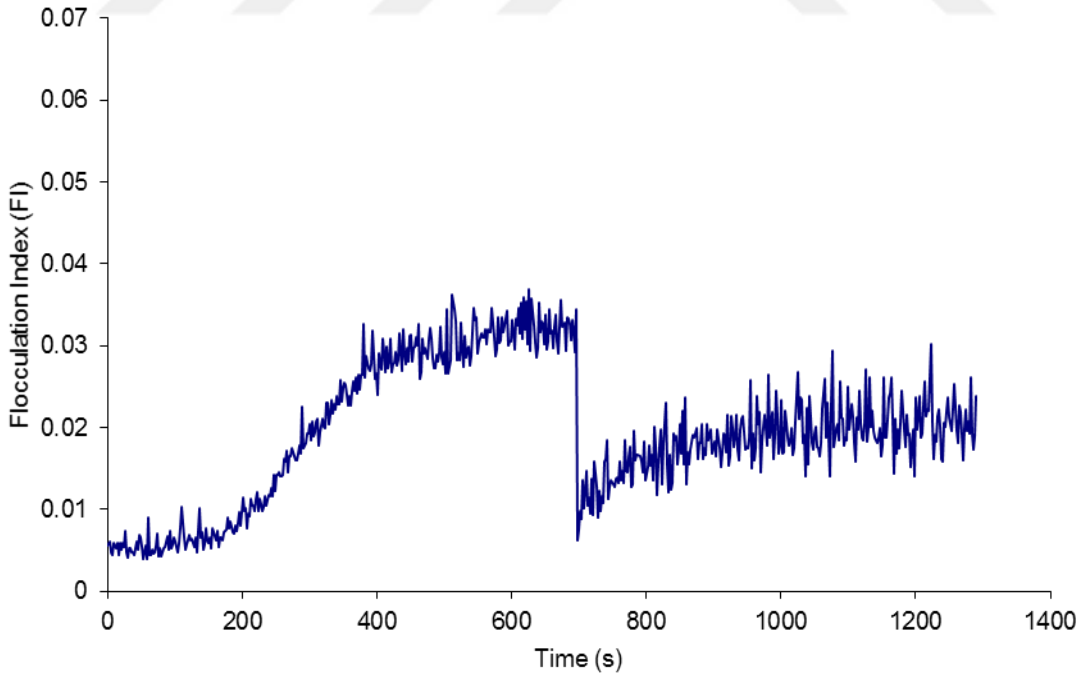

Figure 3.108. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

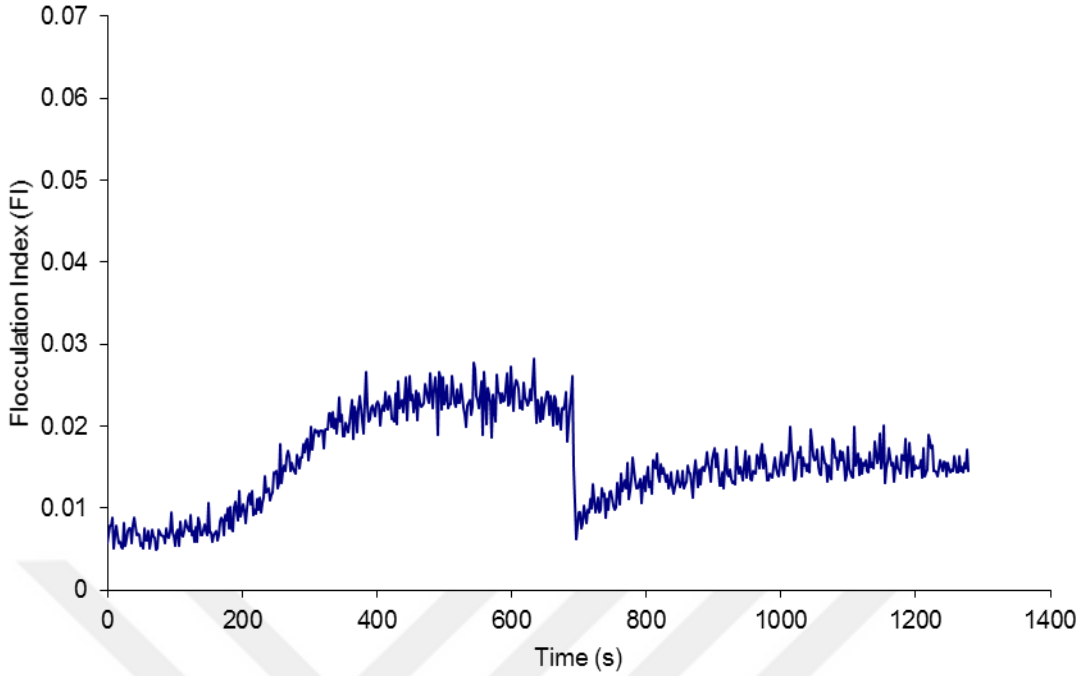

Figure 3.109. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

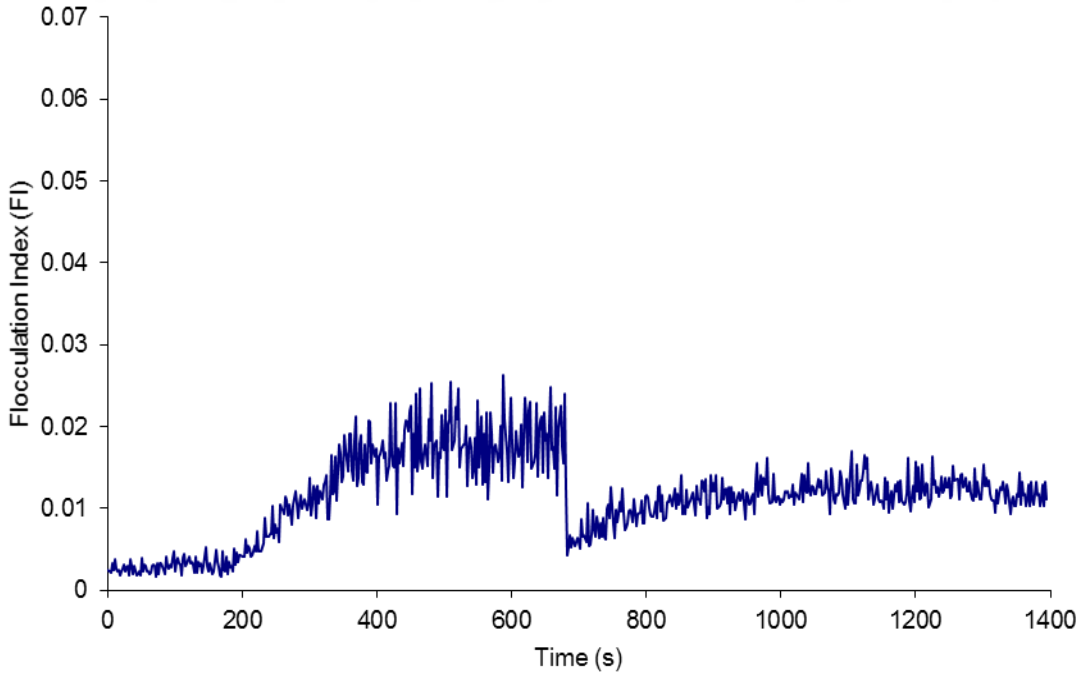

Figure 3.110. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

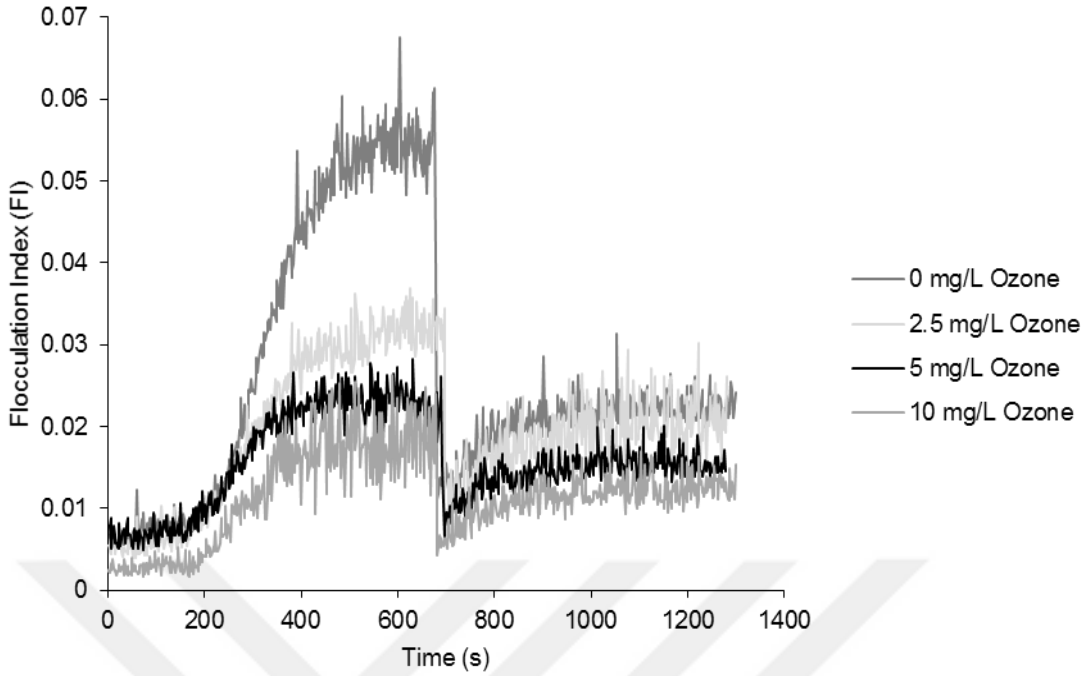

Figure 3.111. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid

state size distribution of fully grown flocs was longer with increasing ozone dose. These findings suggest that pre-ozone dose apparently hindered flocculation.

3.3.1.2. Experiments with synthetic raw waters containing 10 mg/L humic acid

The difference between the previous set of experiments performed with synthetic waters with 5 mg/L humic acid concentration was found to be larger floc formation when the humic acid concentration was raised to 10 mg/L. This might be because of increased number of collisions with increasing humic acid concentration.

The same observation as that with 5 mg/L humic acid containing synthetic raw waters is also valid for flocculation tests with 10 mg/L humic acid containing synthetic raw waters: smaller flocs were formed with increasing ozone dose (Figures 3.112-3.115). This observation was also the same for flocs regrown after breakage (Figure 3.116). Obviously, increasing pre-ozone dose negatively affected floc formation in terms of floc size.

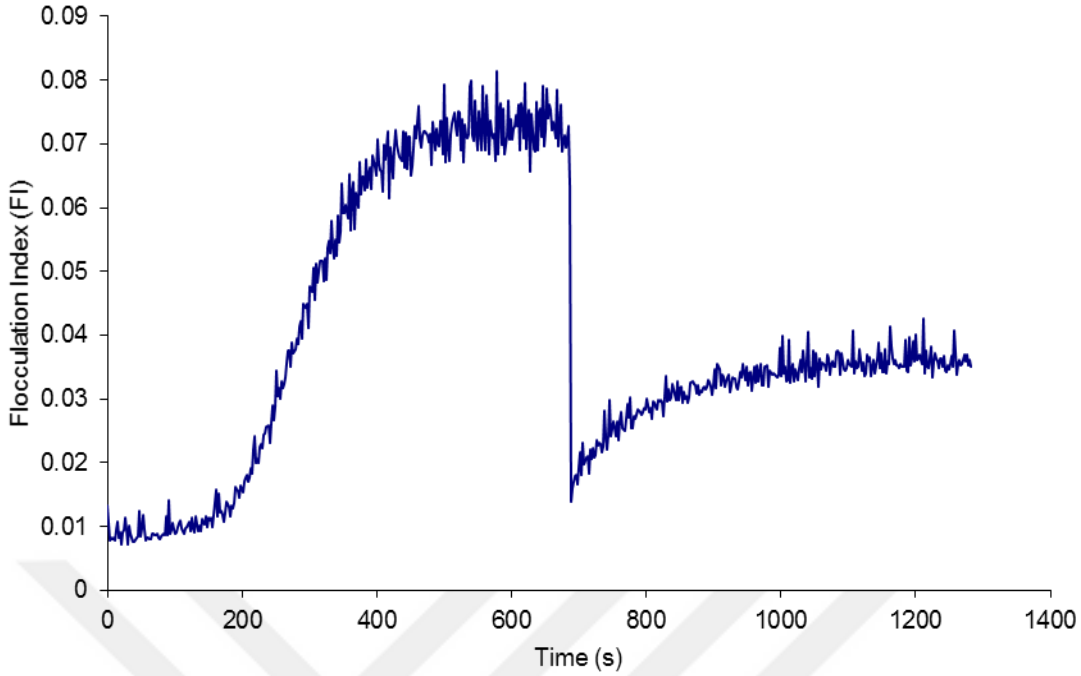

Figure 3.112. Floc growth and regrowth with alum in un-ozonated synthetic raw water containing 10 mg/L humic acid

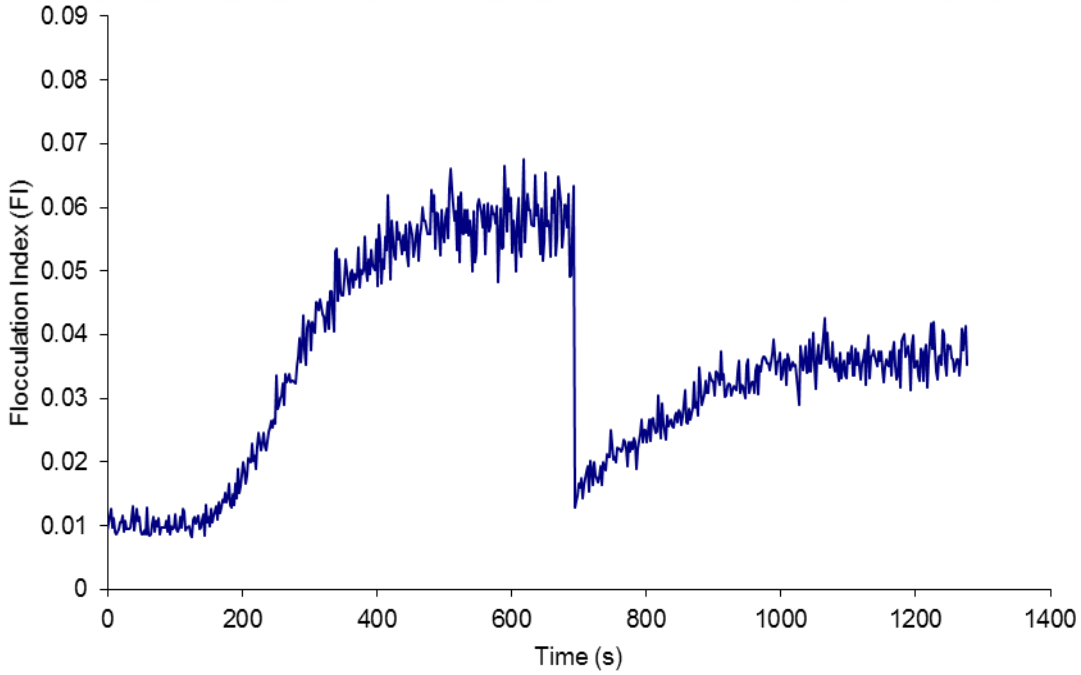

Figure 3.113. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

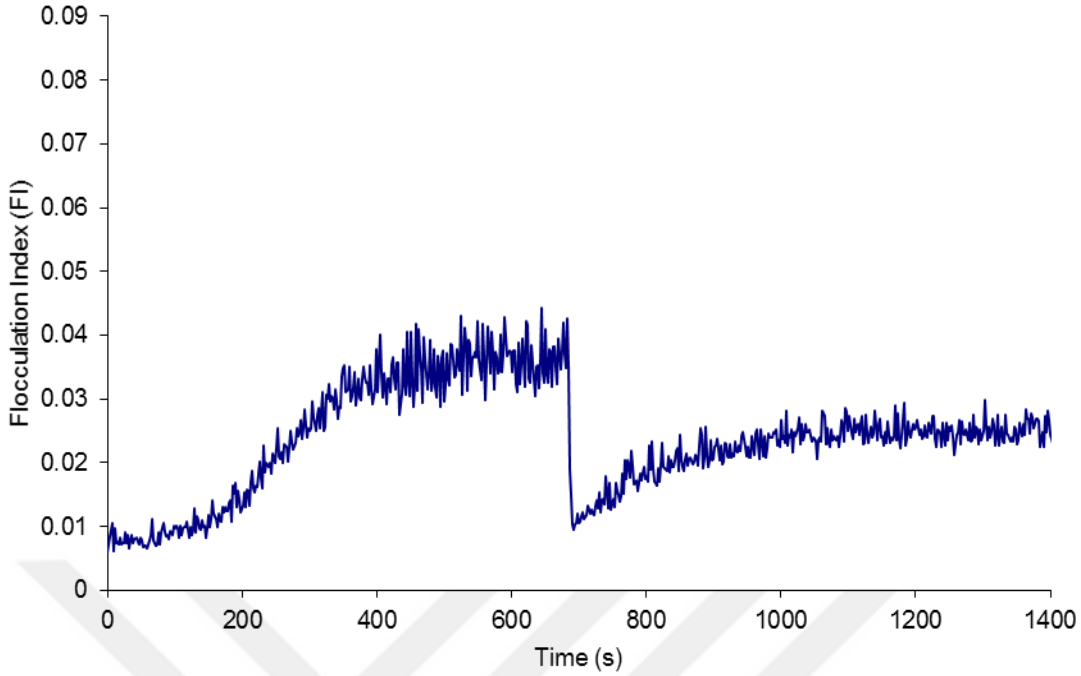

Figure 3.114. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

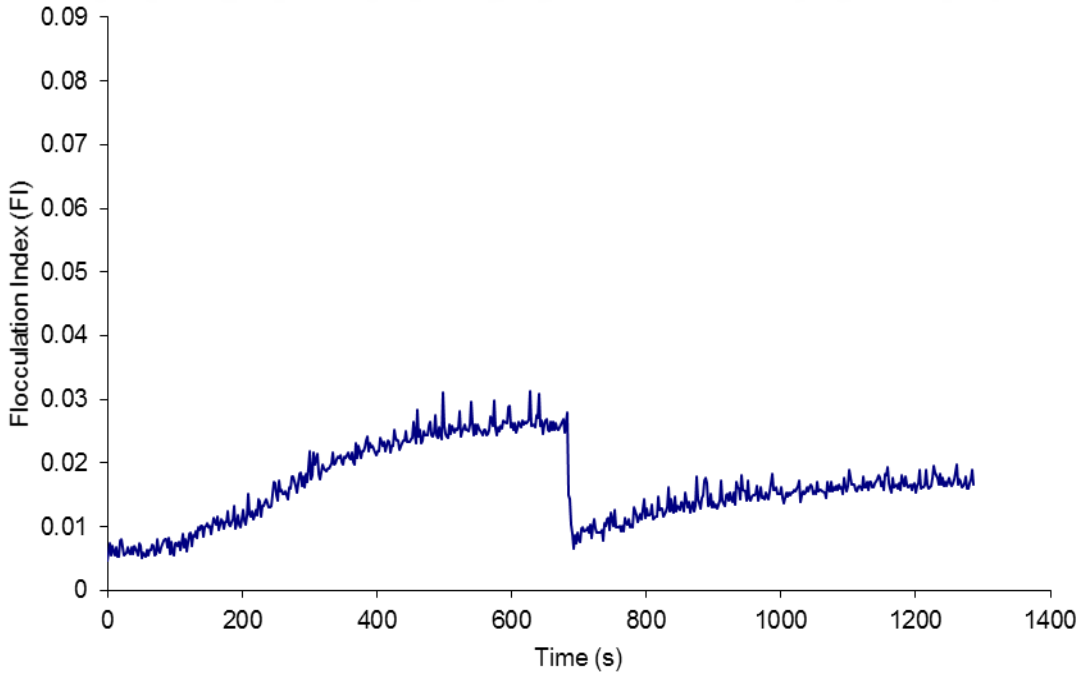

Figure 3.115. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

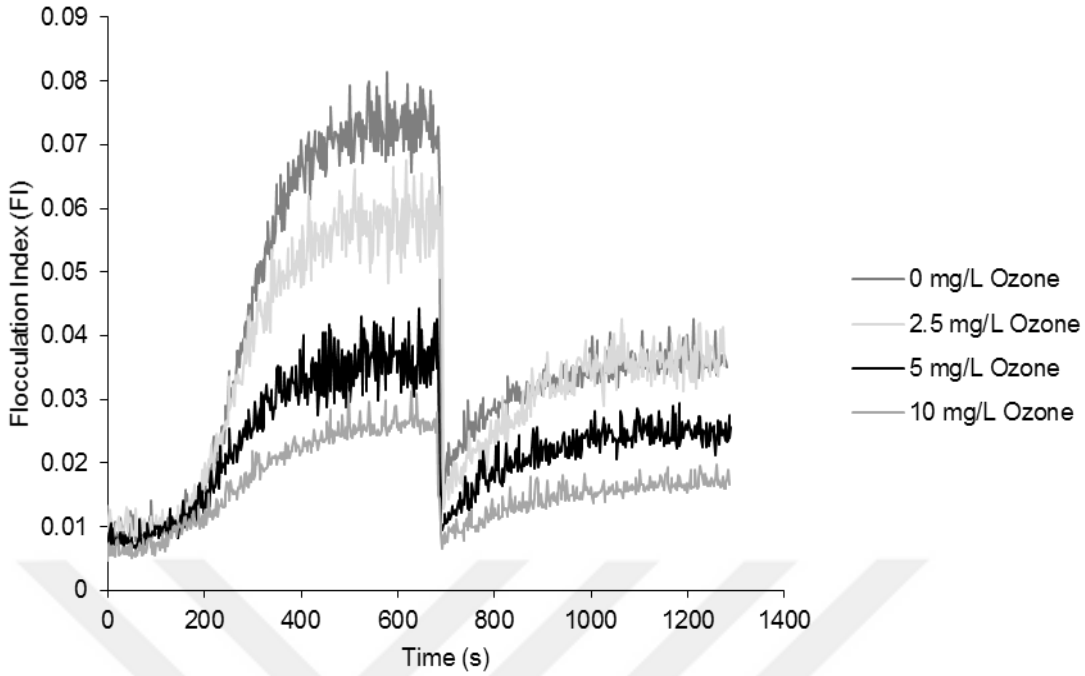

Figure 3.116. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid

Same as in the jar tests performed with 5 mg/L humic acid containing synthetic raw waters, flocculation started later as the pre-ozone dose was increased. It also took longer to reach steady-state floc size distribution with increasing pre-ozone dose. These are other findings pointing out that flocculation was negatively affected by pre-ozonation.

In all of the jar tests, limited floc size recovery after breakage was observed, which is peculiar to sweep flocculation regime.

3.3.1.3. Experiments with synthetic raw waters containing 20 mg/L humic acid

As in the previous experiments executed with 5 and 10 mg/L concentrations of humic acid, relative floc size was observed to increase with increasing humic acid concentration. Increase in collision efficiency with increasing humic acid concentration

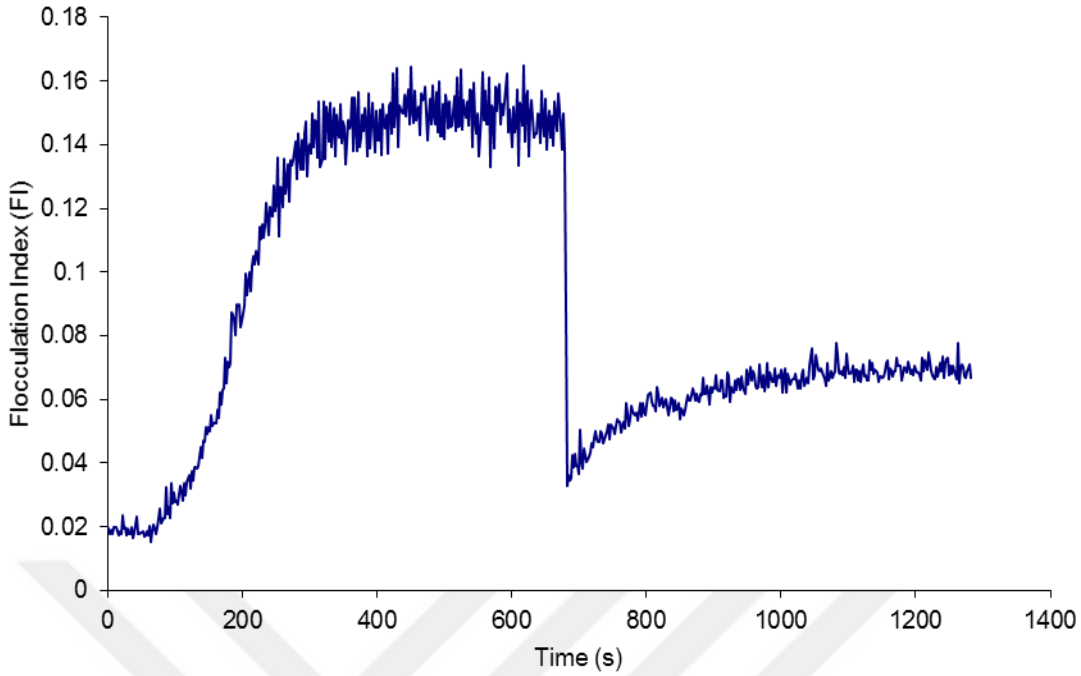

Figure 3.117. Floc growth and regrowth with alum in un-ozonated synthetic raw water containing 20 mg/L humic acid

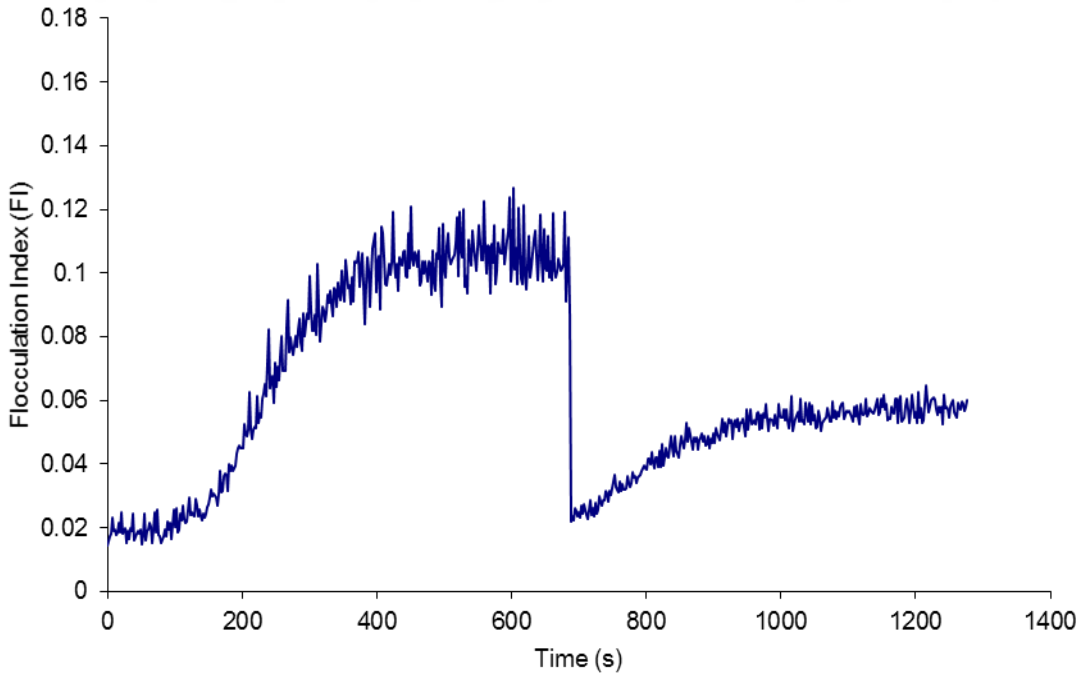

Figure 3.118. Floc growth and regrowth with alum in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

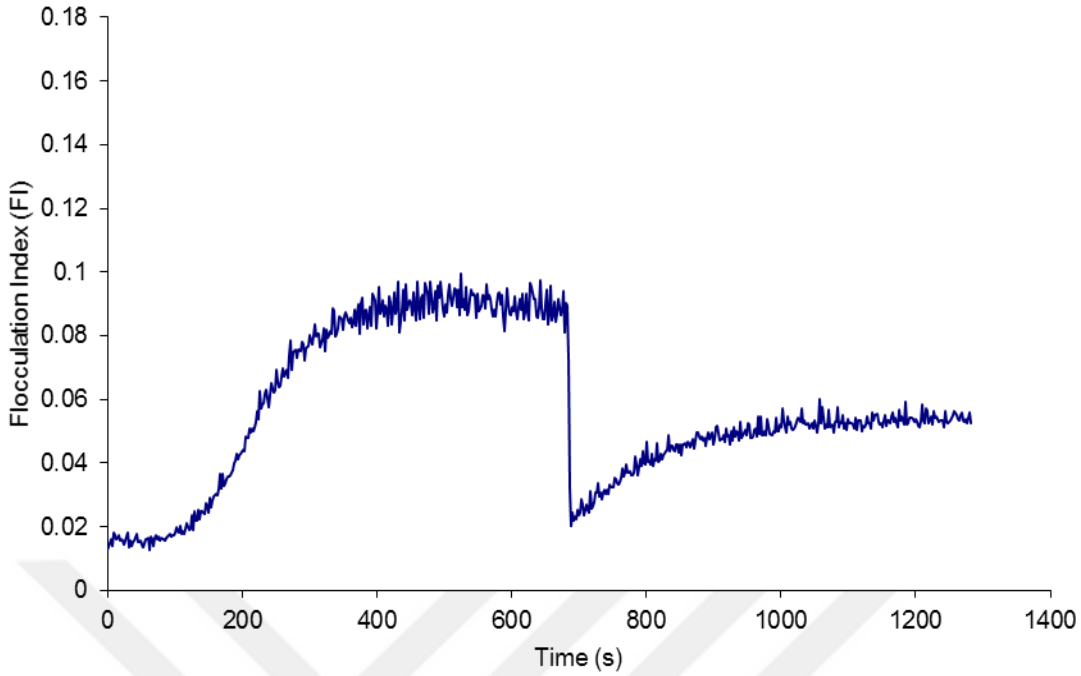

Figure 3.119. Floc growth and regrowth with alum in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

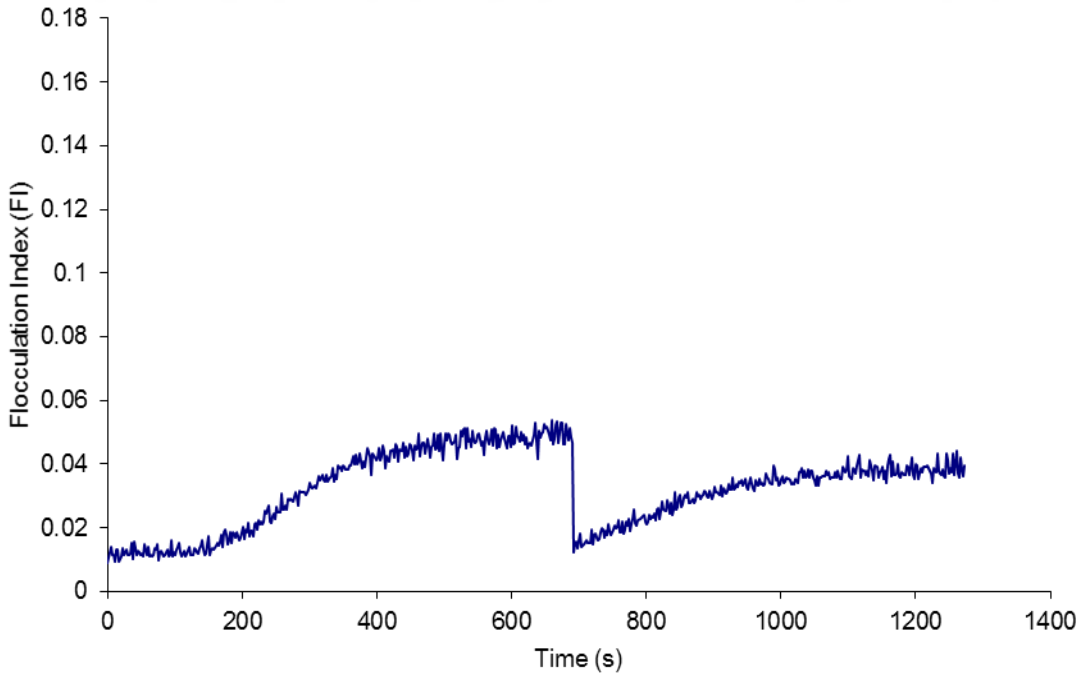

Figure 3.120. Floc growth and regrowth with alum in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

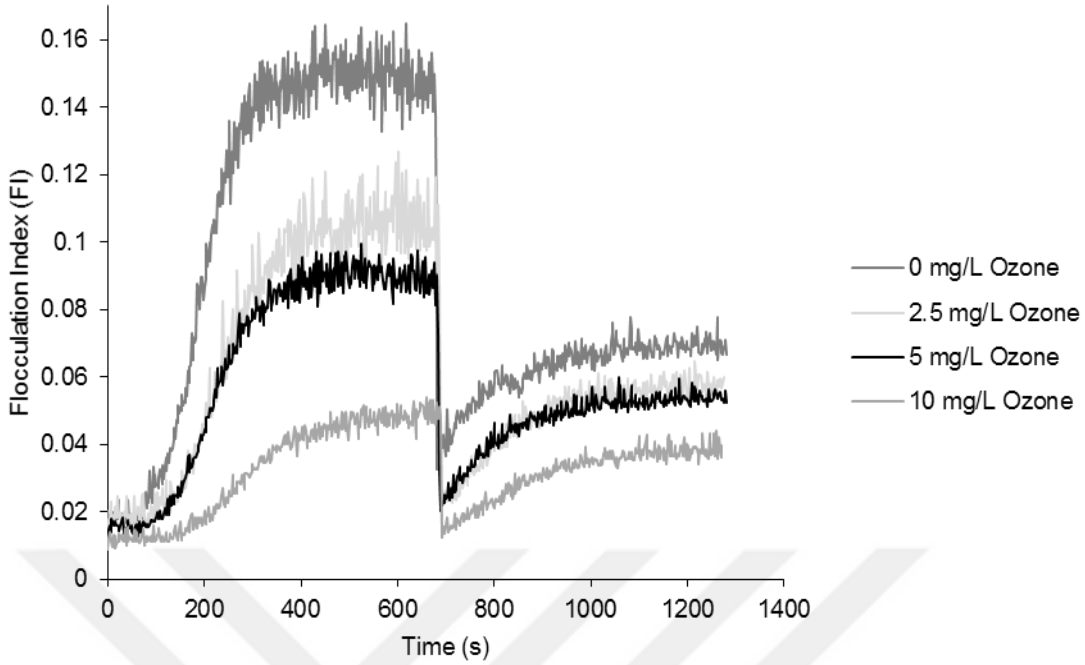

Figure 3.121. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid

might be the probable reason. Also, relative size of flocs reformed after breakage increased with increasing humic acid concentration.

Similar to what was observed at previous humic acid concentrations, relative floc size diminished as the pre-ozone dose was increased (Figures 3.117-3.120). The very same observation was also valid for flocs regrown after exposure to high shear rate (Figure 3.121). Clearly, aggregation was negatively affected by increasing pre-ozone dose.

Again, flocculation started earlier and steady-state floc size distribution was reached in shorter time as the pre-ozone dose was decreased, which together make the floc growth curve steeper with reducing pre-ozone dose. These also indicate that increasing pre-ozone dose negatively affected flocculation.

Similarly, once broken, flocs could only grow to some extent of their sizes before breakage, which is seen in sweep flocculation.

3.3.2. Experiments with polyaluminium chloride (PACl)

3.3.2.1. Experiments with synthetic raw waters containing 5 mg/L humic acid

Similar to flocculation with alum, flocs exposed to high shear rate could not grow back to their sizes before break-up process. This feature is characteristic of sweep flocculation, in which aggregation is in the form of entrapment of particles/adsorption of dissolved organic molecules in growing amorphous metal hydroxide precipitates rather than electrostatic attraction between destabilised particles.

When floc growth curves depicted in Figures 3.123-3.126 are examined, it is seen that floc size was gradually decreased with increasing pre-ozone dose. Also, from Figure 3.126 it is seen the onset of flocculation was delayed and the time required to reach a steady-state size distribution of fully grown flocs was longer with increasing ozone dose. These indicate hindrance of flocculation by pre-ozonation.

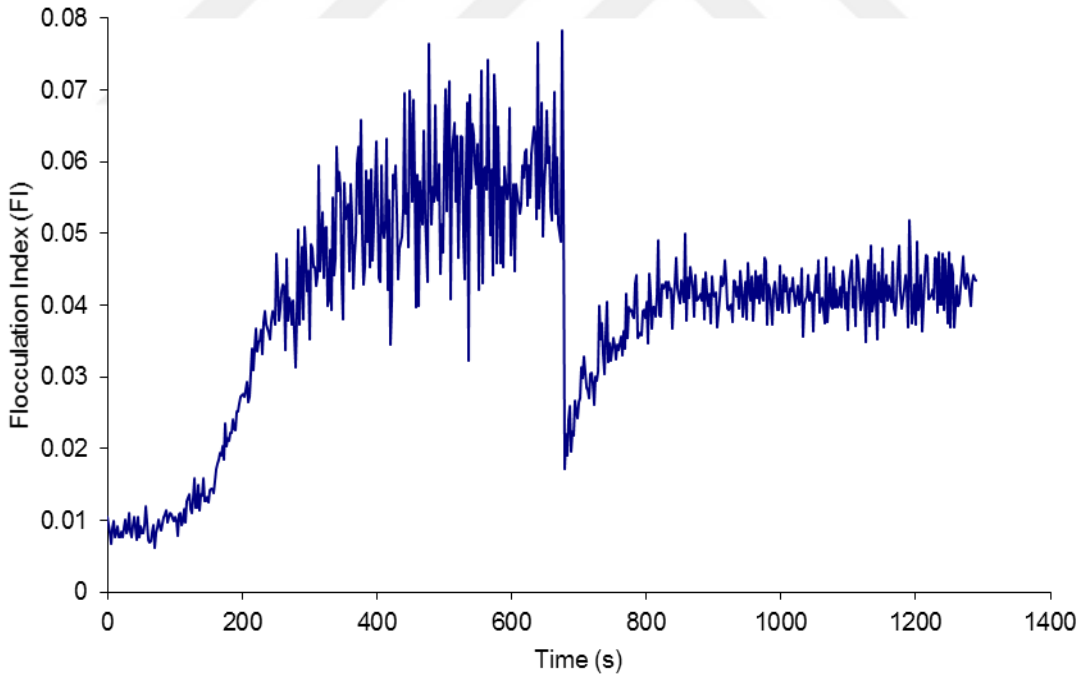

Figure 3.122. Floc growth and regrowth with PACl in un-ozonated synthetic raw water containing 5 mg/L humic acid

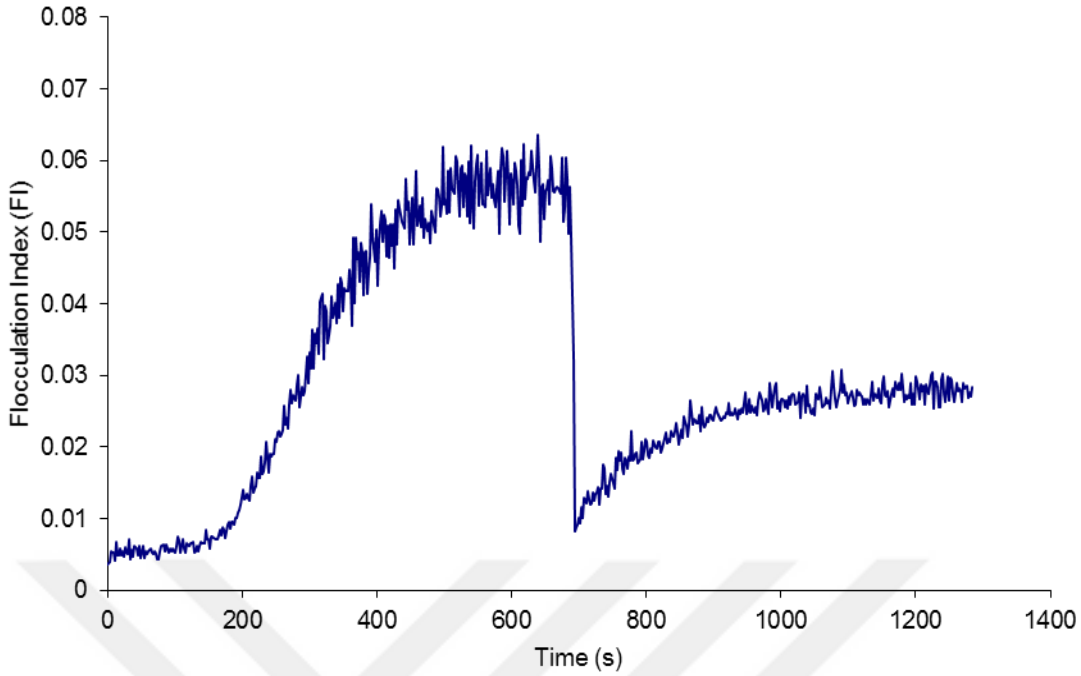

Figure 3.123. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

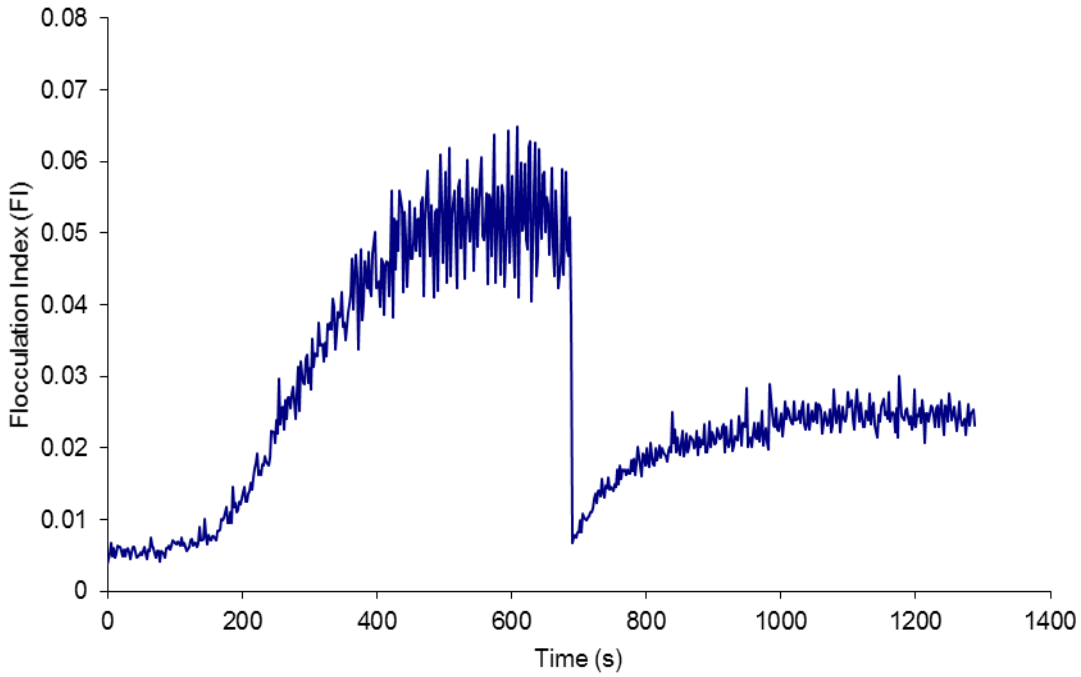

Figure 3.124. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

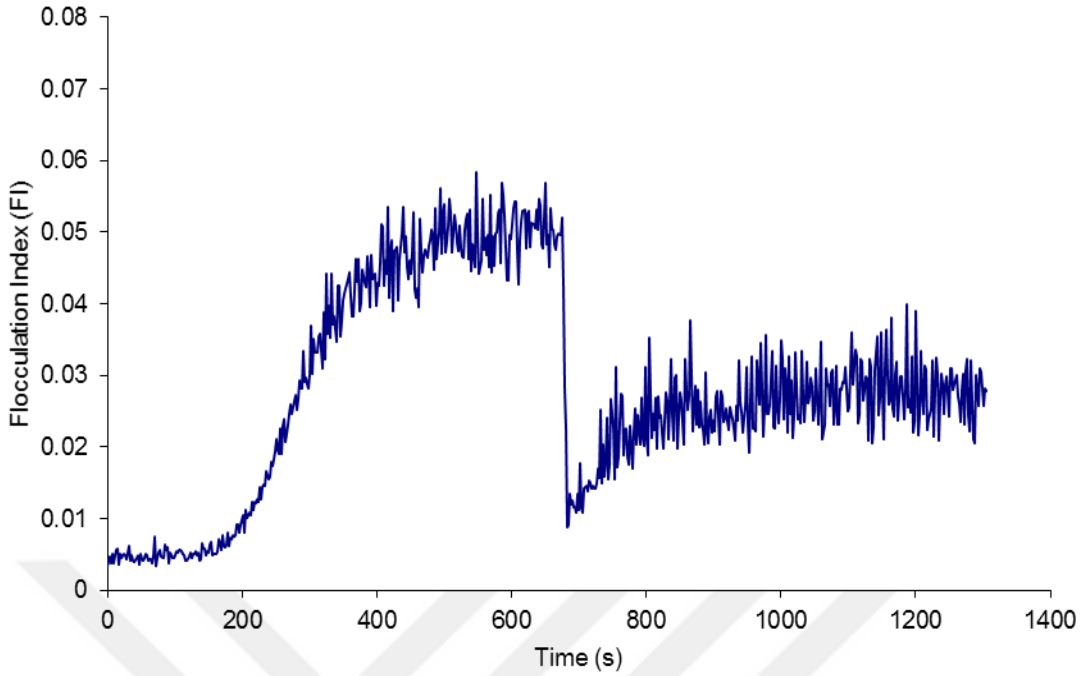

Figure 3.125. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 5 mg/L humic acid

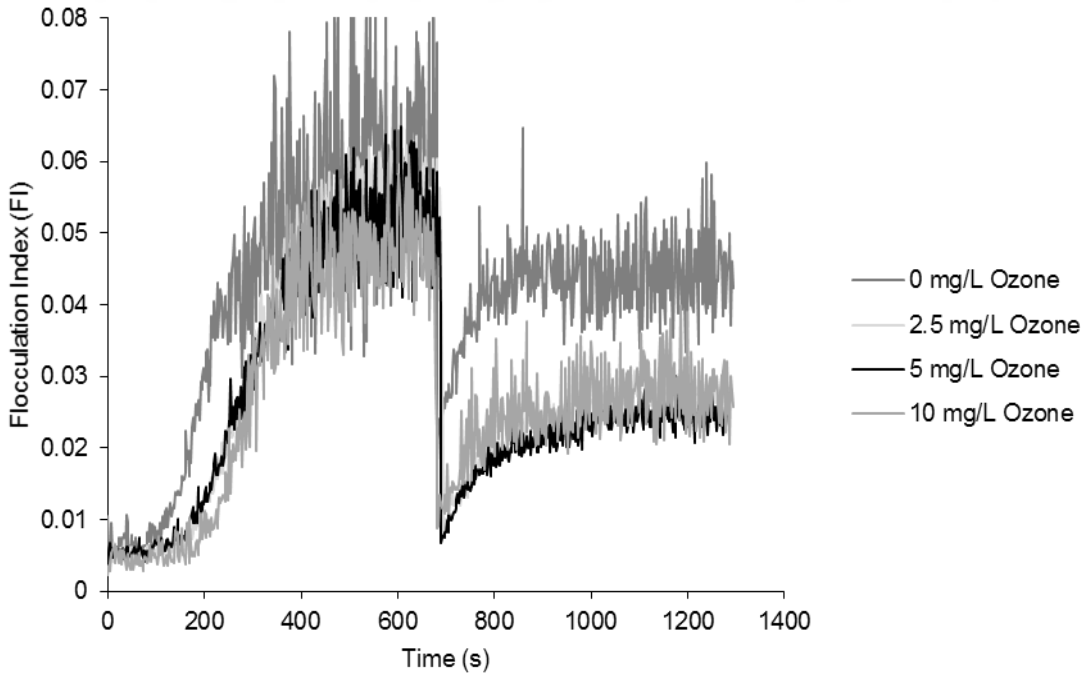

Figure 3.126. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid

3.3.2.2. Experiments with synthetic raw waters containing 10 mg/L humic acid

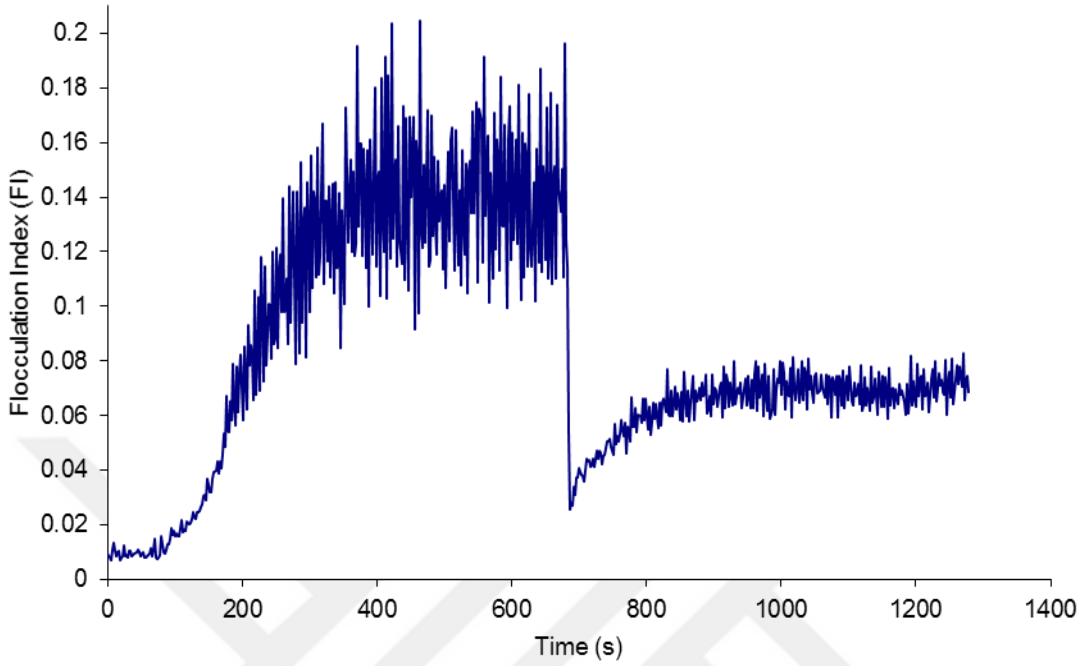

Figure 3.127. Floc growth and regrowth with PACl in un-ozonated synthetic raw water containing 10 mg/L humic acid

Similar to what observed with 5 mg/L humic acid containing synthetic raw waters, in jar tests performed with 10 mg/L humic acid containing synthetic raw waters increasing ozone dose lead to formation of smaller flocs (Figures 3.127-3.130). This was also observed with flocs regrown after rupture (Figure 3.116). Obviously, increasing pre-ozone dose negatively affected floc formation in terms of floc size.

As in the flocculation experiments with 5 mg/L humic acid containing synthetic raw waters, the onset of flocculation was delayed more and more as the pre-ozone dose was gradually increased. Also, time to reach steady-state floc size distribution took longer with increasing pre-ozone dose. These all suggest that increasing pre-ozone dose negatively affected aggregation.

Again, flocs could recover their size only to some extent, which is typical of sweep flocculation regime.

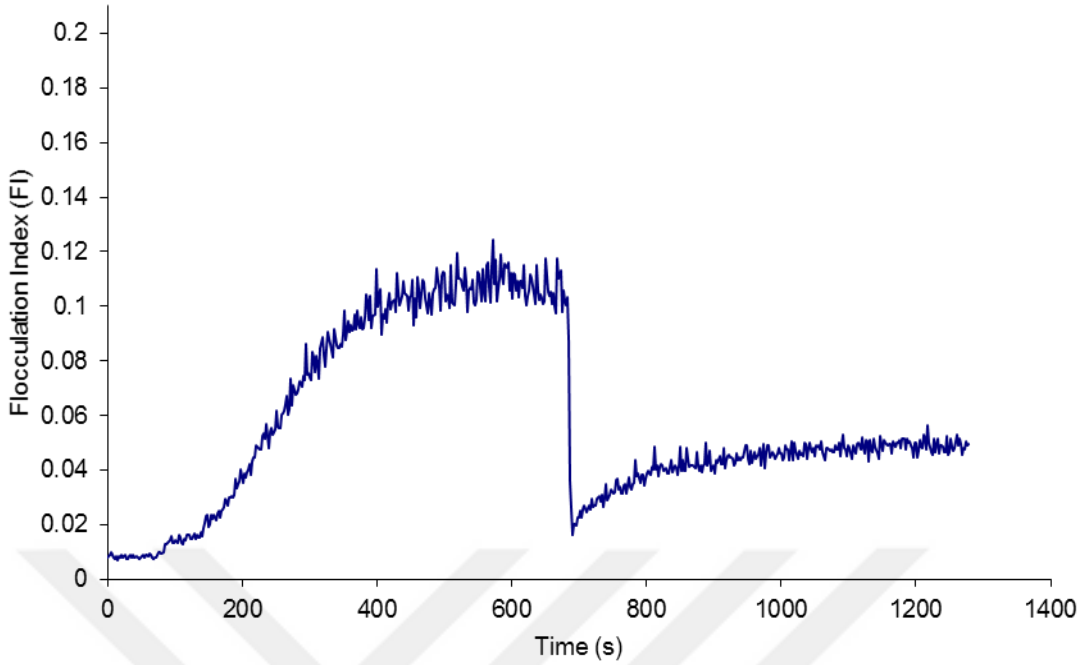

Figure 3.128. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

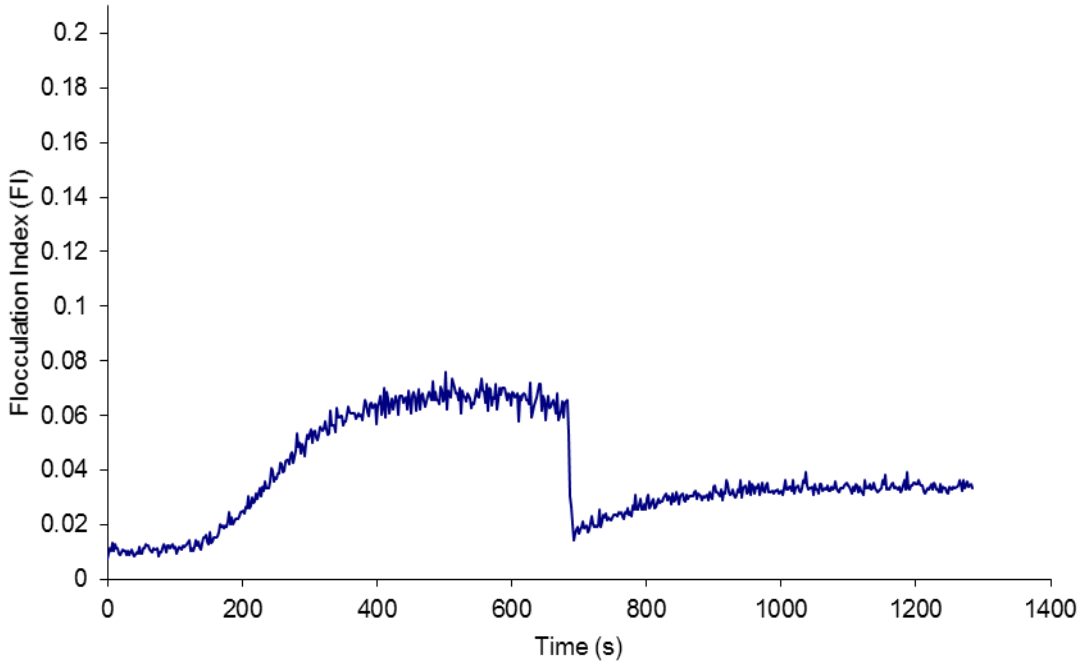

Figure 3.129. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

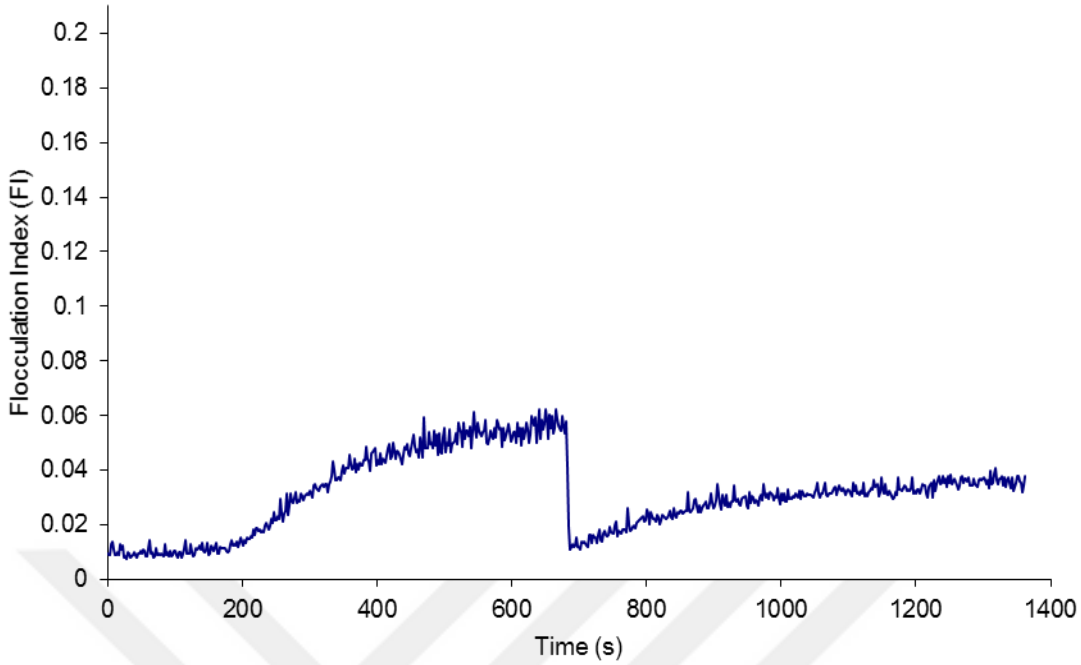

Figure 3.130. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 10 mg/L humic acid

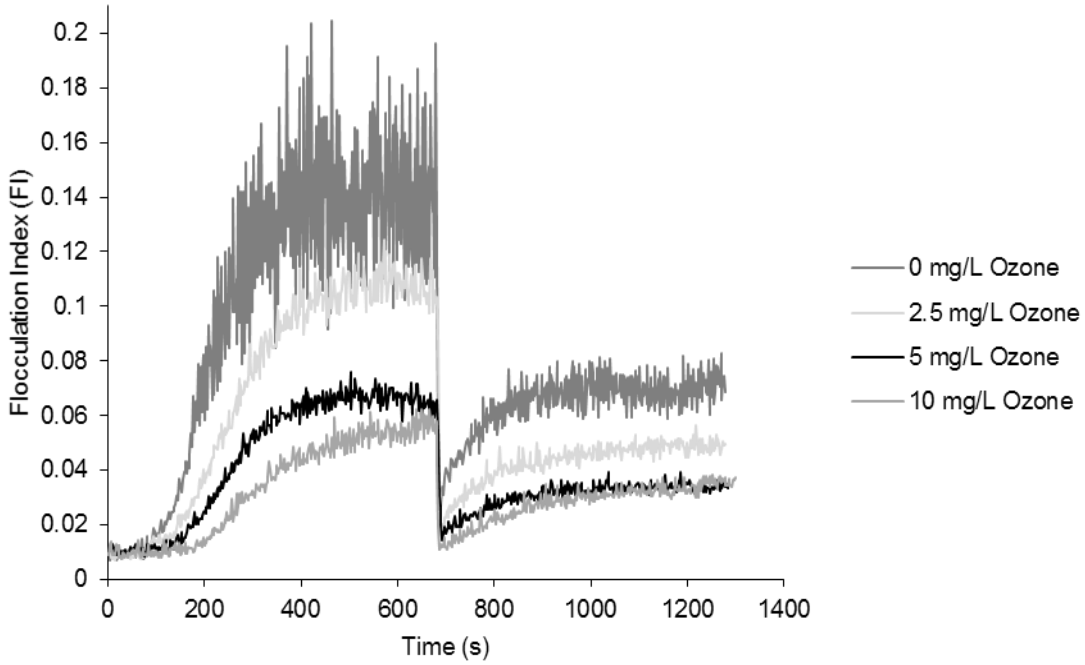

Figure 3.131. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid

3.3.2.3. Experiments with synthetic raw waters containing 20 mg/L humic acid

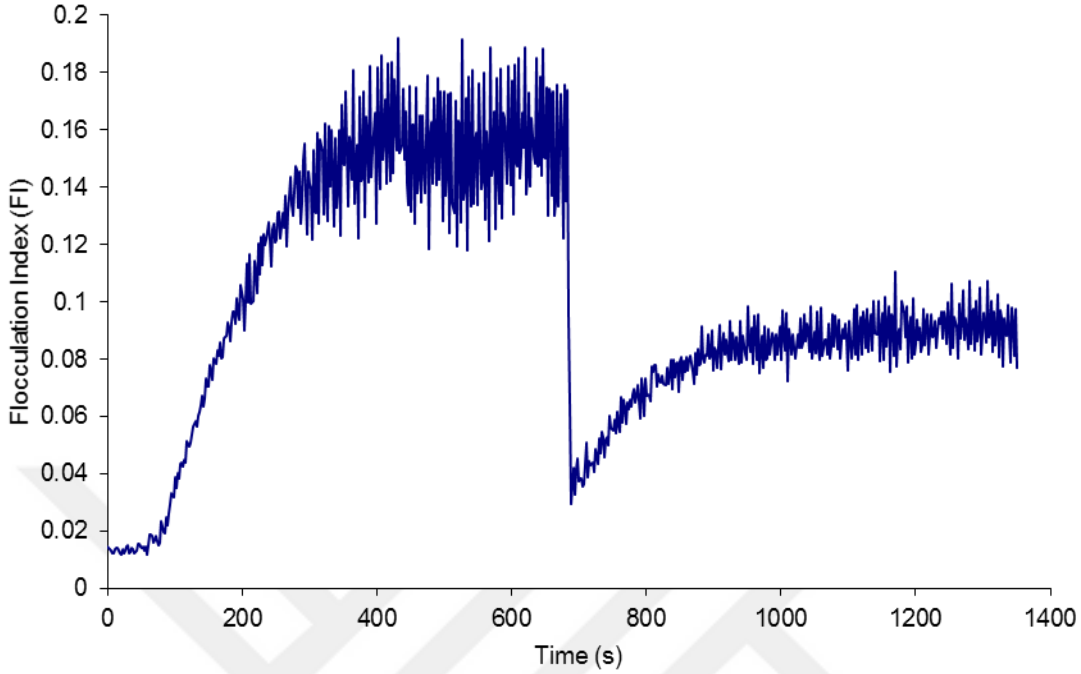

Figure 3.132. Floc growth and regrowth with PACl in un-ozonated synthetic raw water containing 20 mg/L humic acid

Floc size increased with increasing humic acid concentration similar as in the previous experiments when humic acid concentration was increased from 5 mg/L to 10 mg/L. This is likely because of increase in number of collisions with increasing humic acid concentration. Relative size of flocs reformed after breakage also increased as the humic acid concentration was increased.

It was found that relative floc size reduced when the pre-ozone dose was increased (Figures 3.132-3.135), same as that observed with previous humic acid concentrations. This is also valid for flocs regrown after exposure to high shear rate (Figure 3.136). Beginning of aggregation was delayed and steady-state floc size distribution was reached in longer time as the pre-ozone dose was increased, which together made the floc growth period of the curve steeper as the pre-ozone dose was decreased. All of these findings implicate that increasing pre-ozone dose negatively affected flocculation process.

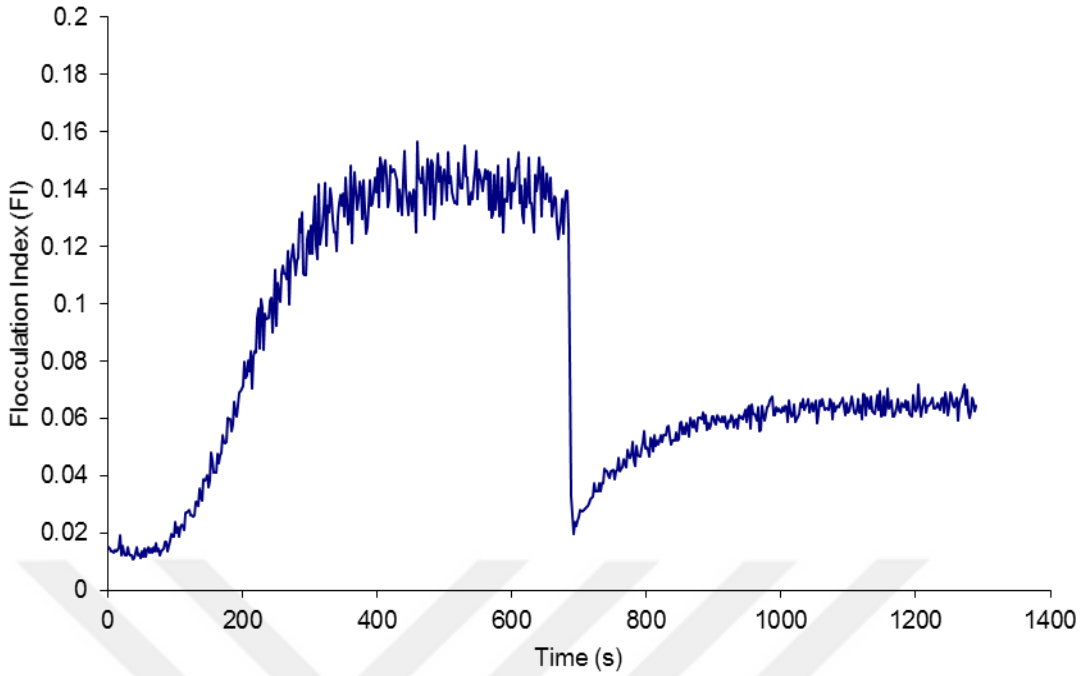

Figure 3.133. Floc growth and regrowth with PACl in 2.5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

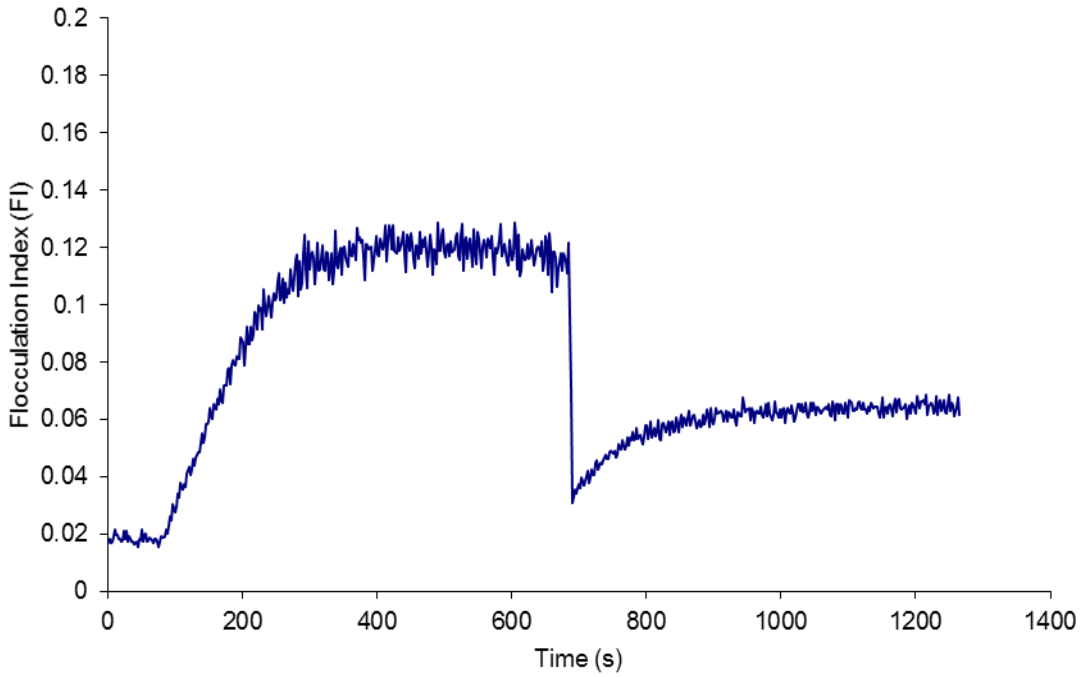

Figure 3.134. Floc growth and regrowth with PACl in 5 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

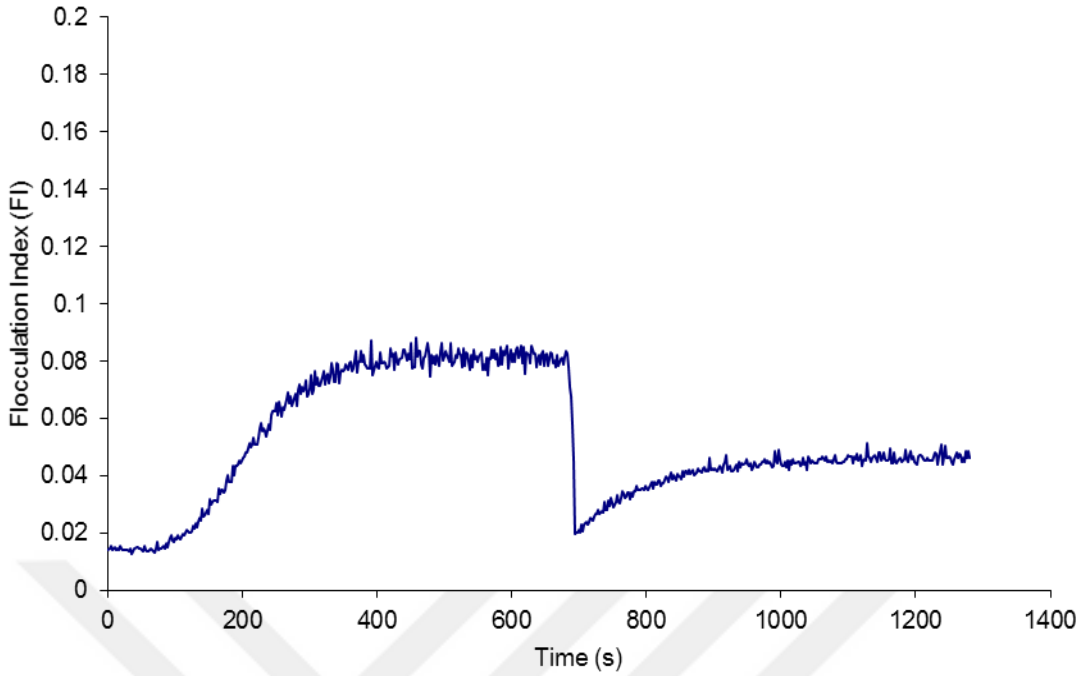

Figure 3.135. Floc growth and regrowth with PACl in 10 mg/L pre-ozonated synthetic raw water containing 20 mg/L humic acid

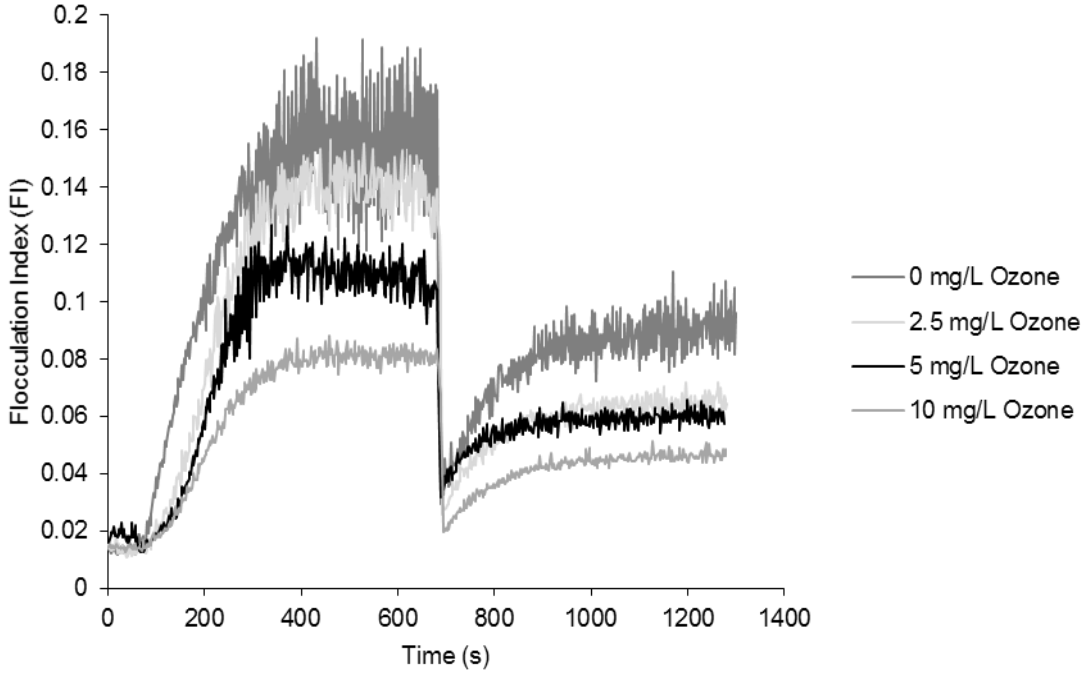

Figure 3.136. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid

Once again, broken flocs could not grow back to their sizes before breakage, which is common in sweep flocculation.

3.3.3. Comparison of floc sizes

Continuous monitoring of floc formation (Figure 3.137) showed that increasing pre-ozone dose resulted in a gradual decrease in floc size. The onset of flocculation was delayed and the time required for fully grown flocs to reach steady-state size distribution was longer with increasing ozone dose. When PACl was used, the resulting flocs were relatively larger. Additionally, PACl exhibited faster floc formation and earlier attainment of steady-state fully grown floc size distribution, both outperformed alum.

Furthermore, irreversible floc breakage was observed with both coagulants, i.e. when fully grown flocs are exposed to higher shear rate, they can only regrow to some extent; this is inherent in sweep flocculation because the nature of aggregation is entrapment of organic molecules in the growing amorphous metal hydroxide precipitate

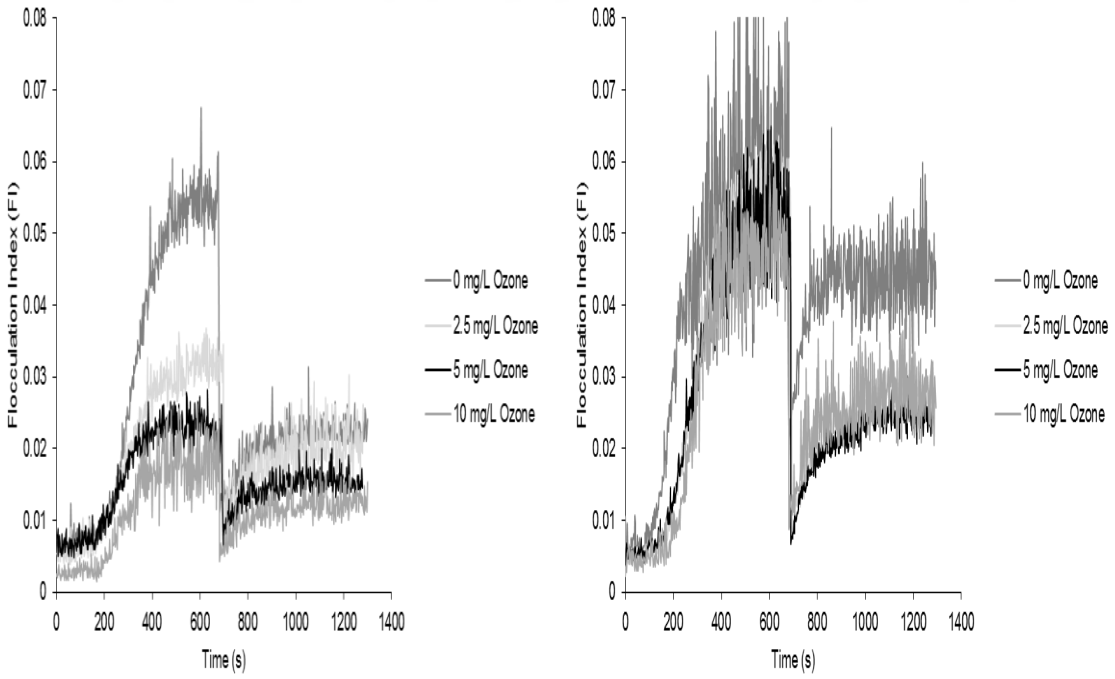

Figure 3.137. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid

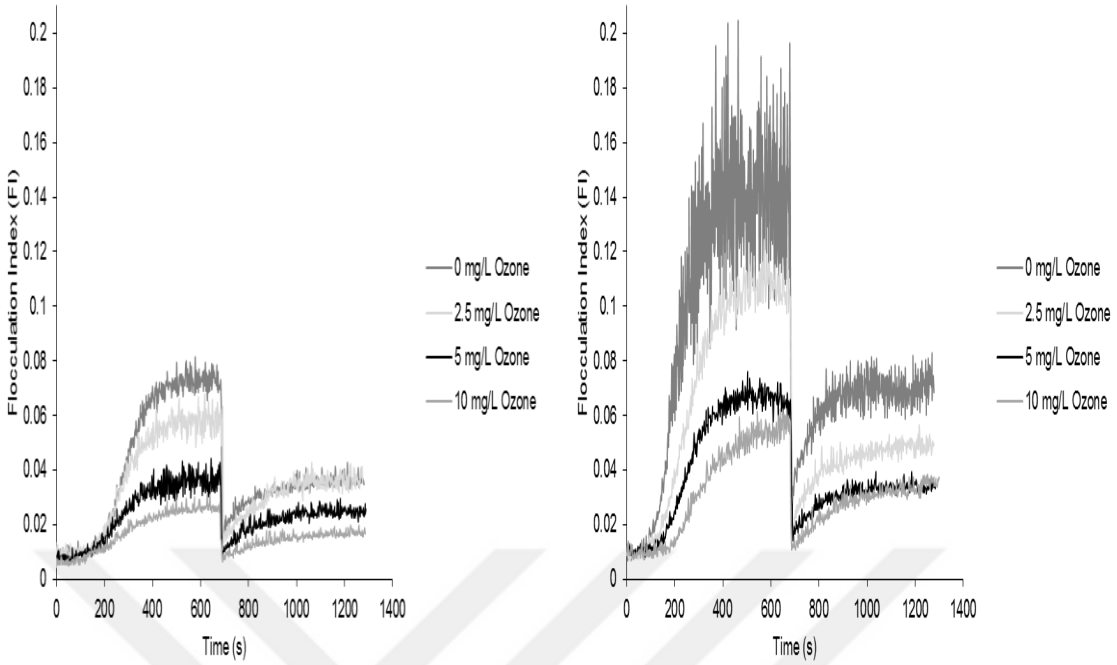

Figure 3.138. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid

rather than electrostatic attraction.

In the jar tests with unozonated 5 mg/L humic acid containing raw waters, the relative size difference between the flocs formed with alum was higher when pre-ozonation was applied. Flocculation with alum appears to be more affected by ozonation than that with PACl, likely due to the presence of pre-hydrolysed aluminium species in PACl.

Figure 3.138 confirms findings similar to those presented in Figure 3.137, where it was observed that increasing pre-ozonation dose had a negative effect on flocculation, i.e., pre-ozonation resulted in the formation of smaller flocs, delayed the onset of aggregation, and extended the time to reach a steady-state fully grown floc size distribution. Larger fully developed flocs, showing comparably higher FI values, were formed with PACl before breakage. PACl formed larger regrown flocs after floc break-up, as well.

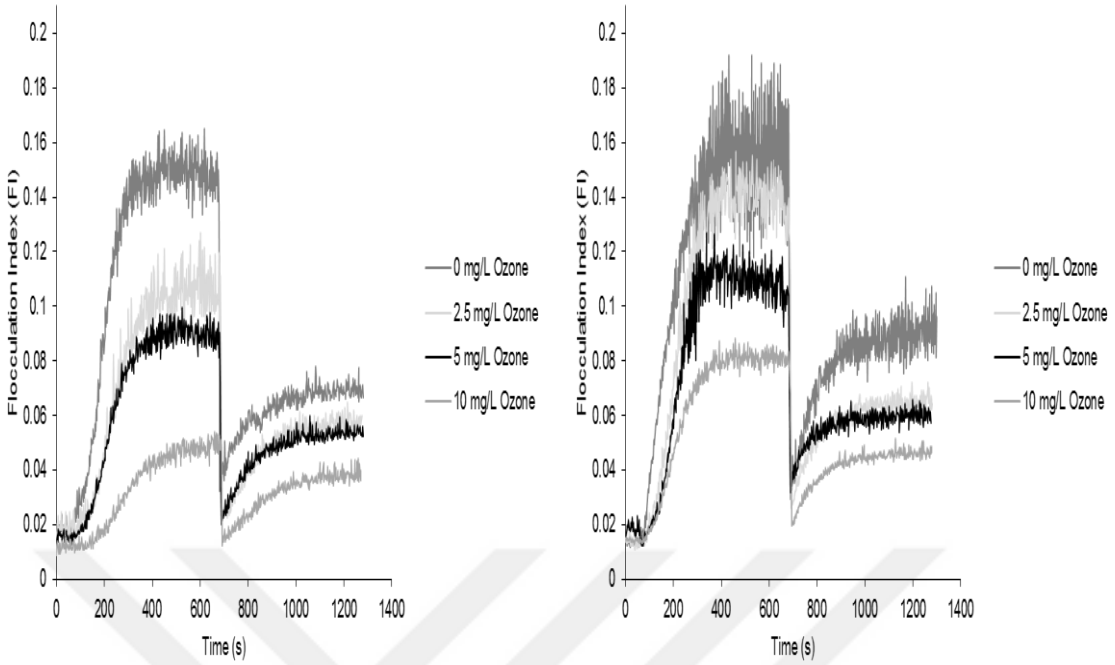

Figure 3.139. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid

What is again evident from Figure 3.139 is that preozonation inhibited floc formation at 20 mg/L humic acid concentration, which is similar to that observed at 5 mg/L and 10 mg/L humic acid concentrations. As the pre-ozone dose was increased, floc size progressively became smaller, the initiation of flocculation was delayed, and the time to reach steady-state floc size distribution was prolonged.

The floc growth-regrowth curves with both coagulants displayed similar shapes, indicating that floc breakage was irreversible. Again, larger flocs were obtained with PACl at each pre-ozonation dose. Examination of the three figures exhibits that the size difference between alum flocs with increasing pre-ozonation dose was higher than that between PACl flocs, which can be interpreted that PACl seems to be less affected by pre-ozonation compared to alum. Both features are probably due to the pre-hydrolysed Al hydroxide content of PACl.

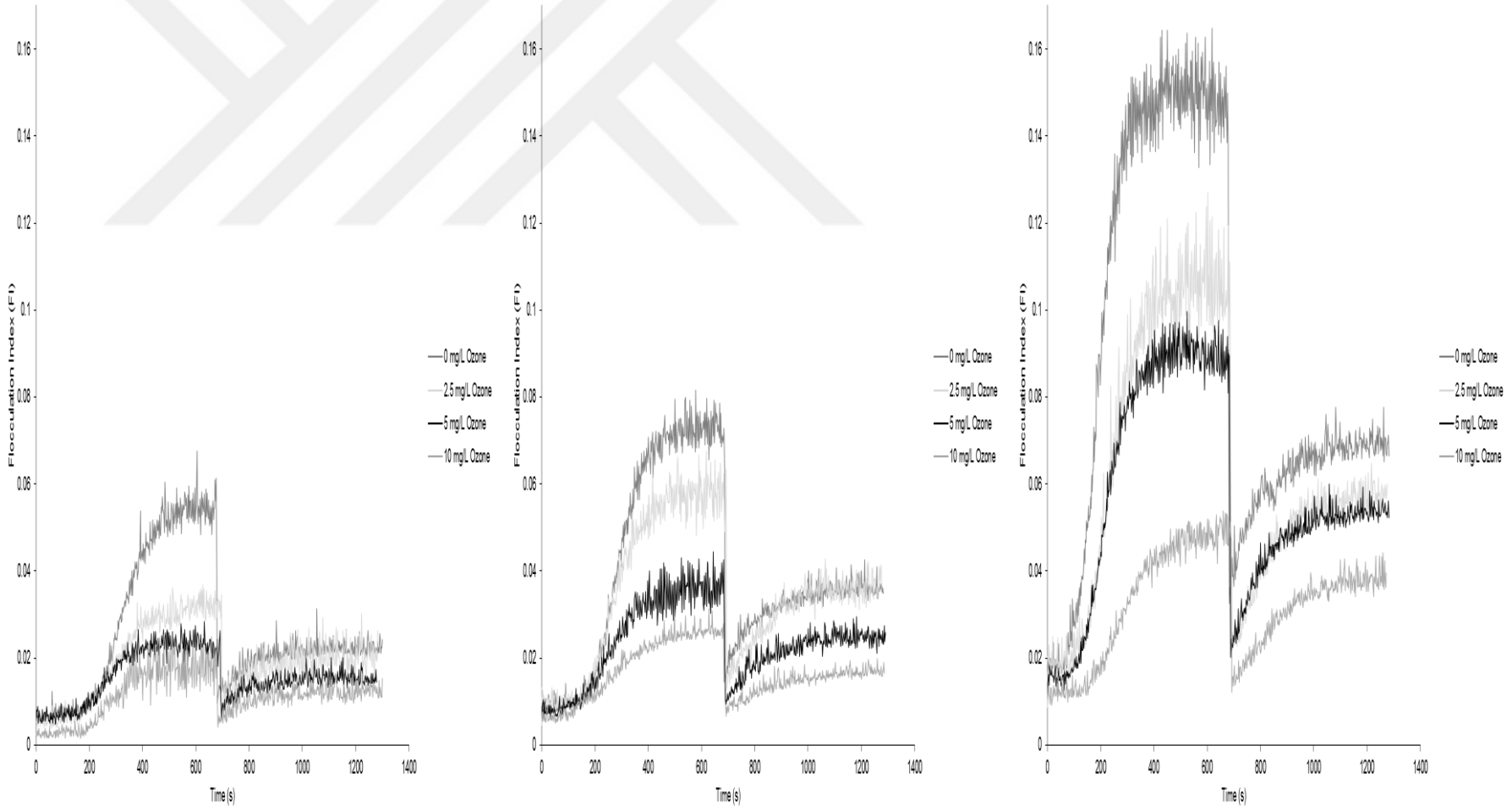

Figure 3.140. Floc growth and regrowth with alum in flocculation of pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid (from left to right)

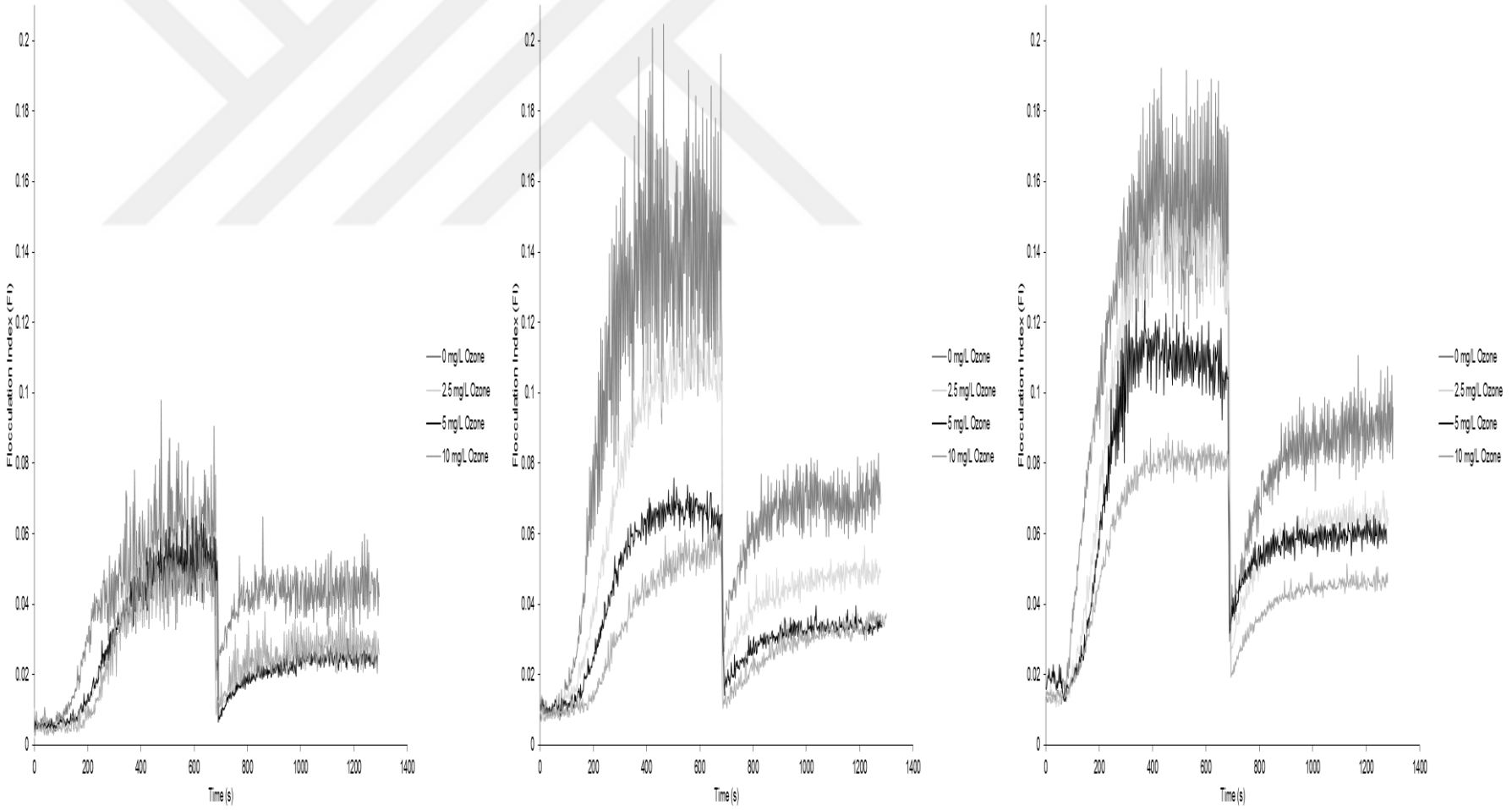

Figure 3.141. Floc growth and regrowth with PACl in flocculation of pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid (from left to right)

With both of the coagulants, decrease in floc size as the pre-ozone dose was increased was detected in all three humic acid concentrations. With increasing pre-ozonation dose, the onset of flocculation became more delayed and time to reach a steady-state floc size distribution was longer, making the floc growth curve less steep. It is known that in sweep flocculation regime once broken, flocs can grow back to some extent but not to their sizes before break-up. It is thought that in sweep flocculation the aggregation is in the form of entrapment of particles/adsorption of dissolved organic molecules in growing amorphous metal hydroxide precipitates rather than electrostatic attraction between destabilised particles. This is seen in Figures 3.140 and 3.141, and in all of the floc growth monitoring where also, flocs regrown after breakage alined in decreasing size order with increasing ozone dose.

3.3.4. Organic carbon removal with $Al_2(SO_4)_3$

3.3.4.1. Removals in synthetic raw waters containing 5 mg/L humic acid

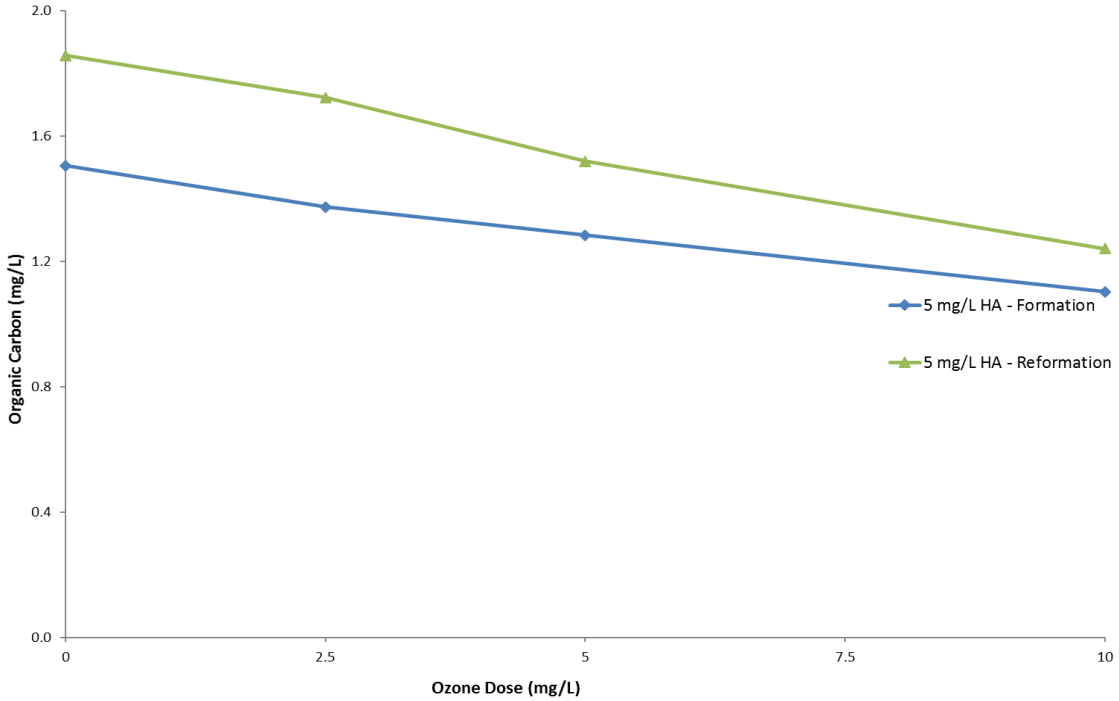

Figure 3.142. Residual TOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum

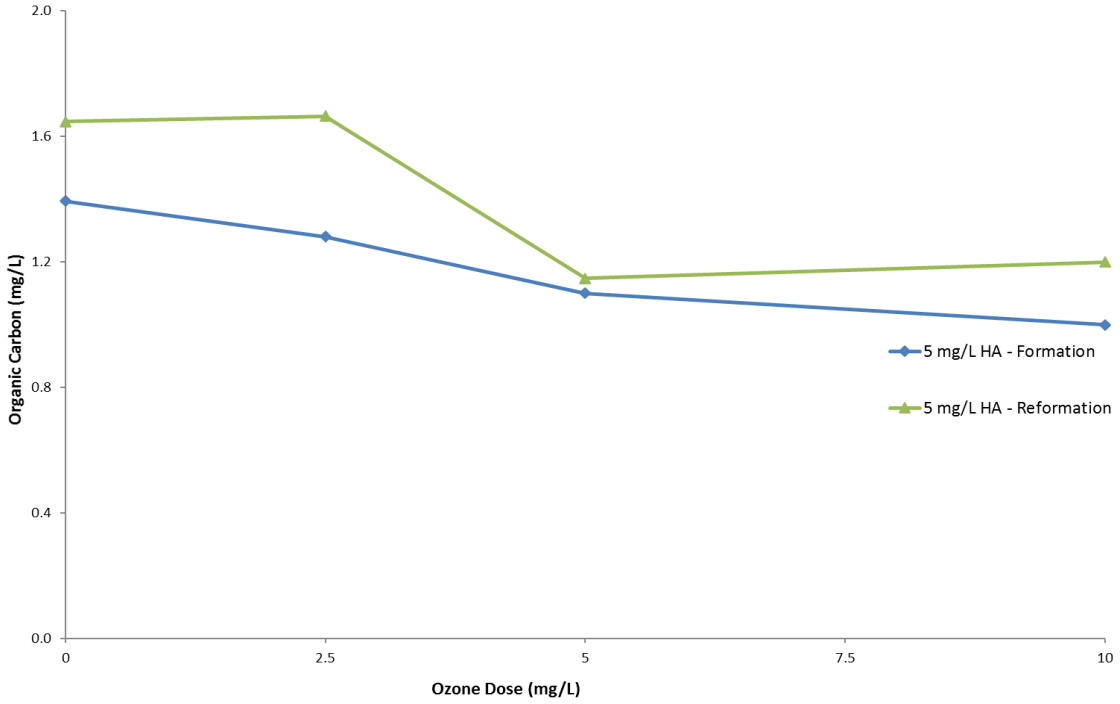

Figure 3.143. Residual DOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum

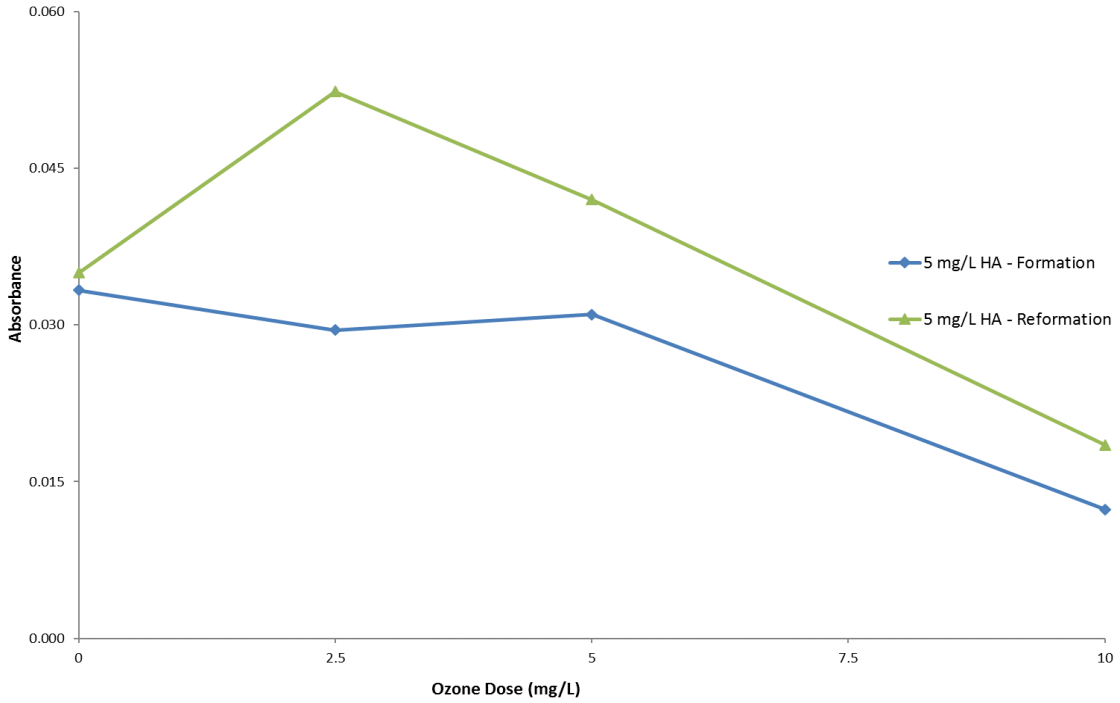

Figure 3.144. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum

Figure 3.142 and Figure 3.143 present how residual organic carbon concentrations (total and dissolved organic carbon, respectively) after alum flocculation changed when the unozonated synthetic raw water containing 5 mg/L humic acid was pre-ozonated with 2.5, 5 and 10 mg/L ozone. Residual organic carbon concentrations were measured to decrease as the pre-ozone dose was increased. Similarly, a decreasing trend was observed with residual UV_{254} absorbance after flocculation as the raw waters were ozonated more.

Whilst UV absorbance at 254 nm is useful for comparing organic matter concentrations, it is also used to calculate Specific UV absorbance (SUVA) by taking the ratio of it to dissolved organic carbon concentration. SUVA gives insight into hydrophobicity/hydrophilicity of humic matter. SUVA can be used to specify hydrophilic and hydrophobic composition of water; SUVA < 3 essentially represents the hydrophilic matter (Edzwald and Tobiason, 1999) whereas SUVA > 4 points out hydrophobic and particularly aromatic matter. Although there is no specific relationship between SUVA and removal, it is observed that the higher the SUVA is, the better the removal of DOC gets.

It was attempted to find evidences for the molecular size distribution of humic material by taking the ratio of light absorbance at 465 nm (E_4) to 656 nm (E_6). A high E_4/E_6 ratio indicates the presence of small molecules in solution, whilst a low value points out large molecules (Maartens et al., 1999).

Change of Specific UV absorbance in the supernate after flocculation by increasing pre-ozone dose is depicted in Figure 3.145. Up to 5 mg/L pre-ozone dose, residual SUVA measurements were in the intermediate range and showed an increasing trend (residual UV_{254} absorbance slightly decreased but not as much as residual dissolved organic carbon concentration did), indicating that there were aromatic structures absorbing UV radiation at 254 nm in the residue. Relatively low pre-ozone dose oxidised higher molecular weight organic matter to smaller organic molecules, which had more affinity to interact with alum possibly and were removed better consequently. Ozone probably broke the aliphatic chains but those intermediate size molecules still had aromatic structures which absorbed UV radiation at 254 nm (slight decrease in residual UV_{254} absorbance data in Figure 3.144), they were smaller organic

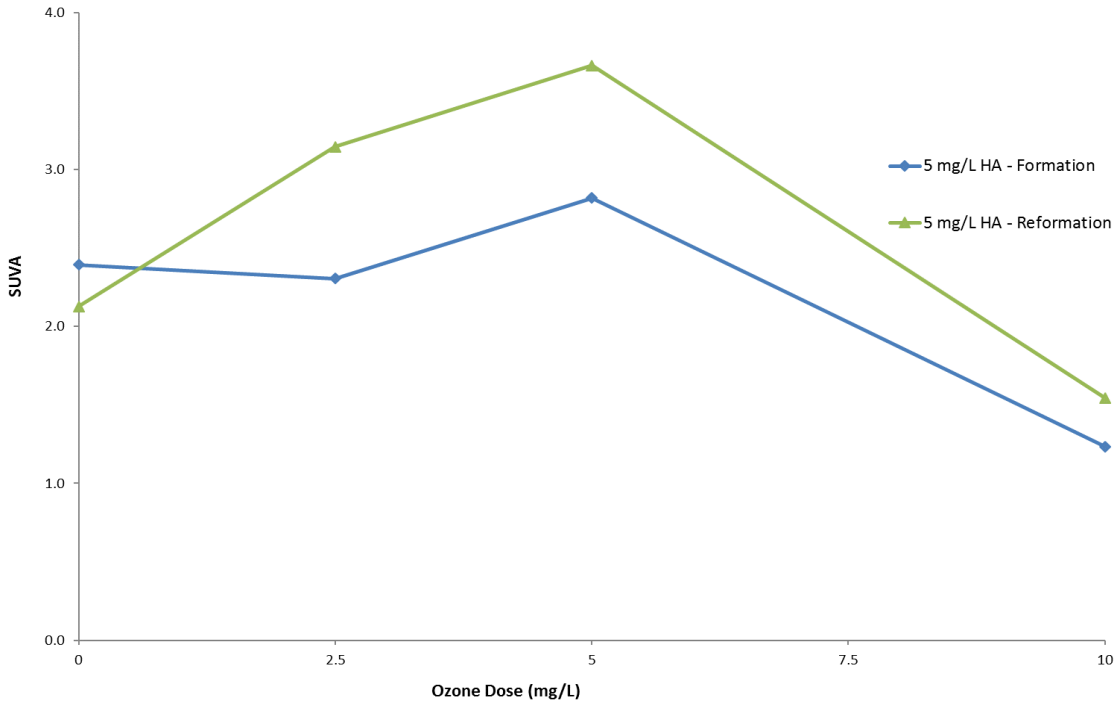

Figure 3.145. SUVA after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum

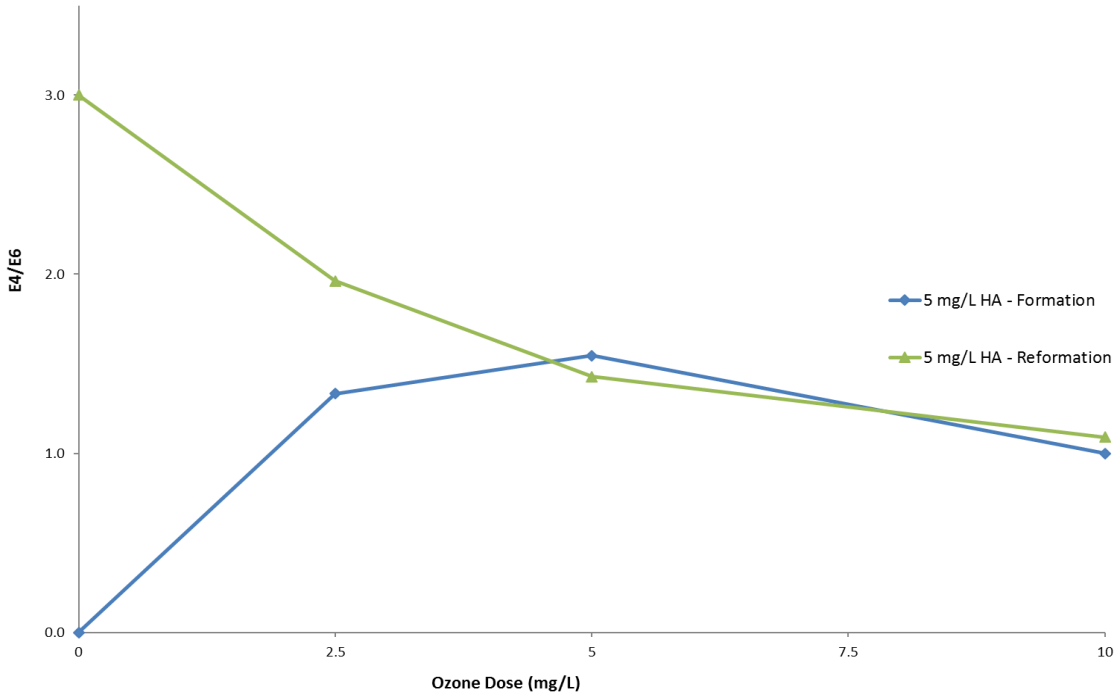

Figure 3.146. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum

molecules (E_4/E_8 ratio in Figure 3.146) but were not removed as much (residual SUVA data in Figure 3.145). Further increasing the pre-ozone dose to 10 mg/L might over-oxidise higher molecular weight organic matter and this time break most of the aromatic rings which resulted in the observed residual UV_{254} absorbance and residual SUVA reductions. Decrease in E_4/E_6 indicate that relatively larger molecules were left unremoved in the supernate. Although shorn by oxidation, smaller molecules still having aromaticity might not be removed as well as smaller molecules without aromatic structures. Despite the finding that floc size decreased with increasing pre-ozone dose, organic carbon removal relatively improved. It is likely that smaller organic molecules released by ozonation were prone to interact with alum, by which smaller floc formation may be explained, they possibly adsorbed to floc surfaces or formed complexes and since more number of smaller flocs had more surface, their removal improved consequently.

3.3.4.2. Removals in synthetic raw waters containing 10 mg/L humic acid

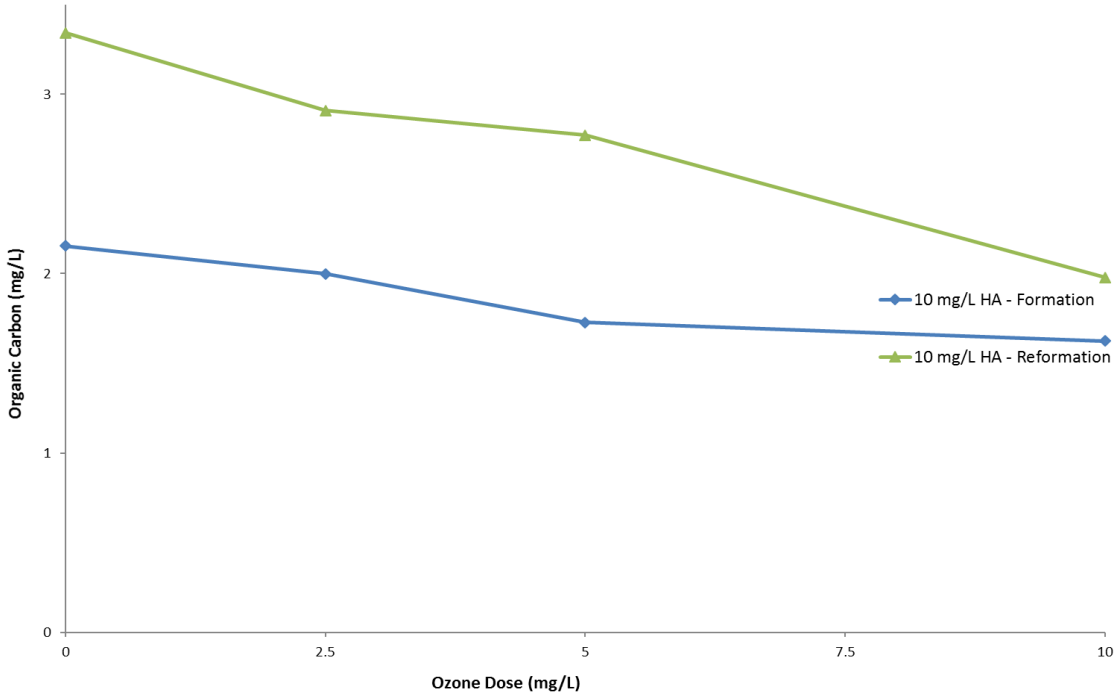

Figure 3.147. Residual TOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum

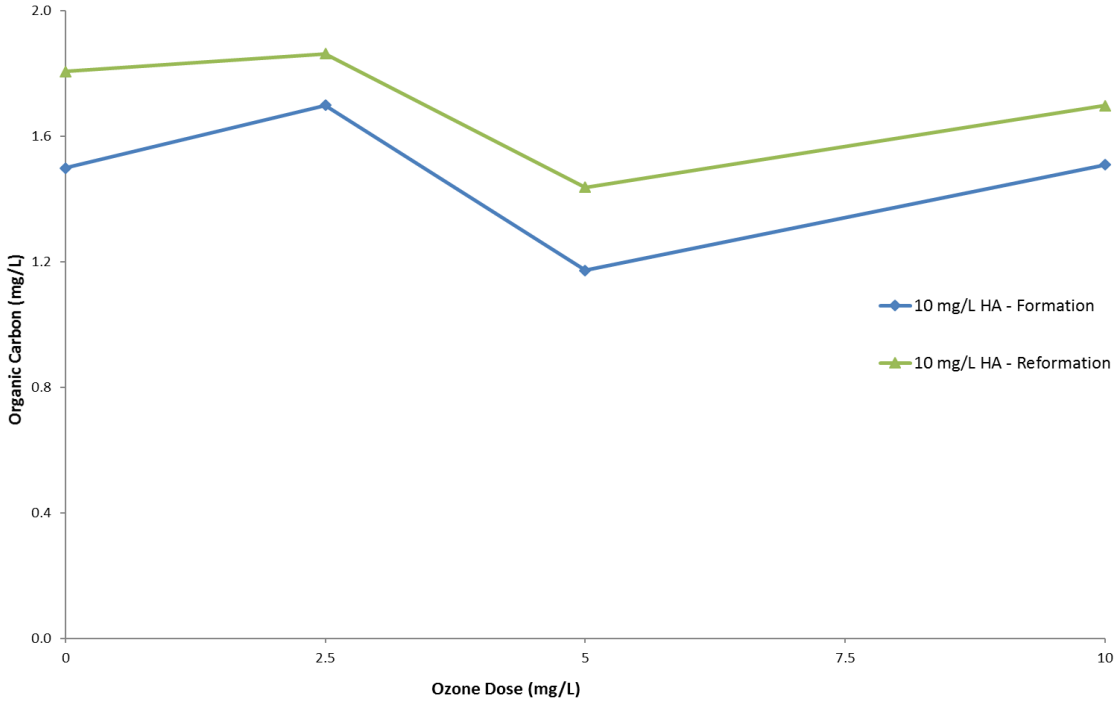

Figure 3.148. Residual DOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum

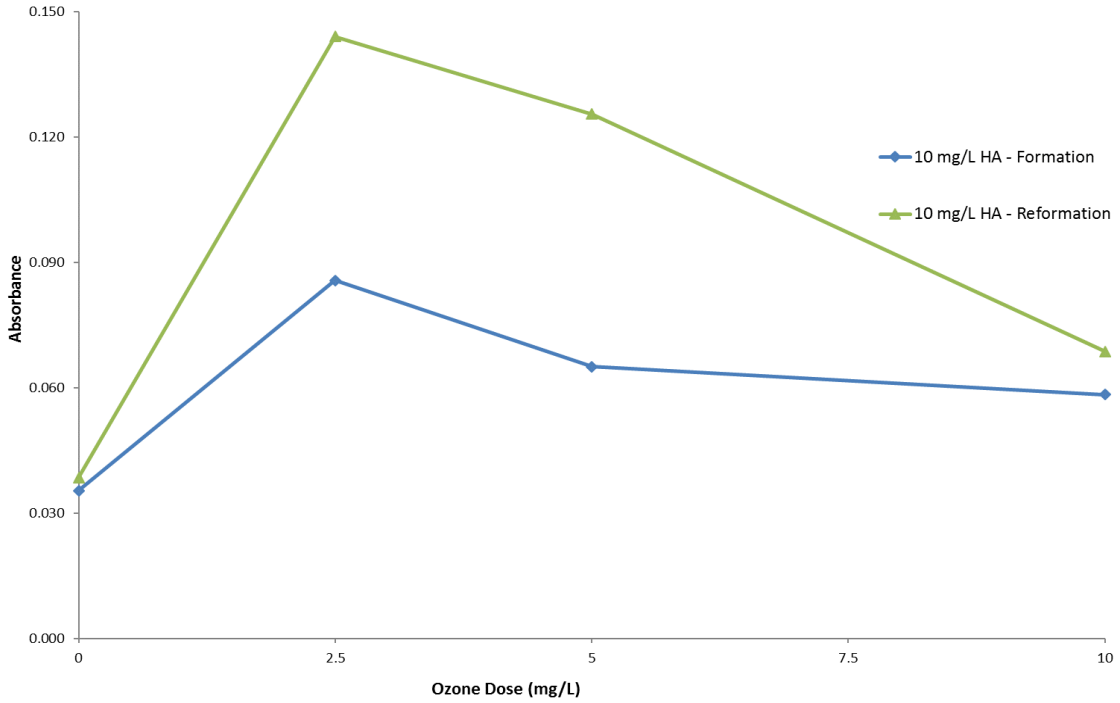

Figure 3.149. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum

When the humic acid concentration of raw water was increased from 5 mg/L to 10 mg/L, residual total organic carbon concentrations measured in the supernates of settled suspensions after flocculation of pre-ozonated raw waters displayed a decreasing trend with increasing pre-ozone dose (Figure 3.147). Residual dissolved organic carbon concentration was observed to increase when pre-ozonation applied first, then to decrease when the dose of pre-ozonation was 5 mg/L and to increase again when the pre-ozone dose was further increased to 10 mg/L (Figure 3.148). Residual UV_{254} absorbance exhibited a similar trend up to 5 mg/L pre-ozone dose and slightly decreased when the pre-ozone dose was 10 mg/L (Figure 3.149). It is likely that pre-ozonation of 10 mg/L humic acid by 2.5 mg/L ozone released more amount of smaller organic molecules than that of 5 mg/L humic acid and these smaller molecules had more affinity for alum, thus they flocculated and were removed better whilst intermediate organics containing aromatic structures were not removed that well, hence the increases observed in residual dissolved organic carbon concentration, residual UV_{254} absorbance and SUVA value. When the pre-ozone dose was further increased to 5 mg/L, organic molecule size became even smaller; those absorbing less UV radiation at 254 nm but still having some aromaticity were found in the supernate; indicating that oxidised smaller organics without aromatic structures were removed better. Probably, this much of ozone dose cleaved some more aromatic rings, which is why less UV_{254} absorbance was measured in the supernatant phase of settled waters and those oxidised organic molecules containing less amount of aromatic rings were removed better showing lower residual dissolved organic carbon concentration. When the pre-ozone dose was further increased to 10 mg/L, the unremoved dissolved organic carbon increased in concentration, absorbing less UV radiation at 254 nm and having much less aromaticity. It is likely that at this much dose, ozone over-oxidised higher molecular weight organic matter and broke most of the aromatic rings leading to the observed residual UV_{254} absorbance and residual SUVA reductions, also decrease in E_4/E_6 ratio suggests larger molecules; broken aromatic rings might have generated relatively longer chains. However, over-oxidation might have caused the release of too much amount of soluble smaller organics, more than the coagulant dose used could sufficiently neutralise, and it is possible that these smaller molecules interacted with alum and formed smaller flocs but relatively larger molecules were not removed that well, leading to the increased con-

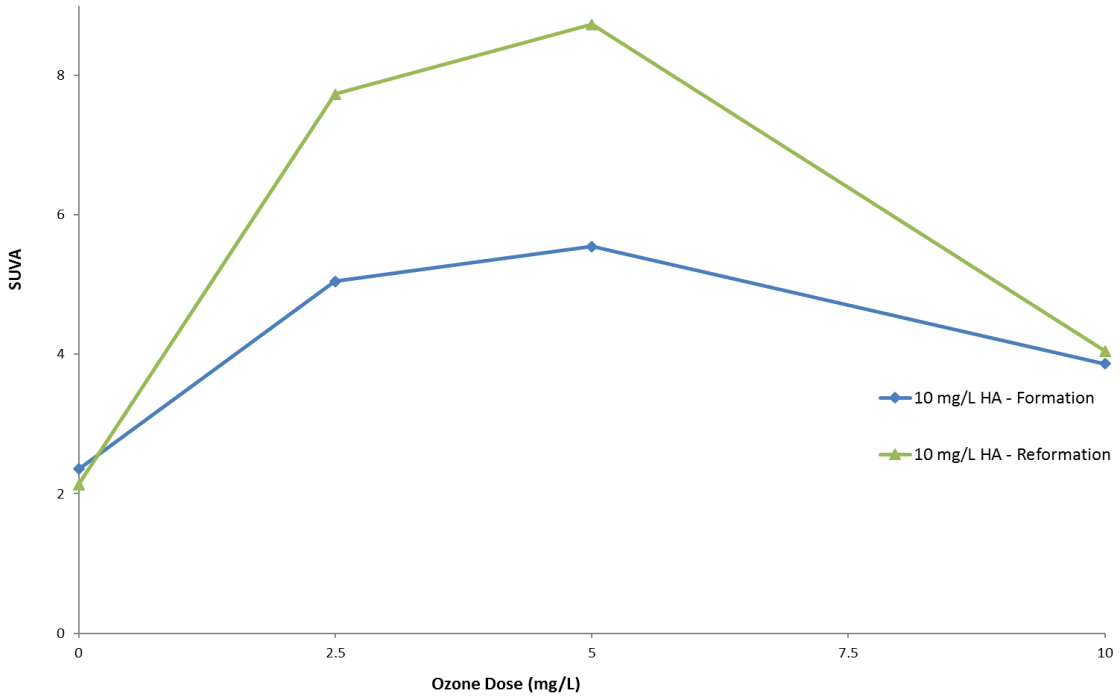

Figure 3.150. SUVA after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum

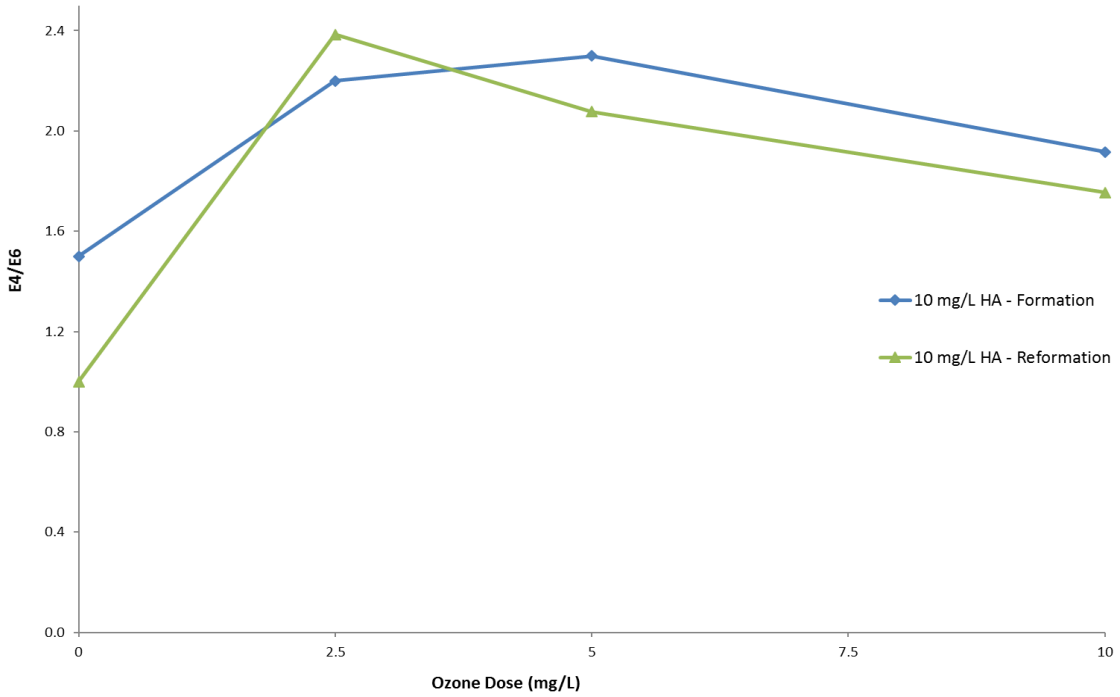

Figure 3.151. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum

centration of dissolved organic carbon measured in the supernate.

3.3.4.3. Removals in synthetic raw waters containing 20 mg/L humic acid

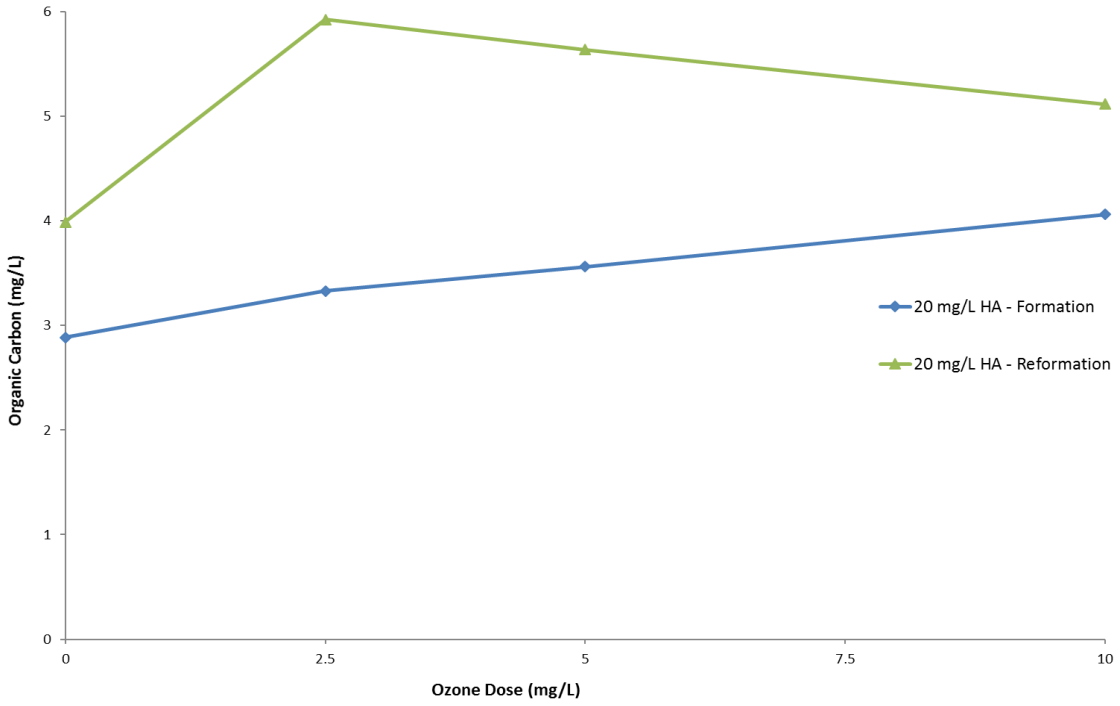

Figure 3.152. Residual TOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum

The changes of residual total and dissolved organic carbon concentrations after alum flocculation of unozonated synthetic raw water containing 20 mg/L humic acid ozonated with 2.5, 5 and 10 mg/L ozone prior to flocculation were plotted in Figures 3.152 and Figure 3.153, respectively. Residual total organic carbon concentration exhibited an increasing trend with increasing pre-ozone dose. Residual dissolved organic carbon concentration showed an increase when pre-ozonation applied first, then a decrease when the dose of pre-ozonation was 5 mg/L and a higher increase this time when the pre-ozone dose was further increased to 10 mg/L. Residual UV_{254} absorbance exhibited a relatively steep increase when pre-ozonation applied first, then

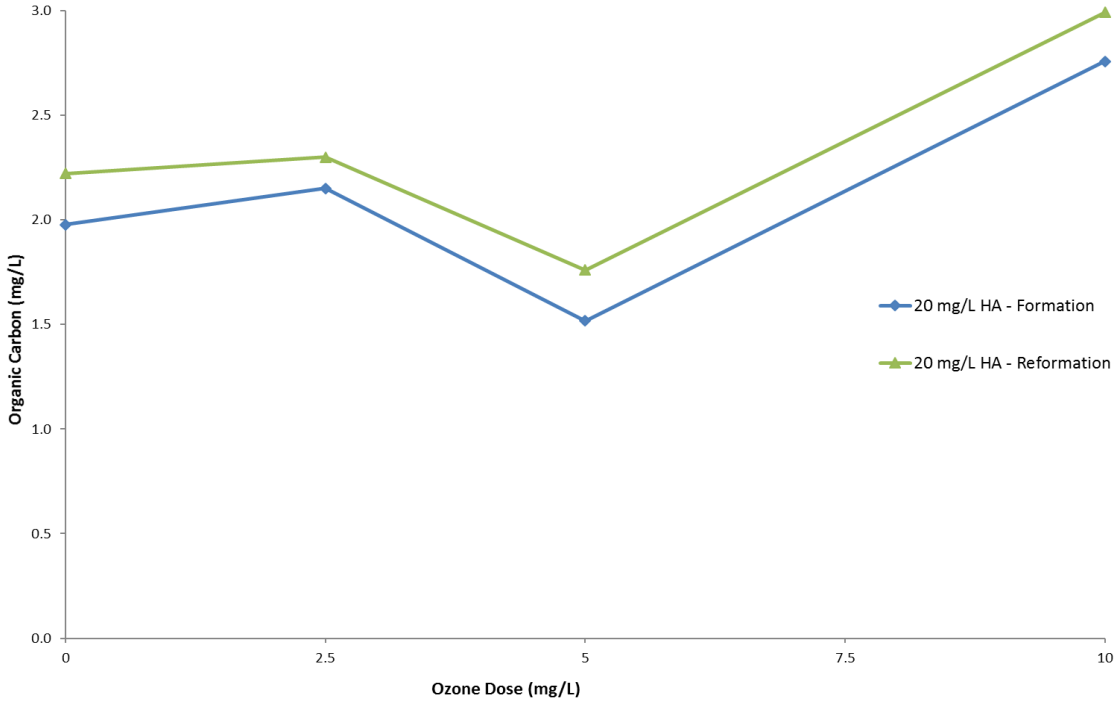

Figure 3.153. Residual DOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum

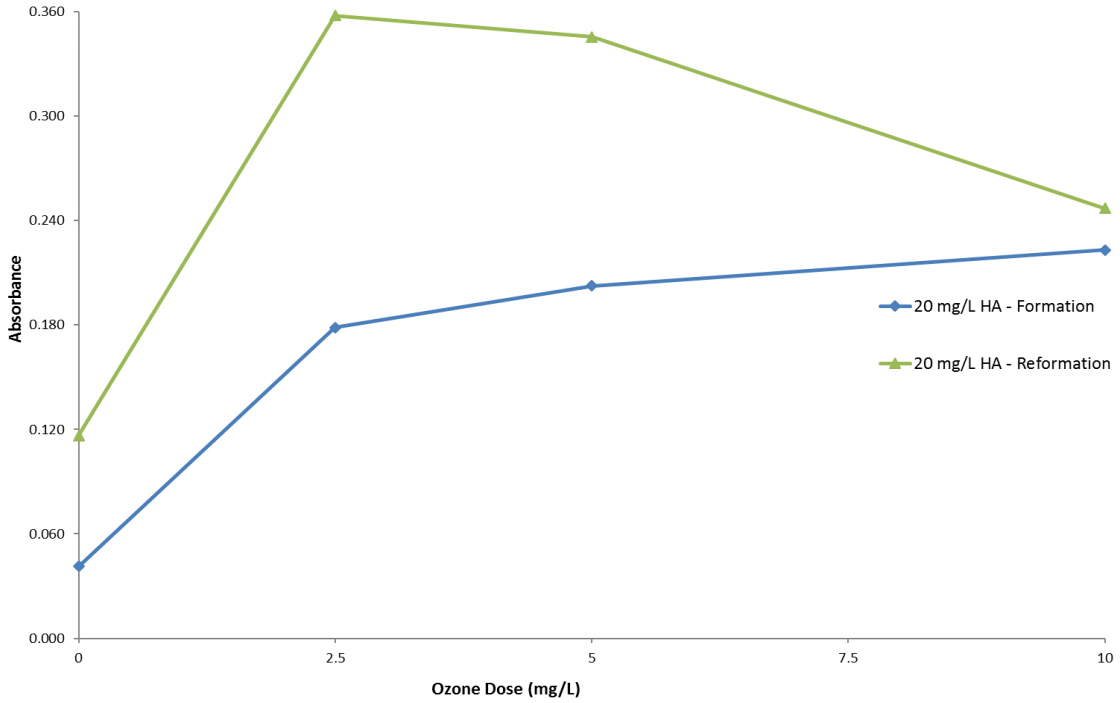

Figure 3.154. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum

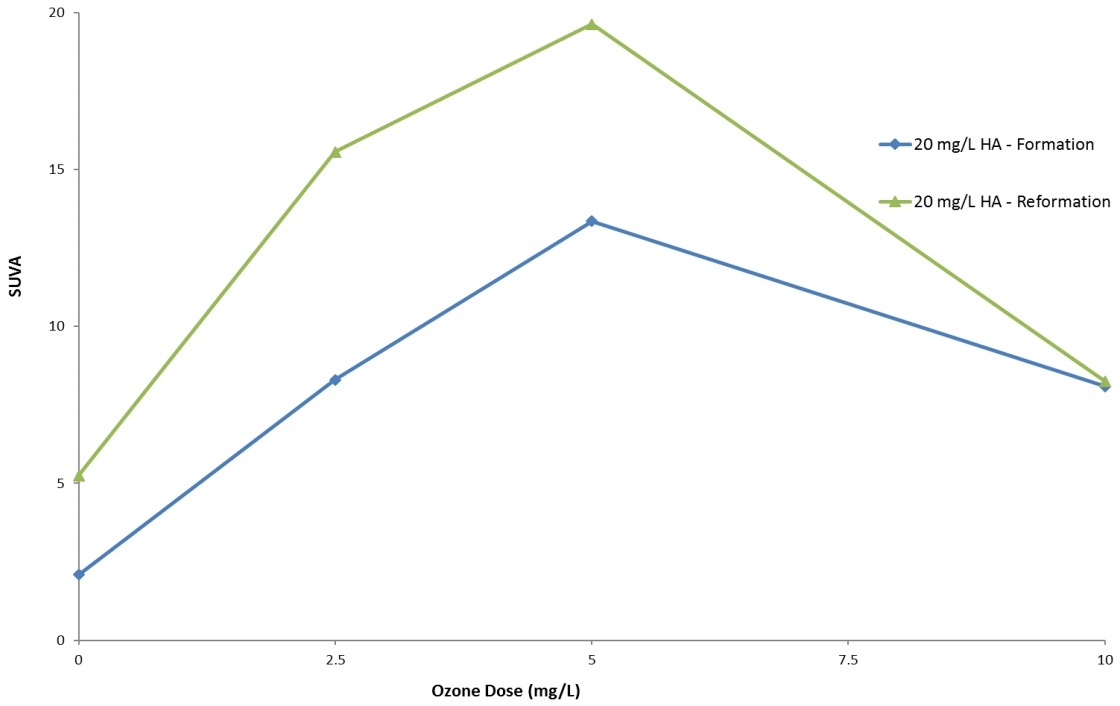

Figure 3.155. SUVA after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum

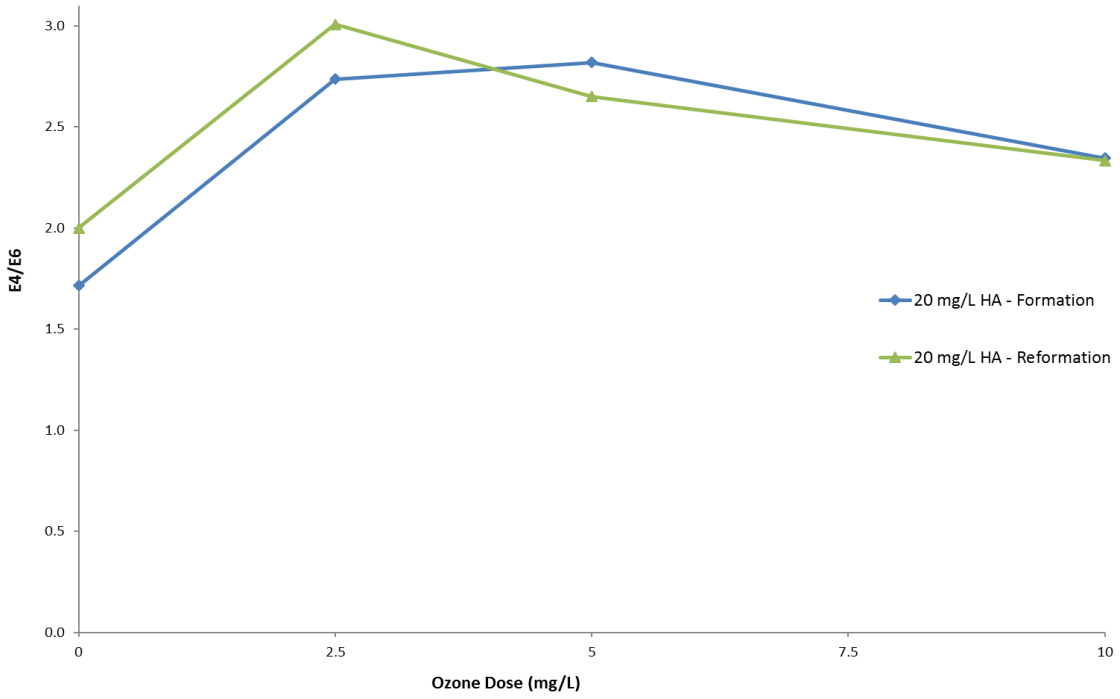

Figure 3.156. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum

kept increasing smoothly (Figure 3.154). It is likely that oxidation of 20 mg/L humic acid with increasing pre-ozone dose resulted in release of more and more smaller organic molecules that were in abundance for the alum dose used to sufficiently neutralise, leading to the hinderance of total organic carbon removal. After the application of the lowest pre-ozone dose followed by flocculation, residual dissolved organic carbon concentration was measured to increase relatively slightly. It is likely that oxidation generated small organic molecules and intermediate size organic molecules which still had aromatic structures, small molecules were more prone to interact with alum which were removed better in the form of smaller flocs compared to intermediate organic molecules containing aromatic structures, leading to the observed increases in the residual UV_{254} absorbance and aromaticity (SUVA), however those small organic molecules were not in abundance in terms of mass concentration, consequently a higher residual dissolved organic carbon concentration was observed. When a higher dose of pre-ozone (5 mg/L) was applied, probably ozone-generated small organic molecules became abundant and since they were more prone to interact with the coagulant hence reduced dissolved organic carbon concentration. It is likely that 5 mg/L pre-ozone also generated intermediate organic molecules that contained aromatic structures and as indicated by the increases in residual UV_{254} absorbance and residual SUVA, the unremoved part of the organic matter was those intermediate size molecules. Further increasing the pre-ozone dose to 10 mg/L followed by flocculation resulted in an increase in the concentration of residual dissolved organic carbon, which showed a higher absorbance at 254 nm and a reduced SUVA that was still higher than 4, indicating presence of some aromaticity. That much of ozone might have destructed some of the aromatic structures but some oxidised molecules with intermediate size which still had aromatic structures might not have been completely removed by flocculation, showing the measured increase in residual UV_{254} absorbance and a SUVA value in the aromatic range. Smaller size molecules were probably more amenable to interact with alum and removed better in the form of smaller flocs but larger molecules were not removed well as indicated by lower E_4/E_6 ratio.

3.3.5. Organic carbon removal with polyaluminium chloride (PACl)

3.3.5.1. Removals in synthetic raw waters containing 5 mg/L humic acid

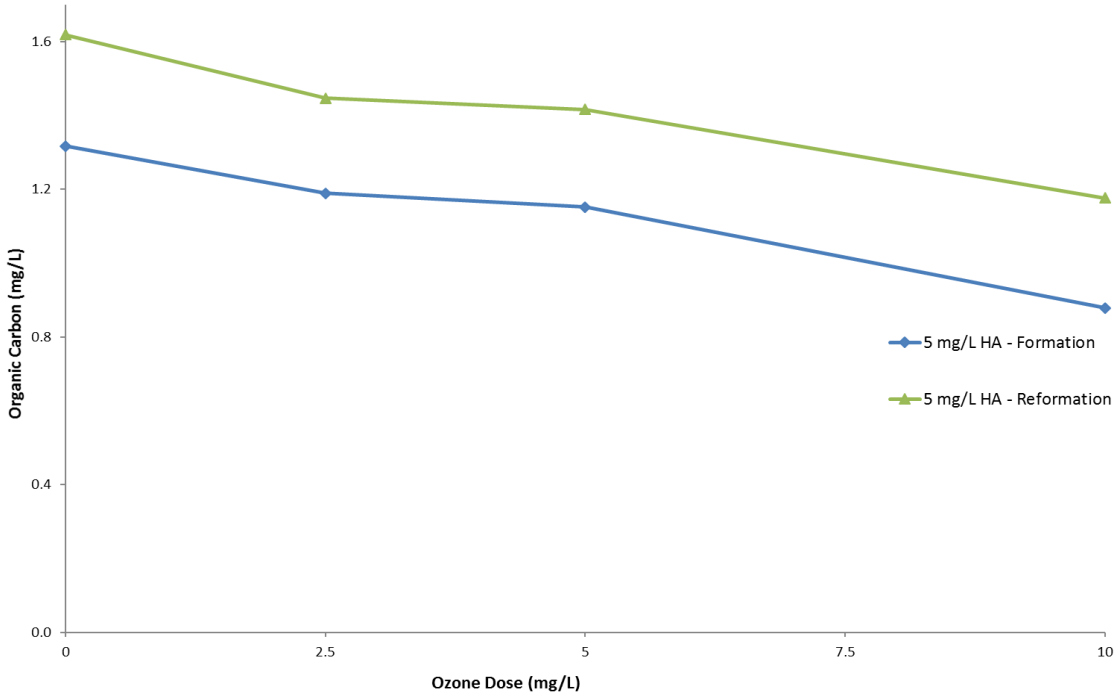

Figure 3.157. Residual TOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl

In Figure 3.157 and Figure 3.158, how residual organic carbon concentrations (total and dissolved organic carbon, respectively) after alum flocculation changed when the unozonated synthetic raw water containing 5 mg/L humic acid was pre-ozonated with 2.5, 5 and 10 mg/L ozone was plotted. Both the residual total and dissolved organic carbon concentrations were measured to decrease as the pre-ozone dose was increased. Similarly, a decreasing trend was observed with residual UV_{254} absorbance after flocculation as the raw waters were ozonated more. These residual parameters showed very similar trends with those after alum flocculation, only lower values were measured with PACl (Appendix Figures 25-27). That is also in correlation with the finding that larger flocs were generated with PACl, indicating that PACl exhibited a higher performance compared to alum or it can be said that in flocculation of waters containing 5 mg/L humic acid, compared to alum, PACl was affected less by pre-ozona-

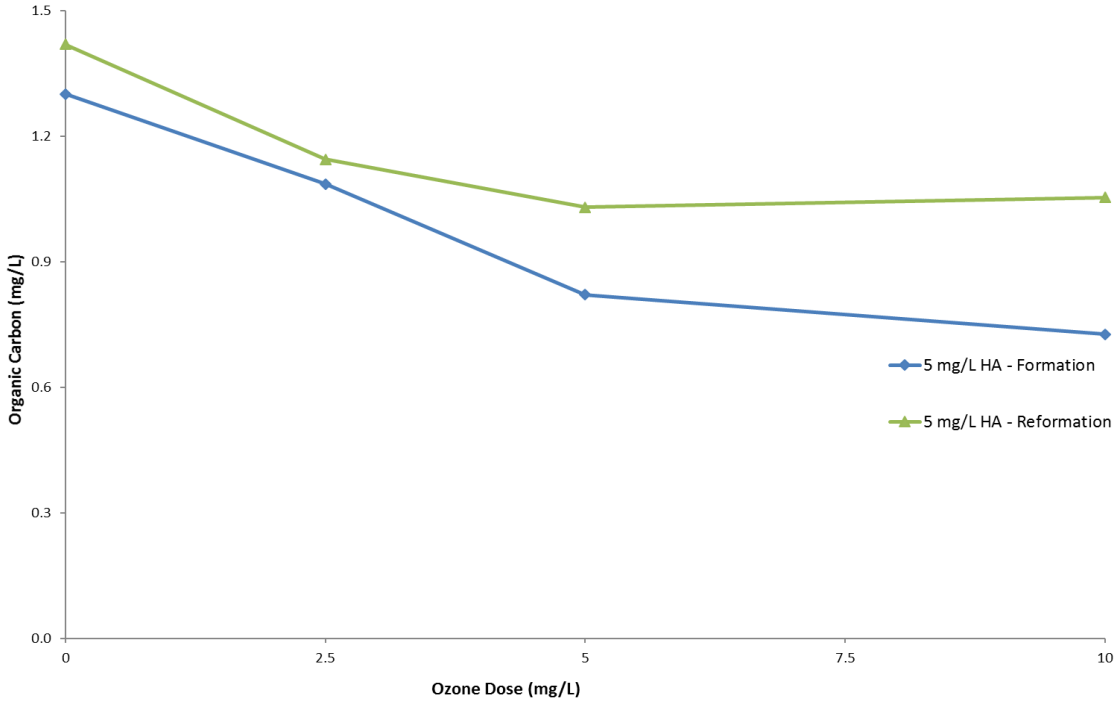

Figure 3.158. Residual DOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl

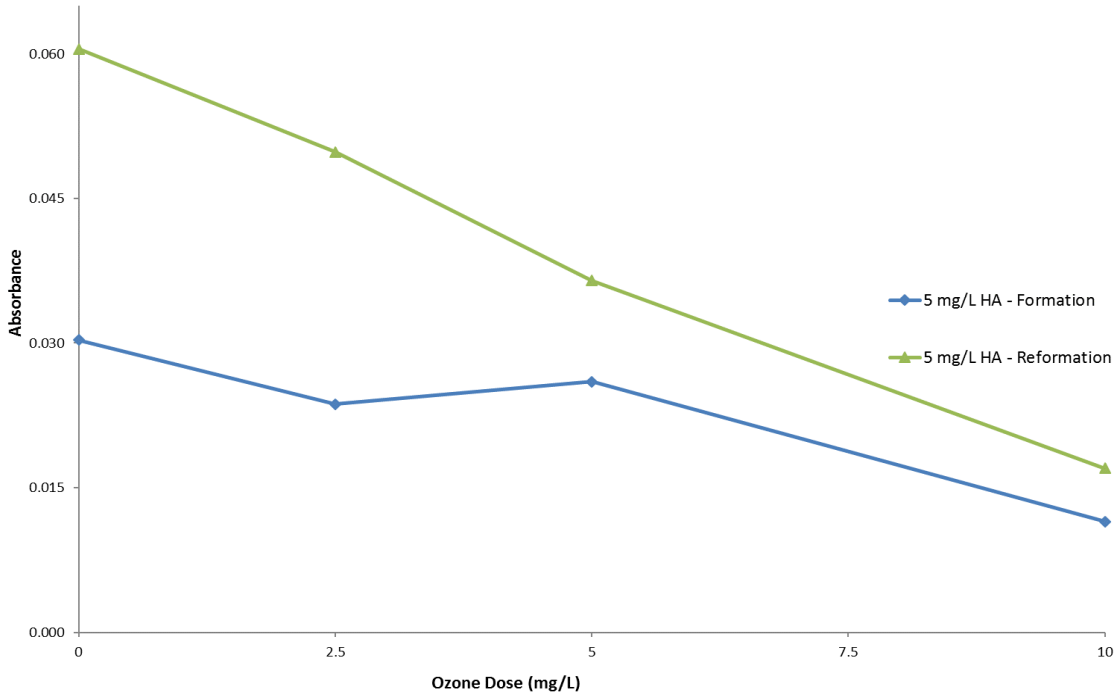

Figure 3.159. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl

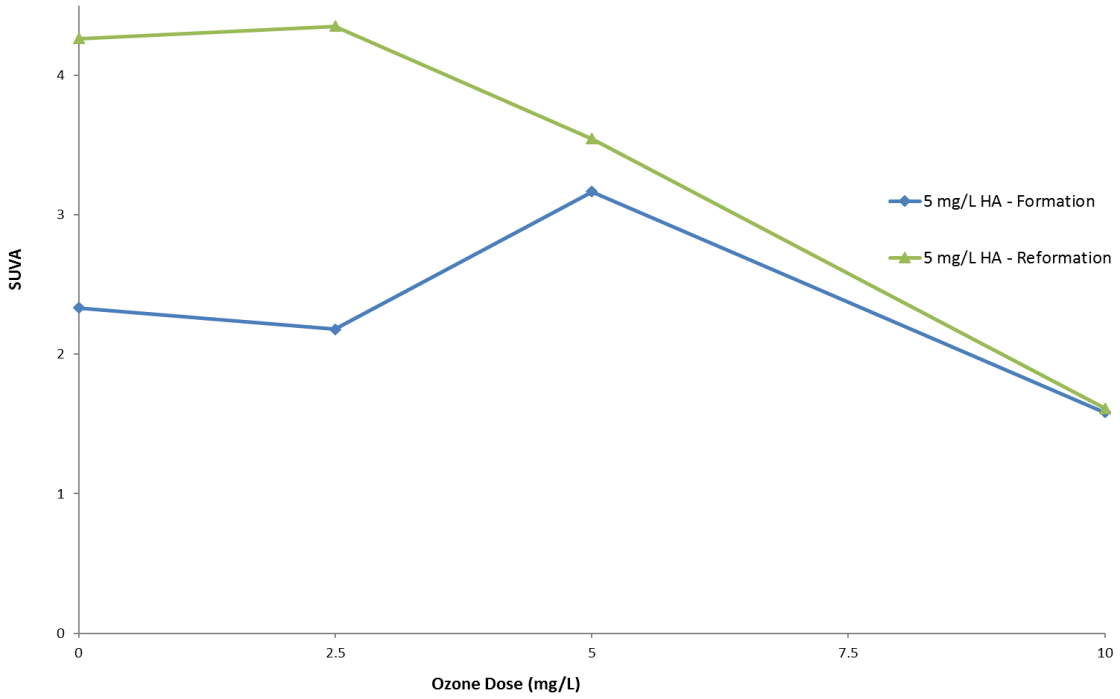

Figure 3.160. SUVA after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl

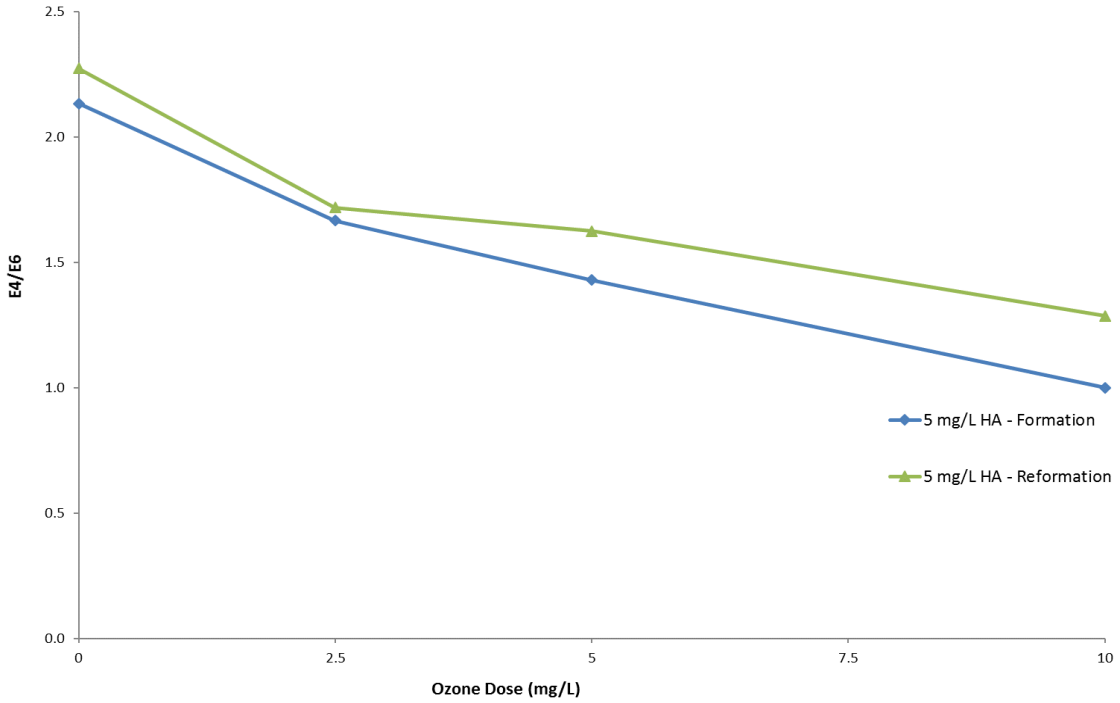

Figure 3.161. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with PACl

tion. The superiority of PACl's performance can be attributed to its pre-hydrolysed Al species content.

Figure 3.160 illustrates the change of specific UV absorbance in the supernate after flocculation as function of increasing pre-ozone dose. Residual SUVA values remained within the intermediate range up to 5 mg/L pre-ozone dose and exhibited an increasing trend. This was due to the fact that the decrease in residual UV_{254} absorbance was less pronounced than the reduction in residual dissolved organic carbon, suggesting the presence of aromatic structures in the supernate capable of absorbing UV radiation at 254 nm. At relatively low pre-ozonation doses, high molecular weight organic matter was partially oxidised into smaller molecular fragments, which likely exhibited enhanced affinity for complexation with PACl, thereby facilitating more efficient removal. Ozonation might have cleaved aliphatic chains, the resulting intermediate molecular weight fractions retained UV-absorbing aromatic functionalities, as evidenced by the modest reduction in residual UV_{254} absorbance (Figure 3.159). It is likely that these ozonation products, characterised by reduced molecular size (Figure 3.161), were less amenable to interact with the coagulant and they were not removed as much, as reflected in the elevated residual SUVA value (Figure 3.160). A further increase in the pre-ozonation dose to 10 mg/L might have led to over-oxidation of high molecular weight organic matter, resulting in cleavage of most of the aromatic rings, as evidenced by the pronounced reductions in both residual UV_{254} absorbance and residual SUVA values. The observed gradual decrease in the E_4/E_6 ratio suggests that relatively larger molecular structures remained in the supernate, potentially due to their limited reactivity with the coagulant and removal via flocculation. Although truncated by oxidation, smaller organic molecules retaining aromatic character might have been less efficiently removed compared to their non-aromatic analogues. Interestingly, despite the reduction in floc size with increasing pre-ozone dose, organic carbon removal improved. This may be explained by the formation of smaller, more reactive organic molecules upon ozonation, which exhibited enhanced affinity for PACl. These molecules likely adsorbed onto floc surfaces or formed complexes, leading to the generation of a high number of small flocs with greater total surface area, thereby facilitating more effective removal. Higher residual SUVA values were obtained with PACl, that is because the reduction in residual dissolved organic carbon concentration

with PACl was more pronounced than the decrease in residual UV_{254} absorbance. Unlike the trend observed with alum, the E_4/E_6 ratio gradually declined with increasing pre-ozonation dose, suggesting that the fraction of organic matter remaining after flocculation comprised relatively larger molecular structures. These findings imply that as the pre-ozone dose was increased, more amount of smaller organic molecules were generated and they were more prone to interact with PACl compared to relatively larger molecules, also better removed by PACl than alum, likely because of highly charged pre-hydrolysed Al species content of PACl. This is also the probable reason of larger floc formation with PACl.

3.3.5.2. Removals in synthetic raw waters containing 10 mg/L humic acid

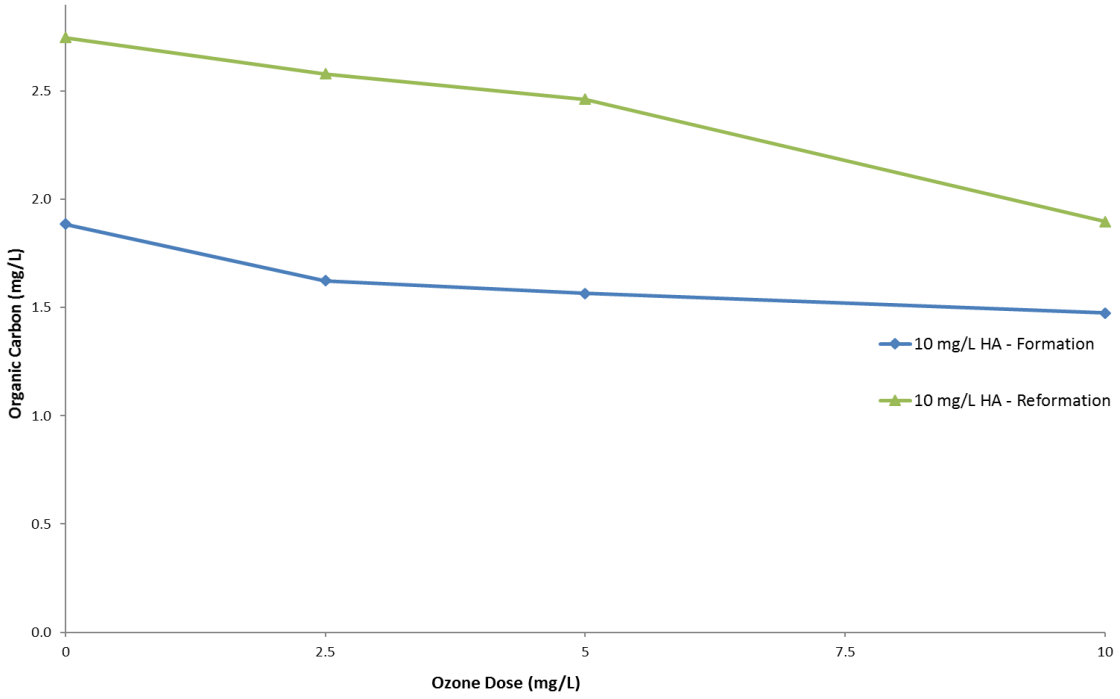

Figure 3.162. Residual TOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl

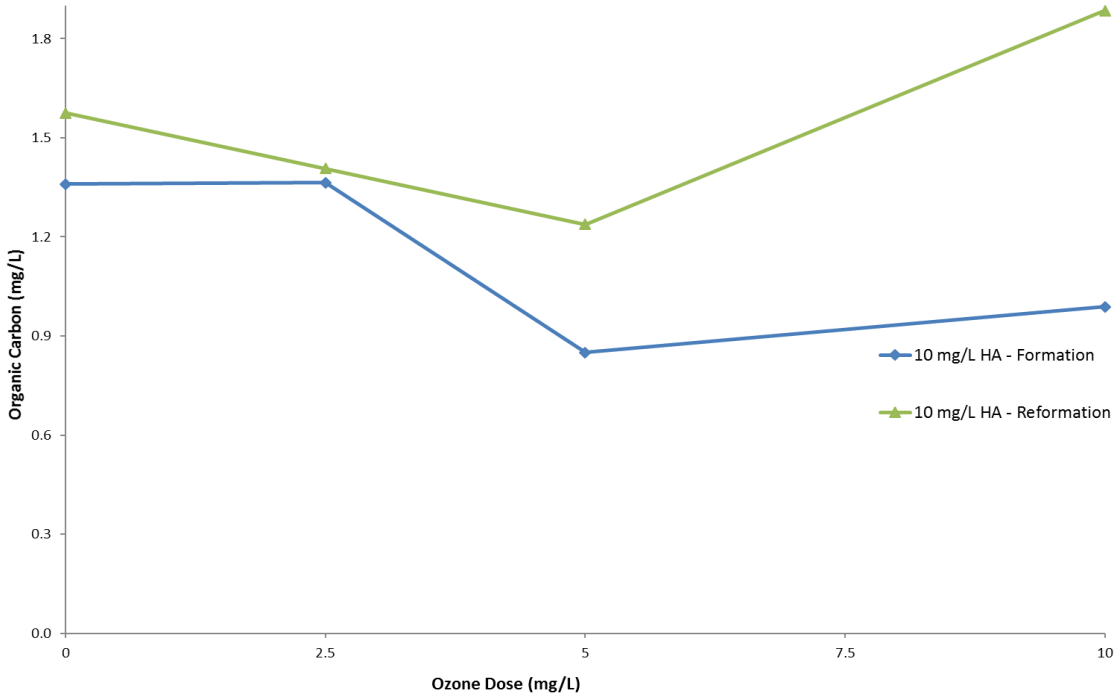

Figure 3.163. Residual DOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl

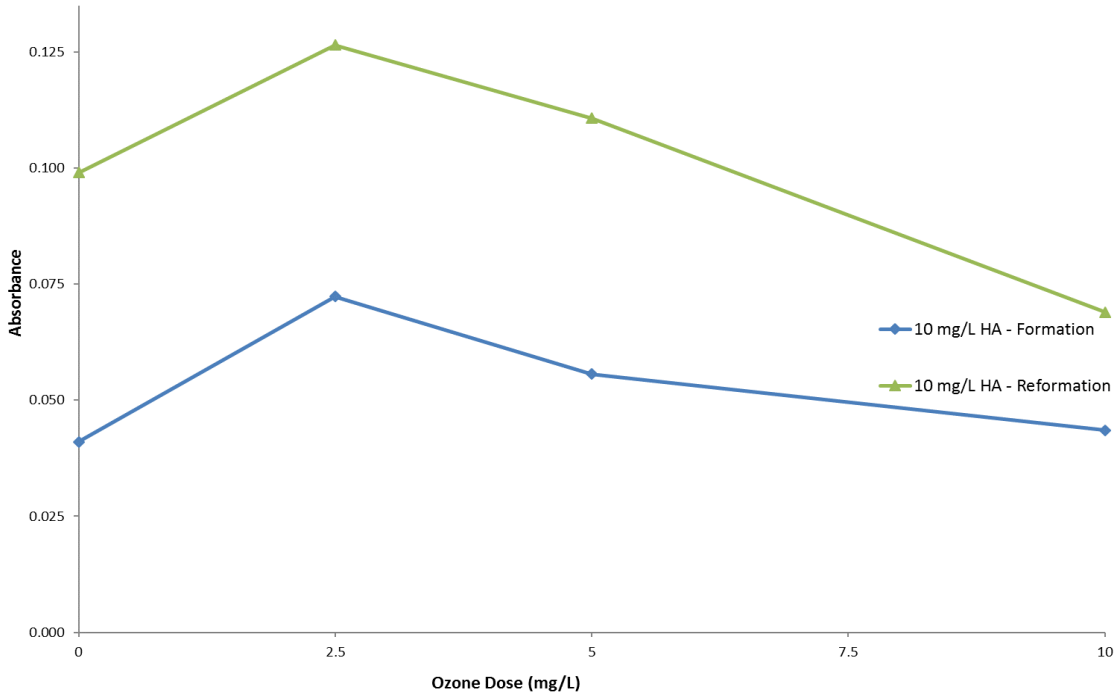

Figure 3.164. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl

Residual total organic carbon concentrations measured in the supernates after flocculation of pre-ozonated suspensions exhibited a decreasing trend with increasing ozone dose when the humic acid concentration in raw water was increased from 5 mg/L to 10 mg/L (Figure 3.162). Residual dissolved organic carbon initially increased slightly upon pre-ozonation, declined at 5 mg/L ozone dose, and then increased again when the pre-ozone dose was elevated to 10 mg/L (Figure 3.163). Residual UV_{254} absorbance first increased upon pre-ozonation and then decreased as the pre-ozone dose was increased (Figure 3.164). It is plausible that pre-ozonation of 10 mg/L humic acid with 2.5 mg/L ozone generated a greater quantity of low molecular weight organic compounds compared to the pre-ozonation of 5 mg/L humic acid. These smaller molecules likely exhibited higher affinity toward PACl, thereby were flocculated more effectively and removed better subsequently. In contrast, intermediate molecular weight compounds retaining aromatic character were either less amenable to flocculation or were kinetically disadvantaged in competing for interaction with the coagulant, relative to the more reactive, oxidised low molecular weight species. This competitive limitation may account for the observed increases in residual dissolved organic carbon, residual UV_{254} absorbance, and residual SUVA values. At 5 mg/L pre-ozone dose, further molecular fragmentation may have occurred, generating smaller compounds that absorbed less UV_{254} radiation, yet still exhibited some degree of aromaticity, suggesting that non-aromatic, oxidised organics were removed more efficiently. This observation may be explained by partial ring-opening of aromatic structures, reducing their UV_{254} absorbance and enhancing their amenability to coagulation. When the pre-ozone dose was further increased to 10 mg/L, an increase in residual dissolved organic carbon concentration was detected, whilst residual UV_{254} absorbance and residual SUVA values declined. This much ozone might have oxidised high molecular weight organic matter excessively, leading to the breakdown of most of the aromatic rings, which resulted in the observed reductions in residual UV_{254} absorbance and residual SUVA. The concurrent decrease in the E_4/E_6 ratio suggests the presence of larger molecular structures, possibly consisting of linearised fragments resulting from aromatic ring cleavage. Nevertheless, over-oxidation might have generated an abundance of soluble, low molecular weight organics that exceeded the charge neutralisation capacity of the applied coagulant dose. These smaller compounds might have interacted with PACl to

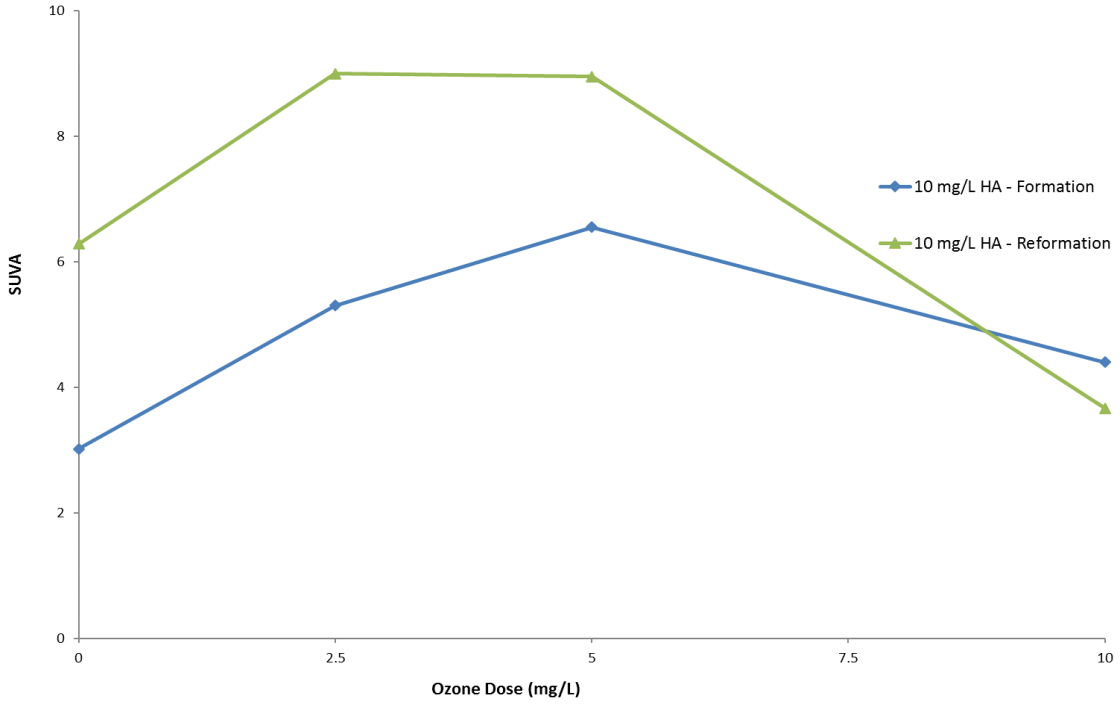

Figure 3.165. SUVA after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl

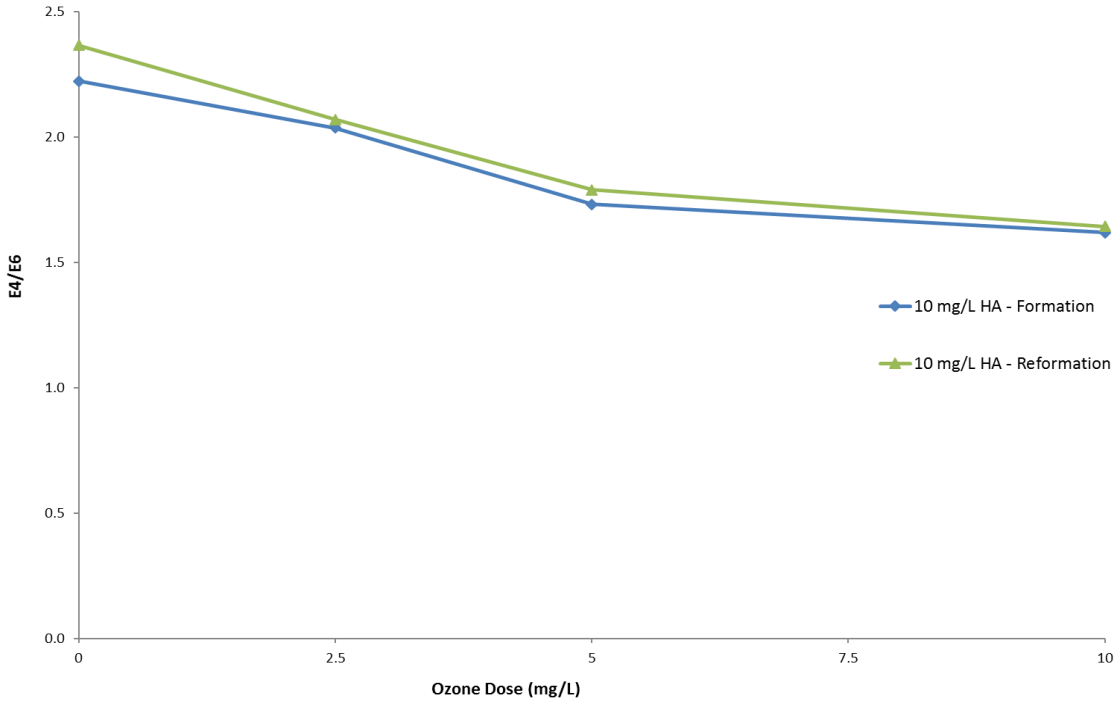

Figure 3.166. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with PACl

form fine flocs, whilst relatively larger, less reactive species remained in suspension, culminating in elevated residual dissolved organic carbon concentration in the supernate.

Residual total and dissolved organic carbon concentrations, along with residual UV_{254} absorbance, exhibited similar trends to those observed following alum flocculation, with lower values when PACl was used (Appendix Figures 30-32). This observation aligns with the finding that PACl produced larger flocs, suggesting superior flocculation performance relative to alum. Moreover, in flocculation of waters containing 10 mg/L humic acid, PACl appeared to be less affected by pre-ozonation. The enhanced performance of PACl is likely attributable to the presence of pre-hydrolysed, highly charged aluminium species that promote more efficient interaction with organic matter.

Higher residual SUVA values were observed with PACl, which can be attributed to the more substantial reduction in residual dissolved organic carbon concentration compared to the decrease in residual UV_{254} absorbance. In contrast to the trend observed with alum, the E_4/E_6 ratio progressively decreased with increasing pre-ozone dose, suggesting that the fraction of organic matter remaining after flocculation predominantly consisted of relatively larger molecular structures. These findings indicate that increasing the pre-ozone dose led to the formation of a greater proportion of low molecular weight organic compounds, which exhibited higher affinity toward PACl than high molecular weight organics, and were consequently removed more effectively by PACl than by alum. The superior performance of PACl is likely attributable to the presence of highly charged, pre-hydrolysed aluminium species in it, which may also explain the formation of larger flocs observed with this coagulant.

3.3.5.3. Removals in synthetic raw waters containing 20 mg/L humic acid

Figures 3.167 and 3.168 display the changes of residual total organic carbon and dissolved organic carbon concentrations after alum flocculation of synthetic raw water containing 20 mg/L humic acid ozonated with 2.5, 5, and 10 mg/L ozone prior to flocculation, respectively. Residual total organic carbon concentration exhibited an in-

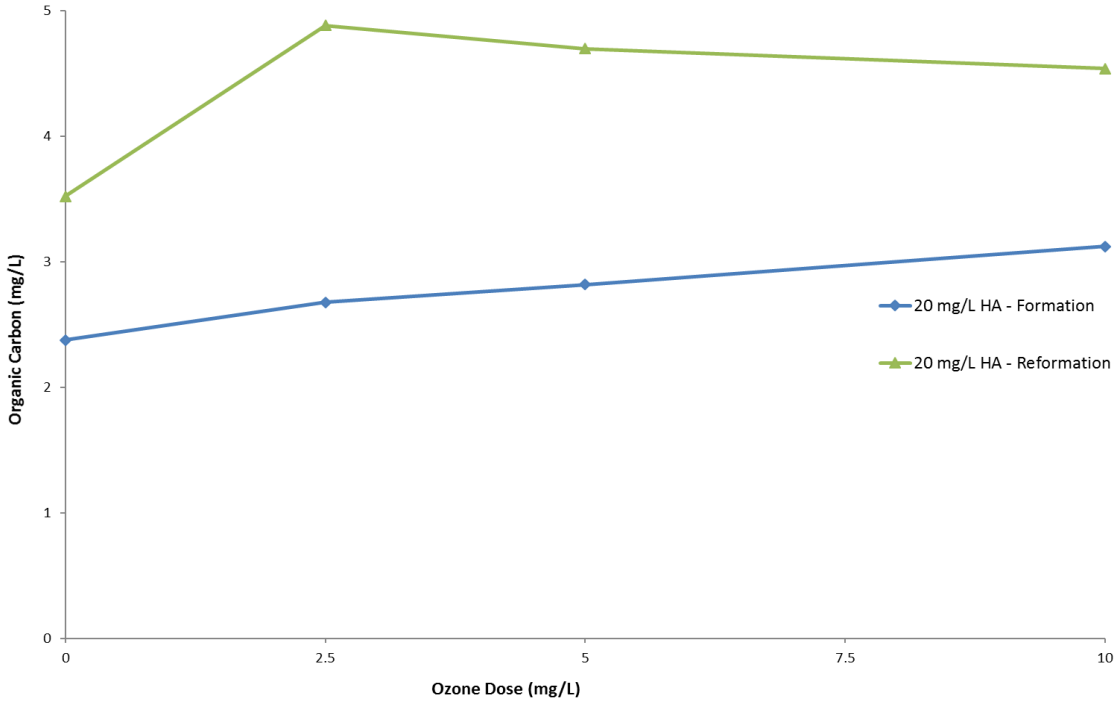

Figure 3.167. Residual TOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl

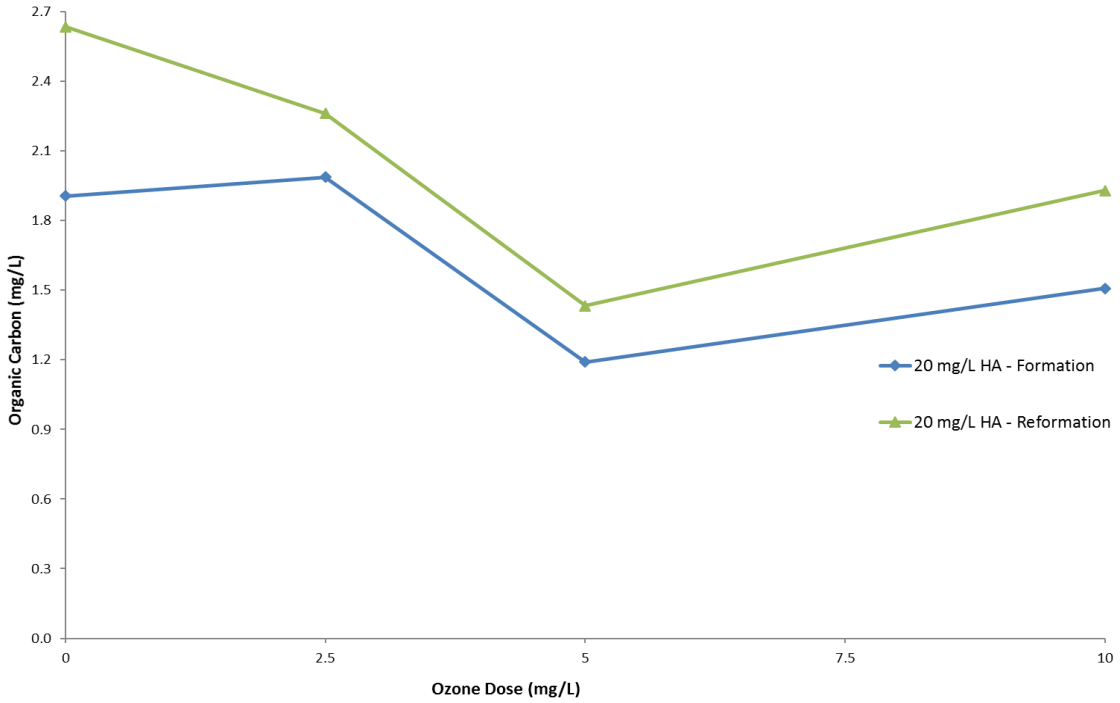

Figure 3.168. Residual DOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl

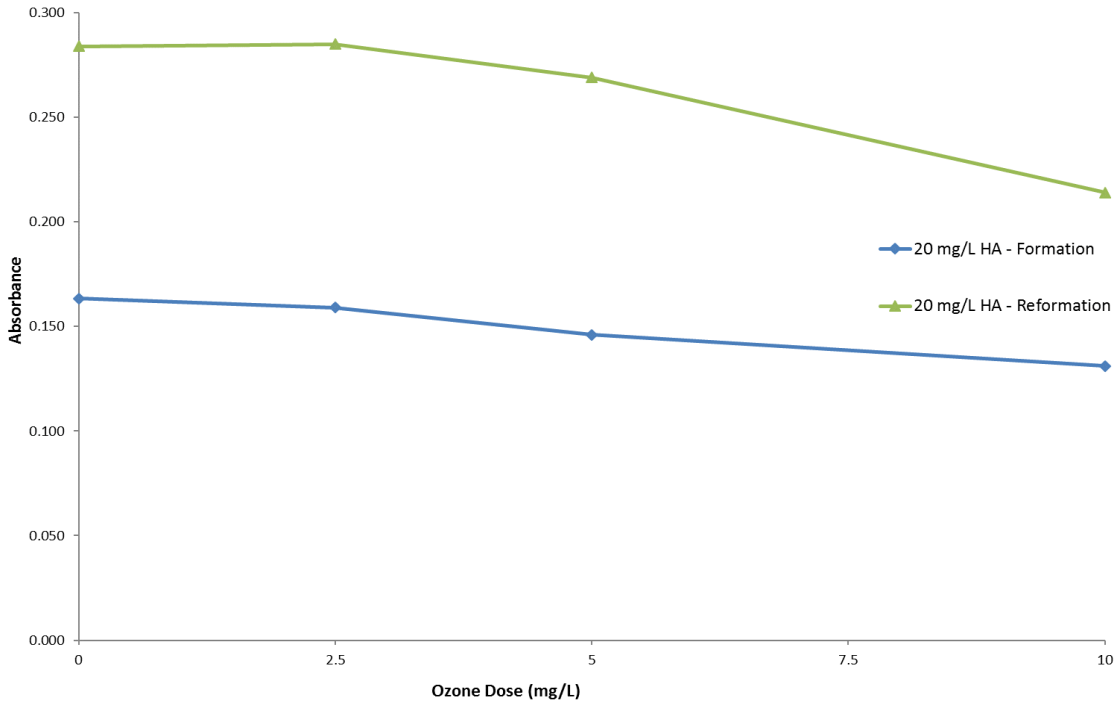

Figure 3.169. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl

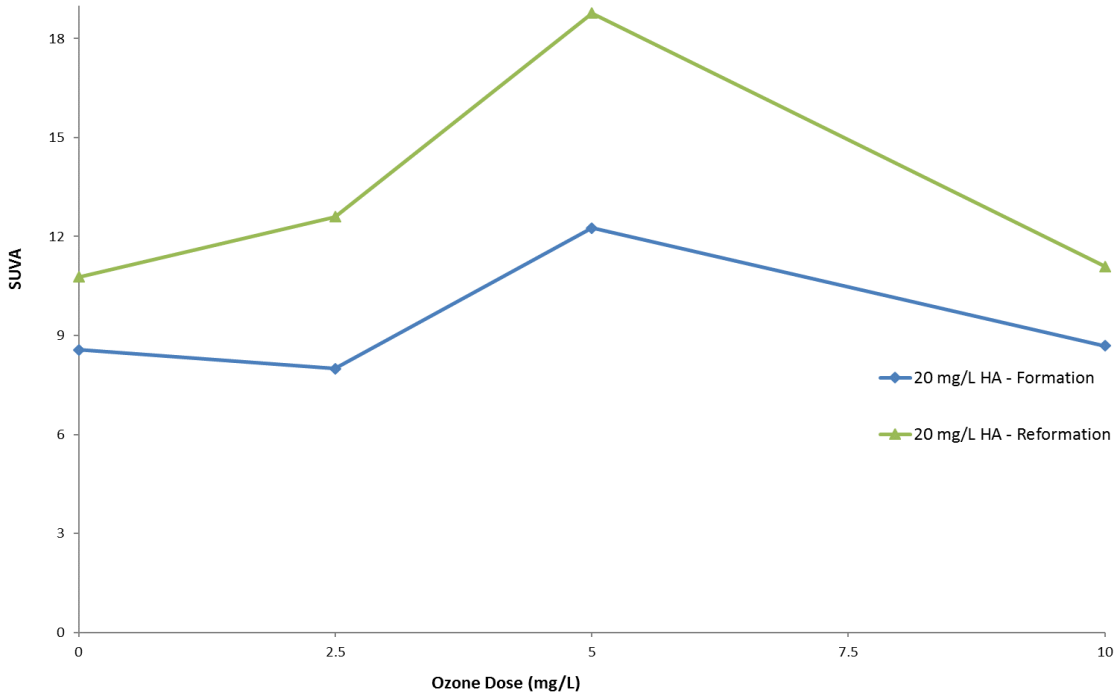

Figure 3.170. SUVA after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl

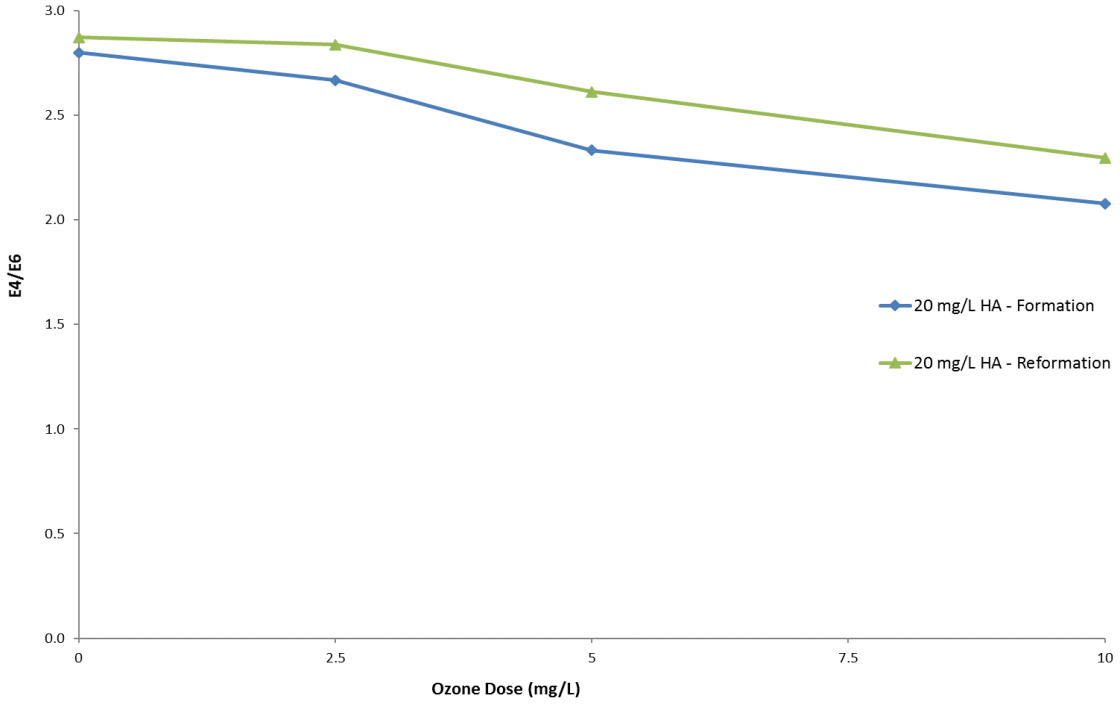

Figure 3.171. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with PACl

creasing trend with increasing pre-ozonation dose. Residual dissolved organic carbon concentration initially increased slightly upon the application of the lowest ozone dose (2.5 mg/L), decreased at 5 mg/L, and subsequently increased again at 10 mg/L. Residual UV_{254} absorbance demonstrated a slightly decreasing trend with increasing pre-ozone dose (Figure 3.169). Following the lowest ozone dose (2.5 mg/L), the slight increase in residual dissolved organic carbon concentration can be attributed to the formation of both low molecular weight and intermediate molecular weight compounds. Whilst low molecular weight organics, which were likely more reactive and less aromatic, exhibited higher affinity for PACl and were effectively removed as small flocs, intermediate molecular weight organics retaining aromatic structures were less efficiently flocculated (SUVA value indicates presence of aromaticity). Larger size molecules generated by pre-ozonation were probably abundant in concentration than smaller size ones and since they were not removed as efficiently, residual total organic carbon concentration was measured to increase. The moderate decrease in residual UV_{254} absorbance may indicate that PACl was more successful in flocculating those intermediate molecular weight

organics than alum. At the 5 mg/L pre-ozone dose, the higher abundance of low molecular weight organics enhanced interaction with PACl, improving dissolved organic carbon removal. However, the presence of oxidised intermediate molecular weight compounds with residual aromatic character still contributed aromaticity (SUVA was higher than 4), indicating incomplete removal of these species. This much ozone dose probably cleaved some aromatic rings, leading to reduced concentration of larger organics retaining some aromatic structures, hence the observed decrease in residual UV_{254} absorbance. It is likely that these molecules are also not as prone as oxidised smaller molecules to interact with the coagulant, leading to the observed higher residual total organic carbon concentration. This level of ozonation might have induced excessive oxidation of high molecular weight organic matter, leading to extensive cleavage of aromatic structures and consequently resulting in the observed decrease in residual UV_{254} absorbance and residual SUVA value. Nevertheless, residual SUVA remained above 4 L/mg·m, implying the persistence of aromaticity. The simultaneous decline in the E_4/E_6 ratio implies the presence of relatively larger molecular structures, probably composed of linearised fragments derived from aromatic ring disruption. Nonetheless, on further increasing the pre-ozone dose, over-oxidation might have generated a substantial concentration of soluble, low molecular weight organic species that surpassed the charge neutralisation capacity of the applied coagulant. These smaller compounds may have preferentially interacted with PACl to form fine flocs, whereas the remaining larger and less reactive organic fractions persisted in the aqueous phase, thereby contributing to the elevated residual organic carbon concentrations measured in the supernate.

When the performances of the two coagulants are compared, lower residual values were measured when PACl was used (Appendix Figures 35-37). This observation is consistent with the finding that PACl generated larger flocs, indicating superior flocculation efficiency compared to alum. In particular, for waters containing 20 mg/L humic acid, PACl appeared less susceptible to the effects of pre-ozonation. This enhanced performance is likely attributable to the presence of highly charged, pre-hydrolysed aluminium species in PACl, which facilitate more efficient interactions with organic matter.

Slightly higher residual SUVA values were observed in PACl-treated samples, which can be ascribed to a more pronounced reduction in residual dissolved organic carbon than in UV_{254} absorbance. Unlike the trend observed with alum, the E_4/E_6 ratio declined gradually with increasing pre-ozone dose, suggesting that the remaining organic fraction after flocculation was dominated by relatively larger molecular structures. These findings imply that higher pre-ozone doses led to increased generation of low molecular weight organic species, which exhibited greater affinity toward PACl than their high molecular weight counterparts and were more effectively removed. The superior removal efficiency and formation of larger flocs are both likely consequences of the unique chemical characteristics of PACl, particularly its content of pre-hydrolysed, polymeric aluminium species with high charge density. There are many reports in the literature on the higher performance of polymeric inorganic coagulants like PACl over monomeric ones like alum, just to give a recent example; Kong et al. (2021) reported that larger flocs were formed and better humic acid removal was achieved with a commercial PACl compared to $AlCl_3$ at pH ≥ 7, with PACl less affected by the changes in pH.

Numerous studies in the literature have reported contradicting findings regarding the impact of pre-ozonation on the removal of organic matter (Xie et al., 2016). Whilst some researchers observed that pre-ozonation impaired organic matter removal (Schneider and Tobiason, 2000; Hailong et al., 2007; Bose and Reckhow, 2007), others reported enhanced removal following ozonation (Marhaba and Pipada, 2000; Singer et al., 2003; Yükselen et al., 2007; Pei et al., 2007; Jasim et al., 2008). Still, some studies indicated that the effect of ozonation is highly dependent on the initial concentration of organic matter (O'Melia et al., 1999) or on the applied ozone dose (Singer, 1990; Edwards et al., 1993). For example, Edwards et al. (1993) noted that pre-ozonation improved removal by directly degrading organic matter through mineralisation, volatilisation, or stripping. However, they also highlighted that ozonation could decrease the surface charge of flocs formed during coagulation with hydrolysing metal salts, thus reducing the adsorptive removal of anionic organic compounds and potentially leading to the formation of more stable, less settleable flocs, which were outcomes that could hinder removal relative to unozonated systems. Edwards et al. (1994) stated, “Because ozonation could, in theory, either increase or

decrease NOM removal by either sorption or precipitation, it is difficult to predict the overall effect of NOM behavior in a coagulation process. However, in practice, when alum or $FeCl_3$ is used alone, ozonation generally increases or has no effect on coagulant demand". Schneider and Tobiason published an article in 2000 with a punchline "Depending on the type of coagulant used, pre-ozonation can help or hinder the removal of organic matter". They reported that when alum is used as a coagulant, pre-ozonation led to increases in settled water turbidity, total organic carbon, and dissolved organic carbon at the conditions tested (0.5 and 0.8 mg/L ozone) whereas when polyaluminium chloride was used as the coagulant for several natural waters, pre-ozonation aided turbidity and dissolved organic matter removal in one instance and hindered removal of turbidity and organic materials in another instance. They hypothesised that pre-ozonation reduced the surface charge of particulates, leading to better coagulation by charge neutralisation.

In a recent review article, it was stated that there were little consistency in the conditions used in flocculation research, complained about lack of crucial information related to important parameters like the nature or source of the NOM, ionic strength of the water, sometimes even pH and temperature and lack of standard conditions, which all made it quiet difficult to compare flocculation research in one class, let alone to compare between different combinations (Dayarathne et al., 2021). These contradictory findings may largely stem from variations in the characteristics of the raw waters used across different studies. Waters sampled from diverse geographic regions and climatic conditions can exhibit significant variability in the composition and reactivity of natural organic matter. Parameters such as molecular weight distribution, structural complexity, charge density, and acidity of organic substances are known to fluctuate seasonally and geographically (Edzwald, 1993; Popov et al., 2020). Consequently, humic substances originating from different sources may not respond uniformly to ozonation (Gilbert, 1988), potentially explaining the contradicting results reported in the literature.

In a study, the results indicated that pre-treatment of natural water (containing low calcium hardness and hydrophobic humic substances) with increasing ozone doses led to a decline in total organic carbon removal rates during the subsequent coagulation process. Notably, the highest total organic carbon removal rate (33%) was achieved in

the absence of ozonation, through flocculation alone. This adverse effect of ozonation was less pronounced in synthetic solutions containing higher levels of calcium hardness and humic substances (Rodríguez et al., 2012).

Shen et al. (2020) studied flocculation of different model NOM concentrations (as humic acid concentration) of 5, 10, 20, 50 and 100 mg/L with PAC (polyaluminium chloride), PAC-PolyDMDAAC mixture and PAC + PolyDMDAAC. They reported that turbidity removal was deteriorated with increasing NOM concentration with PAC and PAC-PolyDMDAAC mixture where turbidity removal got even under 0% (around -20% and -30%). With PAC, dissolved organic carbon removal first increased to about 50% at 10 mg/L and 20 mg/L NOM concentrations, then reduced to around 30% at 50 mg/L NOM concentration and a little lower at 100 mg/L. It was similar with PAC- PolyDMDAAC mixture, only removals were little higher. When PAC + PolyDMDAAC dual coagulant was added, dissolved organic carbon removal increased with increasing NOM concentration with the highest removal of about 65% at 50 mg/L NOM concentration, then decreased to around 45% at 100 mg/L NOM concentration. Those removals were not very consistent with floc sizes; when PAC was used, from largest to smallest floc sizes were measured at 20 mg/L, 10 mg/L and 50 mg/L (similar sizes), 5 mg/L and 100 mg/L NOM concentrations, when PAC-PolyDMDAAC mixture was used from largest to smallest floc sizes were at 20 mg/L, 50 mg/L, 10 mg/L, 5 mg/L and 100 mg/L NOM concentrations, and with PAC + PolyDMDAAC dual coagulant system similar largest floc sizes were observed at three NOM concentrations (20 mg/L, 50 mg/L, and 10 mg/L), smaller at 5 mg/L and the smallest at 100 mg/L NOM concentration. If emphasis is placed on PAC flocculation, dissolved organic carbon removals from highest to lowest were at 10, 20, 5, 50, 100 mg/L NOM concentrations whereas similar largest floc sizes were measured at 20 mg/L, 10 mg/L and 50 mg/L NOM concentrations.

Pre-ozonation was suggested to be able to enhance the removal of dissolved organic matter in flocculation (Farvardin and Collins, 1989; Sadrnourmohamadi and Gorczyca, 2015) when it produces some hydrophobic neutral and intermediate molecular weight dissolved organic matter at appropriate doses of ozone (Yan et al., 2007). Ozone might favour flocculation when oxygenated functional groups, such as

carboxylic and hydroxyl groups, are produced in pre-ozonation, which then can interact and form complexes with hydrolysing coagulants in the subsequent flocculation process (Reckhow et al., 1986). The favourable ozone doses in those researches were criticised for being low (Liu et al., 2021). For instance, a low dose of pre-ozone (1.0 mg/L) was claimed to promote, whereas a higher dose (2.0 mg/L) was claimed to hinder the removal of organic matter (Yan et al., 2007). Similar findings were reported in more recent works; a pre-ozone dose of 3.51 mg/L was recommended for optimum removal of dissolved organic carbon, whilst a higher dose of 6.63 mg/L was reported to be avoided for natural organic matter removal (Chiang et al., 2009). Van Geluwe et al. (2011) stated that the dosing quantity of ozonation was very important for the combined ozonation and flocculation process. At higher ozone dosing quantities, the NOM was oxidised into hydrophilic and low molecular weight compounds, which were more difficult to aggregate in the flocculation process, but at a lower dosing quantity, the ozonation process produced hydrophobic neutral compounds, which could be efficiently removed in the flocculation process. Hu et al. (2021) reported that removal efficiency of humic acid could be improved by pre-ozone doses lower than 3.85 mg/L. It was claimed that at high ozone doses more amounts of hydrophilic and lower molecular weight organic matter were generated, which were amenable to low capability of flocculation and complexation, leading to the inhibition of the overall performance of pre-ozonation followed by flocculation (Novotna et al., 2020; Liu et al., 2021; Jin et al., 2023). Hydrophobic organic matter with intermediate molecular weight and proper structure such as aromatic structures with carboxyl or hydroxyl groups (which were products of ozonation with lower doses) were reported to facilitate flocculation (Yan et al., 2007; Song et al., 2019). The findings of this research align with those of the reports mentioned above: oxidation of relatively low concentrations of humic acid with lower pre-ozone doses enhanced the removal of organic carbon in flocculation, whereas oxidation of higher concentrations of humic acid with elevated pre-ozone doses impeded organic carbon removal.

4. CONCLUSION

This study systematically investigated the impact of pre-ozonation on the flocculation performance and organic carbon removal efficiency in synthetic waters containing varying concentrations of humic acid (5, 10, and 20 mg/L), using two widely employed coagulants: aluminium sulphate (alum) and polyaluminium chloride (PACl) under different pre-ozone doses (0, 2.5, 5, and 10 mg/L). Floc growth was dynamically monitored with an on-line monitoring device, the Photometric Dispersion Analyser. Multiple parameters, including relative floc size, residual organic carbon concentrations (total and dissolved), residual UV_{254} absorbance, residual Specific UV Absorbance (SUVA), and E_4/E_6 ratio, were measured to elucidate the effects of varying ozone doses (0, 2.5, 5, and 10 mg/L). The findings offer valuable insights into the complex interactions between the pre-oxidation process and the physicochemical characteristics of flocculation, particularly within the sweep flocculation regime.

The flocculation behaviour exhibited by alum and PACl followed a similar trend; increasing humic acid concentration resulted in the formation of larger flocs with both of the coagulants. This can be primarily attributed to enhanced collision efficiency among particles. When there are more particles in suspension there is more opportunity for more number of collisions, thus aggregation of those particles which come into contact with each other is more possible. An additional observation supporting this interpretation is that flocculation set on earlier and time to reach a steady-state fully grown floc size distribution was shorter as the humic acid concentration was increased. In other words, it took longer to complete flocculation as the humic acid concentration was decreased.

In every humic acid concentration, compared to alum, larger flocs were formed with PACl; this is attributed to PACl's highly positively charged pre-hydrolysed Al species content, which enhanced its flocculation efficiency by promoting stronger interactions with negatively charged organic matter. The initiation of floc growth was accelerated, and the time to attain a steady-state floc size distribution was reduced when PACl was used as coagulant or it can be said that it took longer with alum to complete flocculation compared to PACl.

Floc breakage was irreversible with both coagulants; flocs, once exposed to high shear rates, broke up and when the mixing rate was restored to the low speed before breakage, flocs could only regrow to some extent of their size before rupture. This is typical of sweep flocculation because the nature of aggregation is entrapment of organic molecules in the growing amorphous metal hydroxide precipitate rather than electrostatic attraction.

In all pre-ozonation scenarios, for both coagulants, an increase in humic acid concentration resulted in higher residual total and dissolved organic carbon concentrations, as well as increased residual UV_{254} absorbance values. At first glance, this may seem contradictory, especially considering that larger flocs were also formed under these conditions. However, this disappears when one considers that increasing humic acid concentrations results in a greater load of organic matter to be removed with the same coagulant dose. When the data are assessed in terms of removal efficiency (i.e., percent removed), a trend of improved removal efficiencies of both total and dissolved organic carbons with increasing humic acid concentration attracts attention. This aligns well with the observation of larger floc formation, which is likely due to the higher frequency of particle collisions at higher humic acid concentrations. Although organic carbon removal efficiency generally increased with increasing humic acid concentration, in waters containing 20 mg/L initial humic acid concentration, the enhancement in removal efficiency diminished when pre-ozonated raw waters were used. Specifically, increasing the pre-ozonation dose to 5 mg/L resulted in little to no improvement, and a further increase to 10 mg/L led to a decline in removal efficiency with alum and virtually no change with PACl, indicating that PACl is less affected by pre-ozonation compared to alum. The removal efficiency of UV absorbance at 254 nm improved with increasing humic acid concentration in unozonated waters; however, this trend reversed upon the application of pre-ozonation. These findings suggest that pre-oxidation of humic acid with increasing ozone dose altered the chemical characteristics of the organic matter.

In the perspective of increasing pre-ozone dose, examining the dynamic monitoring of floc formation showed that increasing pre-ozone dose led to gradual reduction in floc size in all three humic acid concentrations with both of the coagulants.

The onset of flocculation was delayed and it took longer to reach a steady-state size distribution of fully grown flocs as the pre-ozone dose was increased. These findings suggest that increasing pre-ozone dose hindered floc formation. Larger flocs were formed with PACl, and larger flocs regrew after breakage when PACl was used, as well. The onset of flocculation was earlier and steady-state floc size distribution of fully grown flocs was reached more quickly with PACl. Consistent with floc size data, lower residual organic carbon concentrations and UV_{254} absorbance were measured after each flocculation experiment performed with PACl. Compared to alum, PACl showed a higher performance and seemed to be affected less by pre-ozonation. These must be owed to its highly charged pre-hydrolysed aluminium species content.

When the humic acid concentration was 5 mg/L, with both of the coagulants, decreasing trends in residual total and dissolved organic carbon concentrations were observed with increasing pre-ozone dose. Residual UV_{254} absorbance exhibited a similar trend in general, as well. Residual SUVA values remained in the intermediate range and showed an increasing trend up to 5 mg/L pre-ozonation dose. This was because residual UV_{254} absorbance did not decrease as much as residual dissolved organic carbon concentration, suggesting the persistence of aromatic structures in the supernate capable of absorbing UV radiation. Relatively low pre-ozone dose partially oxidised high molecular weight organics into smaller fragments with higher affinity for coagulants, enhancing removal efficiency. However, increasing the ozone dose to 10 mg/L likely led to over-oxidation, breaking down most of the aromatic rings and reducing both residual UV_{254} absorbance and residual SUVA, as well as producing larger, less reactive organic structures, as reflected in a decreasing residual E_4/E_6 ratio. Despite floc sizes decreasing with higher ozone doses, organic carbon removal improved, likely due to the formation of small, highly reactive molecules that interacted more efficiently with the coagulant and formed numerous small flocs with greater overall surface area. These reactive organics likely adsorbed onto floc surfaces or formed complexes, contributing to enhanced removal even in the presence of smaller flocs. When comparing coagulants, higher residual SUVA values were observed in PACl-treated samples because the reduction in residual dissolved organic carbon concentration was greater than the decrease in residual UV_{254} absorbance. Additionally, unlike alum, the residual E_4/E_6 ratio consistently decreased with increasing ozone dose

in PACl experiments, suggesting that larger molecular structures dominated the residual organics. This implies that the smaller organic molecules generated via ozonation were more effectively removed by PACl than by alum, most likely due to PACl's highly charged, pre-hydrolysed aluminium species. This also explains the larger floc sizes observed with PACl. Overall, PACl demonstrated greater resilience to the effects of pre-ozonation and superior performance in removing oxidised organic matter compared to alum.

Pre-ozonation of 10 mg/L humic acid with 2.5 mg/L ozone likely produced a greater quantity of low molecular weight organic compounds than the pre-ozonation of 5 mg/L humic acid. These smaller, more reactive molecules probably exhibited higher affinity toward the coagulants, leading to more effective flocculation and removal. In contrast, intermediate molecular weight compounds retaining aromatic structures were either less amenable to flocculation or kinetically disadvantaged in competing for coagulant interaction, relative to their smaller, oxidised counterparts. This competitive limitation may explain the observed increases in residual dissolved organic carbon, residual UV_{254} absorbance, and residual SUVA values. At 5 mg/L pre-ozone dose, further molecular fragmentation might have occurred, generating smaller compounds that absorbed less UV_{254} radiation, but still exhibited some degree of aromaticity, suggesting that non-aromatic, oxidised organics were removed more efficiently. It is likely that this much of ozone dose cleaved additional aromatic rings, resulting in reduced UV_{254} absorbance measured in the supernatant of settled waters. The oxidised organic molecules, now containing fewer aromatic structures, were more effectively removed, as reflected by the lower residual dissolved organic carbon concentrations. When the pre-ozone dose was further increased to 10 mg/L, an increase in residual dissolved organic carbon concentration was detected, whilst UV_{254} absorbance and SUVA values declined. This much of ozone might have oxidised high molecular weight organic matter excessively, leading to the breakdown of most of the aromatic rings, which resulted in the observed reductions in residual UV_{254} absorbance and residual SUVA. The concurrent decrease in the E_4/E_6 ratio suggests the presence of larger molecular structures, possibly consisting of linearised fragments resulting from aromatic ring cleavage. Nevertheless, over-oxidation might have generated an abundance of soluble, low molecular weight organics that exceeded the charge

neutralisation capacity of the applied coagulant dose. These smaller compounds might have interacted with the coagulants to form fine flocs, whilst relatively larger, less reactive species remained in suspension, resulting in increased residual dissolved organic carbon concentration in the supernate.

When synthetic raw waters containing 20 mg/L humic acid were ozonated and then flocculated, residual total organic carbon concentration increased as the pre-ozonation dose was increased. Residual dissolved organic carbon concentration on the other hand, showed a non-linear pattern: a slight increase at 2.5 mg/L pre-ozone dose, followed by a decrease at 5 mg/L, and another increase at 10 mg/L. Residual UV_{254} absorbance gradually decreased with increasing ozone doses when PACl was used, whereas it increased when alum was used. The slight increase in residual dissolved organic carbon concentration at 2.5 mg/L pre-ozone can be attributed to the generation of both low and intermediate molecular weight organic compounds. Whilst the low molecular weight, less aromatic fractions were likely more reactive and better removed via flocculation, the intermediate molecular weight compounds with retained aromaticity were less amenable to removal (SUVA values indicates presence of aromatic structures). Larger size molecules generated by pre-ozonation were probably abundant in concentration than smaller size ones and since they were not removed as efficiently, residual total organic carbon concentration was measured to increase. The moderate decreases in residual UV_{254} absorbance and SUVA may indicate that PACl was more successful in flocculating those intermediate molecular weight organics than alum. At 5 mg/L pre-ozone dose, lower dissolved organic carbon concentrations were observed likely due to even more generation of reactive, oxidised low molecular weight organics, which had higher affinity for the coagulants. However, SUVA values rose, implying the continued presence of aromatic structures, particularly from partially oxidised intermediate molecular weight species. This suggests that although more aromatic rings were cleaved at this dose, the resultant fragments retained some aromatic character and those intermediate molecular weight compounds retaining aromatic character were either less amenable to flocculation or were kinetically disadvantaged in competing for interaction with the coagulant, relative to the more reactive, oxidised low molecular weight species. The decline observed with PACl in the E_4/E_6 ratio whilst the E_4/E_6 ratio increased with alum points out the presence of relatively larger molecular

structures, probably composed of linearised fragments derived from aromatic ring disruption and indicates that oxidised low molecular weight organics were removed better by PACl due to its higher charged pre-hydrolysed Al species. Nevertheless, on further increasing the pre-ozone dose, over-oxidation might have generated a considerable amount of soluble, low molecular weight organic species that exceeded the charge neutralisation capacity of the applied coagulant dose. These smaller compounds may have preferentially interacted with the coagulants to form fine flocs, whereas the remaining larger and less reactive organic fractions remained in the aqueous phase, thereby contributing to the elevated residual organic carbon concentrations measured in the supernate.

Findings suggest that organic carbon concentration should be monitored in raw waters and appropriate doses of ozone should be used accordingly prior to flocculation in practice in order to prevent over-oxidation of organic carbon and consequent hinderance of its removal.

REFERENCES

Alizadeh, H. and Pawlik, M. (2024). Observation on reversibility of flocculation in fine quartz suspensions. Canadian Metallurgical Quarterly, 63, 3, 671-679.

Amirtharajah, A. and O'Melia, C. R. (1990). Coagulation Processes: Destabilization, Mixing, and Flocculation. Water Quality and Treatment (F.W. Pontius, editor), McGraw-Hill, Toronto.

Amy, G. L., Tan, L. and Davis, M. K. (1991). The effects of ozonation and activated carbon adsorption on trihalomethane speciation. Water Research, 25 (2), 191- 202.

Andelmann, J. B. (1990). Total exposure to volatile organic compounds in potable water. Significance and Treatment of Volatile Organic Compounds in Water Supplies (N. M. Ram et al., editors). Lewis Publs., Chelsea, Mich.

Au, K.-K., Yang, S. and O'Melia, C. R. (1998). Adsorption of weak polyelectrolytes on metal oxide surfaces: a hybrid SC/SF approach. Environmental Science and Technology, 32, 2900-2908.

Au, K.-K., Penisson, A. C., Yang, S. and O'Melia, C. R. (1999). Natural organic matter at oxide/water interfaces: complexation and conformation. Geochimica et Cosmochimica Acta, 63 (19-20), 2903-2917.

AWWA Committee Report (1979). Organics removal by coagulation: a review and research needs. Journal of AWWA, 71 (10), 588.

AWWA Committee Report (1989). Coagulation as integrated water treatment process. Journal of AWWA, 81 (10), 72.

Bache, D. H., Johnson, C., Papavasilopoulos, E., Rasool, E., and McGillian, F. J. (1999). Sweep coagulation: structures, mechanisms and practice. Journal of Water Supply: Research and Technology, AQUA, 48 (5), 201-210.

Bache, D. H. and Papavasilopoulos, E. N. (2003). Dewatering of alumino-humic sludge: impacts of hydroxide. Water Research, 37, 3289-3298.

Billica, J. A. and Gertig, K. R. (2000). Optimization of a Coagulation Process to Treat High TOC, Low Alkalinity Water and Its Impact on Filtration Performance. In: *Water Quality Technology Conference*. 5-9 November. Salt Lake City, Utah, USA.

Boller, M. (1993). Removal of organic matter by physico-chemical mechanisms in wastewater treatment plants. Water Science and Technology, 27 (11), 167-183.

Bolto, B., Dixon, D., Eldridge, R., and King, S. (2001). Cationic polymer and clay or metal oxide combinations for natural organic matter removal. Water Research, 35, 2669-2676.

Bose, P. and Reckhow, D. A. (2007). The effect of ozonation on natural organic matter removal by alum coagulation. Water Research, 41, 1516-1524.

Brakalov, L. B. (1987). A connection between orthokinetic coagulation capture efficiency of aggregates and their maximum size. Chemical Engineering Science, 42, 2373-2383.

Buffle, J., Wilkinson, K. J., Stoll, S., Filella, M. and Zhang, J. (1998). A generalized description of aquatic colloidal interactions: the three-colloidal component approach. Environmental Science and Technology, 32, 1887-2899.

Carlson, K. H. and Gregory, D. (2000). Optimizing water treatment with two-stage coagulation. Journal of Environmental Engineering, 126 (6), 556-561.

Chang, S. and Berner, R. A. (1998). Humic substance formation via the oxidative weathering of coal. Environmental Science and Technology, 32, 2883-2886.

Chen, Y., Senesi, N. and Schnitzer, M. (1977). Information provided on humic substance, by E_4/E_6 ratios. Soil Science Society of America Journal, 41 (2), 353-358.

Cheng, W. P. (2002). Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution. Chemosphere, 47, 963-969.

Cheng, W. P. and Chi, F. H. (2002). A study of coagulation mechanisms of polyferric sulfate reacting with humic acid using a fluorescence-quenching method. Water Research, 36, 4583-4591.

Chiang, P.C., Chang, E.E., Chang, P.C., Huang, C.P., 2009. Effects of pre-ozonation on the removal of THM precursors by coagulation. Sci. Total Environ. 407 (21), 5735–5742.

Ching, H. W., Elimelech, M. and Hering, J. G. (1994). Dynamics of coagulation of clay particles with aluminum sulfate. Journal of Environmental Engineering, 120 (1), 160-189.

Chow, C. W. K., van Leeuwen, J. A., Drikas, M., Fabris, R., Spark, K. M. and Page, D. W. (1999). The impact of the character of natural organic matter in conventional treatment with alum. Water Science and Technology, 40 (9), 97-104.

Chow, C. W. K., Fabris, R. and Drikas, M. A. (2004). A rapid fractionation technique to characterize natural organic matter for the optimization of water treatment processes. Journal of Water Supply Research Technology-AQUA, 53 (2), 85-92.

Chow, C. W. K., Fabris, R., Drikas, M. and Holmes, M. (2005). A case study of treatment performance and organic character. Journal of Water Supply Research Technology-AQUA, 54 (6), 385-395.

Cohen, J. M. and Hannah, S. A. (1971). Water Quality and Treatment, 3rd ed, McGraw Hill, New York, 66–122.

Colin, J. L., Dutot, A. L., Bablon, G. and Le Sage, R. V. (1986). Application of factor analysis to surface water test results. Water Research, 20 (6), 675-684.

Collins, M. R., Amy, G. L. and Steelink, C. (1986). Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment. Environmental Science and Technology, 20 (10), 1028.

Cook, R. L. and Langford, C. H. (1998). Structural characterization of a fulvic acid and a humic acid using solid-state Ramp-CP-MAS ^{13}C Nuclear Magnetic Resonance. Environmental Science and Technology, 32, 719-725.

Croue, J.-P., Lefebvre, E., Martin, B. and Legube, B. (1993). Removal of dissolved hydrophobic and hydrophilic organic substances during coagulation. Water Science and Technology, 27 (11), 143-152.

Dayarathne, N., Angove, M. J., Aryal, R., Abuel-Naga, H., Mainali, B. (2021). Removal of natural organic matter from source water: Review on coagulants, dual coagulation, alternative coagulants, and mechanisms. Journal of Water Process Engineering, 40, 101820.

Dempsey, B. A., Ganho, R. M. and O'Melia, C. R. (1984). The coagulation of humic substances by means of aluminum salts. Journal of AWWA, 76 (4), 141-150.

Dennett, K. E., Amirtharajah, A., Moran, T. F. and Gould, J. P. (1996). Coagulation: its effect on organic matter. Journal of AWWA, 88 (4), 129-142.

Dentel, S. K. and Gossett, J. M. (1988). Mechanisms of coagulation with aluminium salts. Journal of AWWA, 80 (4), 187-198.

Diamadopoulos, E. and Vlachos, C. (1996). Coagulation-filtration of a secondary effluent by means of pre-hydrolized coagulants. Water Science and Technology, 33, 193-208.

Dixon, A. M., Myphuong, A. M. and Larive, C. K. (1999). NMR investigation of the interactions between 4'-Fluoro-1'-acetonaphtone and Suwannee River fulvic acid. Environmental Science and Technology, 33, 958-964.

Duan, J., Wang, J., Graham, N. and Wilson, F. (2002). Coagulation of humic acid by aluminium sulphate in saline water conditions. Desalination, 150, 1-14.

Edwards, G. A. and Amirtharajah, A. (1985). Removing color caused by humic acids. Journal of AWWA, 77 (3), 50-57.

Edwards, M. and Benjamin, M. M. (1992). Effect of preozonation on coagulant-NOM interactions. Journal of AWWA, 84 (8), 63-72.

Edwards, M., Boller, M. and Benjamin, M. M. (1993). Effect of pre-ozonation on removal of organic-matter during water-treatment plant-operations. Water Science and Technology, 27 (11), 37-45.

Edzwald, J. K. (1979). Coagulation of humic substances. AIChE Symp Ser 19: Water 75, 54-62.

Edzwald, J. K. (1993). Coagulation in drinking water treatment: particles, organics and coagulants. Water Science and Technology, 27 (11), 21-35.

Edzwald, J. K. and Tobiason, J. E. (1999). Enhanced coagulation: US requirements and a broader view. Water Science and Technology, 40 (9), 63-70.

Edzwald, D. K., Pernitsky, D. J. and Parmenter, W. L. (2000). Polyaluminum coagulants for drinking water treatment: chemistry and selection. in Hahn, H. H., Hoffmann, E., Ødegaard, H. (Eds.). Chemical Water and Wastewater Treatment VI, Berlin, Springer, 3-14.

Eikebrokk, B. and Fettig, J. (1990). Treatment of coloured surface water by coagulation/direct filtration: effect of water quality, type of coagulant and filter aids. in

Hahn, H. H. and Klute, R. (Eds.). Chemical Water and Wastewater Treatment, Berlin, Springer, 361-376.

Eikebrokk, B. (2000). Effects of coagulant type and coagulation conditions on NOM removal from drinking water. in Hahn, H. H, Hoffmann, E., Ødegaard, H. (Eds.). Chemical Water and Wastewater Treatment VI, Berlin, Springer, 211-220.

Exall, K. N. and vanLoon, G. W. (2000). Using coagulants to remove organic matter. Journal of AWWA, 92, 93-102.

Farvardin, M. R. and Collins, A. G. (1989). Preozonation as an aid in the coagulation of humic substances-optimum preozonation dose. Water Research, 23 (3), 307-316.

Fearing, D. A., Goslan, E. H., Banks, J., Wilson, D., Hillis, P., Campbell, A. T. and Parsons, S. A. (2004). Staged coagulation for treatment of refractory organics. Journal of Environmental Engineering, ASCE 130 (9), 975-982.

Fettig, J., Ratnaweera, H. C. and Ødegaard, H. (1990). Simultaneous phophate precipitation and particle destabilization using aluminium coagulants of different basicity, I. in Hahn, H. H. and Klute, R. (Eds.). Chemical Water and Wastewater Treatment, Berlin, Springer, 221-242.

Francois, R. J. and Van Haute, A. A. (1984). Floc strength measurements giving experimental support for a four level hydroxide floc structure. Studies in Environmental Science, 23, 221-234.

Francois, R. J. (1987). Strength of aluminium hydroxide flocs. Water Research, 21, 1023-1030.

Gilbert, E. (1988). Biodegradability of ozonation products as a function of COD and DOC elimination by the example of humic acids. Water Research, 22, 123-126.

Gray, K. A., Yao, C. and O'Melia, C. R. (1995). Inorganic metal polymers: preparation and characterization, Journal of AWWA, 4, 136-143.

Gregor, J. E., Nokes, C. J. and Fenton, E. (1997) Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of Aluminium coagulation. Water Research, 28, 1671-1970.

Gregory, J. and Nelson, D. W. (1986). Monitoring of aggregates in flowing suspensions. Colloids and Surfaces, 18, 175-188.

Gressel, N., McGrath, A. E., McColl, J. G. and Power, R. F. (1995). Spectroscopy of aqueous extracts of forest litter I: suitability of methods. Soil Science Society of America Journal, 41, 1715-1723.

Hailong, L., Dongsheng, W., Min, W., Hongxiao, T. and Min, Y. (2007). Effect of pre-ozonation on coagulation with IPF-PACls: Role of coagulant speciation. Colloids and Surfaces A: Physicochemical Engineering Aspects, 294, 111-116.

Hall, E. S. and Packham, R. F. (1965) Coagulation of Organic Color with Hydrolizing Coagulants. Journal of AWWA, **57**, 1149-1166.

Hu, S., Jin, X., Yang, C., Wang, Y., Xie, X., Zhang, S., Jin, P., Wang, X.C., 2021. Enhanced complexation of humic acids: homogenization of protonated groups in the hybrid ozonation-coagulation process. Chemosphere 280, 130647.

Hundt, T. R. and O'Melia, C. R. (1988). Aluminum-fulvic acid interactions: mechanisms and applications. Journal of AWWA, 80 (4), 176.

Hunter, R. J. (1993). Introduction to Modern Colloid Science. Oxford University Press, New York.

Jasim, S. Y., Ndiongue, S., Johnson, B., Schweitzer, L. and Borikar, D. (2008). The effect of ozone on cold water coagulation. Ozone: Science & Engineering, 30(1): 27-33.

Jarvis P., Jefferson J., Gregory J. and Parsons S. A. (2005). A review of floc strength. Water Research, 39 (14), 3121-3137.

Jiang, J. Q., Graham, N. J. D. and Harward, C. (1993). Comparison of polyferric sulfate with other coagulants for the removal of algae and algae-derived organic matter. Water Science and Technology, 27 (11), 221-230.

Jiang, J. Q. and Graham, N. J. D. (1998a). Preliminary evaluation of the performance of new pre-polymerized inorganic coagulants for lowland surface water treatment. Water Science and Technology, 37 (2), 121-128.

Jiang, J. Q. and Graham, N. J. D. (1998b). Observations of the comparative hdyrolysis/precipitation behaviour of polyferric sulphate and ferric sulphate. Water Research, 32, 930-935.

Jin, X., Liu, M., Zong, Y., Hu, S., Li, Y., Xu, L., Bai, X., Shi, X., Jin, P., Song, J., Wang, X. C. (2023). Unraveling the over-oxidation inhibition mechanism during the hybrid ozonation-coagulation process: Immediate entrapment and complexation between intermediate organic matter and coagulants. Water Research, 232, 119692.

Jung, A. –V., Chanudet, V., Ghanbaja, J., Lartiges, B. S. and Bersillon, J. –L. (2005). Coagulation of humic substances and dissolved organic matter with a ferric salt: An electron energy loss spectroscopy investigation. Water Research, 39, 3849-3862.

Kerc, A., Bekbolet, M. and Saatci, A. M. (2004). Effects of oxidative treatment techniques on molecular size distribution of humic acids. Water Science and Technology, 49 (4), 7-12.

Kim, H. C. and Yu, M. J. (2005). Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. Water Research, 39 (19), 4779-4789.

Knocke, W. R., West, S. and Hoehn, R. C. (1986). Effects of low temperature on the removal of trihalomethane precursors by coagulation. Journal of AWWA, 78 (4), 189.

Kong, Y. L., Ma, Y. Q., Ding, L., Ma, J. Y., Zhang, H. W., Chen, Z. L., Shen, J. M. (2021). Coagulation behaviors of aluminum salts towards humic acid: Detailed analysis of aluminum speciation and transformation. Separation and Purification Technology, 259, 118137.

Krasner, S. W., McGuire, M. J., Jacangelo, J. G., Patania, N. L., Reagani. K. M. and Aieta, E. M. (1989). The occurrence of disinfection by-products in US drinking water. Journal of AWWA, 81, 41-53.

Krasner, S. W. and Amy, G. (1995). Jar test evaluations of enhanced coagulation. Journal of AWWA, 87, 93-107.

Krasner, S. W., Croue, P.-P., Buffle, J. and Perdue, E. M. (1996). Three approaches for characterizing NOM. Journal of AWWA, 88, 66-79.

Kronberg, L. (1987). Mutagenic compounds in chlorinated humic and drinking water. Ph.D. thesis, Department of Chemistry, Åbo Akademi, Turku.

Langlais, B., Reckhow, D. A. and Brink, D. R. (Eds.) (1991). Ozonation in Water Treatment. Applications and Engineering. Cooperative Research Report, AWWRF and Compagnie Generale des Eaux. Lewis Publishers.

Leenheer, J. A. and Noyes, T. I. (1984). A filtration and column adsorption system for on site concentration and fractionation of organic substances from large volumes of water. US Geological Survey Water-Supply Paper, 2230.

Letterman, R. D., Amirtharajah, A. and O'Melia, C. R., (1999). Chapter 6, "Coagulation and Flocculation" in Water Quality and Treatment, 5th edition, McGraw-Hill Inc., NY.

Liao, Y. F., Wang, L. Y., Tian, Y. C., Li, J., Zhou, Q., Li, A. M., Hua, M., Pan, Y. (2025). Effects of ozonation-enhanced coagulation on effluent organic matter and disinfection byproducts. Journal of Cleaner Production, 490, 144801.

Lind C. (1995). Coagulation Choises for Total Organic Carbon Control. Public Works. 126, 35-36.

Lindqvist, N., Korhonen, S., Jokela, J. and Tuhkanen, T. (2002). Comparison of iron and aluminum based coagulants and polymeric flocculant aids to enhance NOM removal. in Hahn, H. H., Hoffmann, E., Ødegaard, H. (Eds.). Chemical Water and Wastewater Treatment VII, 133-142.

Liu, H., Zhang, X., Fang, Y., Fu, C., Chen, Z., 2021. Trade-off control of organic matter and disinfection by-products in the drinking water treatment chain: role of pre-ozonation. Sci. Total Environ. 770, 144767.

Liu, L. B., Lu, S., Jin, Z. Y., Lou, J. W., Zhang, W. J., Wang, D. S. (2025). Hydrolysis of Al_{13} and its coagulation mechanism: Role of speciation stability and transformation. Water Research, 281, 123672.

Liu, M. J., Graham, N., Gregory, J., Elimelech, M., Yu, W. (2024). Towards a molecular-scale theory for the removal of natural organic matter by coagulation with trivalent metals. Nature Water, 2, 285-294.

Lovins, W. A., Duranceau, S. J., Gonzalez, R. M. and Taylor, J. S. (2003). Optimized coagulation assessment for a highly organic surface water supply. Journal of AWWA, 95 (10), 94-108.

Lu, X. Q., Chen, Z. L. and Yang, X. H. (1999). Spectroscopic study of aluminium speciation in removing humic substances by Al coagulation. Water Research, 33 (15), 3271-3280.

Maartens, A., Swart, P. and Jacobs, E. P. (1999). Humic membrane foulants in natural brown water: characterization and removal. Desalination, 115, 215-227.

Marhaba, T. F. and Pipada, N. S. (2000). Coagulation: effectiveness in removing natural organic matter fractions. Environmental Engineering Science, 17 (2), 107-115.

Matilainen, A., Lindqvist, N. and Tuhkanen, T. (2005). Comparison of the efficiency of aluminium and ferric sulphate in the removal of natural organic matter during drinking water treatment process. Environmental Technology, 26 (8), 867-875.

Matsui, Y., Yuasa, A., Furuya, Y. and Kamei, T. (1998). Dynamic analysis of coagulation with alum and PACl. Journal of AWWA, 90 (10), 96-106.

Matsuo, T. and Unno, H. (1981). Forces acting on floc and strength of floc. Journal of Environmental Engineering, ASCE 107, 527-545.

Mejia A. C. and Cisneros, B. J. (2000). "Particle Size Distribution (PSD) Obtained in Effluents from an Advanced Primary Treatment Process Using Different Coagulants", In: *Chemical Water and Wastewater Treatment VI*, H. Hahn, E. Hoffmann and H. Ødegaard (eds.), Springer, pp. 257–268.

Miltner, R. J., Shukairy, H. M. and Summers, R. S. (1992). Disinfection by-product formation and control by ozonation and biotreatment. Journal of AWWA, 84 (11), 53-62.

Morris, J. K. and Knocke, W. R. (1984). Temperature effects on the use of metal-ion coagulants for water treatment. Journal of AWWA, 76 (3), 74.

Mühle, K. (1993). Floc stability in laminar and turbulent flow. In B. Dobias, Ed. Coagulation and Flocculation. New York: Dekker, 355-390.

Narkis, N. and Rebhun, M. (1977). Stoichiometric relationships between humic and fulvic acids and flocculants. Journal of AWWA, 69 (6), 325-328.

Novotna, K., Pivokonský, M., Prokopova, M., Baresova, M., Pivokonska, L., 2020. Consequences of ozonation for the limited coagulation of non-proteinaceous AOM and formation of aldehydes as ozonation by-products. J. Environ. Chem. Eng. 8 (6), 104455.

O'Melia, C. R., Becker, W. C. and Au, K.-K. (1999). Removal of humic substances by coagulation. Water Science and Technology, 40 (9), 47-54.

Ong, H. L. and Bisque, R. E. (1968). Coagulation of humic colloids by metal ions. Soil Science, 106, 220-224.

Owen, D. M., Amy, G. L. and Chowdhury, Z. K., eds (1993). *Characterization of Natural Organic Matter and Its Relationship to Treatability*. AwwaRF, Denver Colarado.

Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G. and Viscosil, K. (1995). NOM - Characterization and treatability. Journal of AWWA, 87 (1), 46-63.

Østerhus S. W. and Eikebrokk B. (1994). Coagulation and corrosion control for soft and coloured drinking water. in Hahn, H. H and Klute, R. (Eds.), Chemical Water and Wastewater Treatment III, Berlin, Springer, 137-153.

Packham, R. E. (1962). Coagulation as a water treatment process. Proceedings Society for Water Treatment and Examination, 11 (2), 106-119.

Pei, Y. S., Yu, J. W., Guo, Z. H., Zhang, Y., Yang, M., Zhang, J. S. and Junji, H. (2007). Pilot study on pre-ozonation enhanced drinking water treatment process. Ozone: Science & Engineering, 29(5): 317-323.

Popov, M., Isakovski, M. K., Jazić, J. M., Tubić, A., Watson, M., Šćiban, M. and Agbaba, J. (2020). Fate of natural organic matter and oxidation/disinfection by-products formation at a full-scale drinking water treatment plant. Environmental Technology, 42 (22), 3475–3486.

Randtke, S. J. (1988). Organic contaminant removal by coagulation and related process combinations. Journal of AWWA, 80 (5), 40-56.

Rebhun, M. and Lurie, M. (1993). Control of organic matter by coagulation and flocs separation. Water Science and Technology, 27 (11), 1-20.

Reckhow, D.A., Legube, B., Singer, P.C., 1986. The ozonation of organic halide precursors: effect of bicarbonate. Water Res. 20 (8), 987–998.

Reckhow, D. A. and Singer, P. C. (1984). The removal of organic halide precursors by preozonation and alum coagulation. Journal of AWWA, 76 (4), 151.

Richardson, S. D. (1998). Drinking water disinfection by-products. In Encyclopedia of Environmental Analysis and Remediation; Wiley: New York.

Rodríguez, F. J., Marcos, L. A., Núnez, L. A., García, M. (2012). Effects of ozonation on molecular weight distribution of humic substances and coagulation processes - a case study: the Úzquiza reservoir water. Ozone: Science & Engineering, 34, 342-353.

Saar, R. A. and Weber, J. H. (1980). Comparison of spectrofluorometry and ion-selective electrode potentiometry for determination of complexes between fulvic acid and heavy-metal ions. Analytical Chemistry, 52, 2095-2100.

Sadrnourmohamadi, M., Gorczyca, B., 2015. Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from high DOC and hardness water. Water Res. 73, 171–180.

Sam, S. and Yukselen, M. A. (2007). Importance of rapid mixing time on sludge dewatering properties. Environment: Survival and Sustainability Symposium, Near East University, Turkish Republic of Northern Cyprus.

Sam, S., Yukselen, M. A., Zorba, M. and Gregory, J., (2010). The Effect of Ozone on the Reversibility of Floc Breakage: Suspensions with High Humic Acid Content. Ozone: Science & Engineering, 32 (6), 435-443.

Schneider, O. D. and Tobiason, J. E. (2000). Pre-ozonation effects on coagulation. Journal of AWWA, 92 (10), 74-87.

Semmens, M. J. and Field, T. K. (1980). Coagulation: experiences in organics removal. Journal of AWWA, 72 (8), 476-485.

Serra, T., Colomer, J. and Casamitjana, X. (1997). Aggregation and breakup of particles in a shear flow. Journal of Colloid and Interface Science, 187, 466-473.

Sharp, E. L., Jarvis, P., Parsons, S. A. and Jefferson, B. (2006). Impact of fractional character on the coagulation of NOM. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 286, 104-111.

Shen, X., Gao, B., Guo, K., Yue, Q. (2020). Characterization and influence of floc under different coagulation systems on ultrafiltration membrane fouling. Chemosphere, 238, 124659.

Singer, P. C., Arlotta, C., Snider-Sajdak, N. and Miltner, R. (2003). Effectiveness of pre- and intermadiate ozonation on the enhanced coagulation of disinfection by-product precursors in drinking water. Ozone: Science & Engineering, 25 (6), 453-471.

Singer, P. C. (1990). Assessing ozonation research needs in water-treatment. Journal of AWWA, 82 (10), 78-88.

Snoeyink, V. L. and Jenkins, D. (1980). Water Chemistry, Wiley, New York.

Song, J., Jin, X., Wang, X.C., Jin, P., 2019. Preferential binding properties of carboxyl and hydroxyl groups with aluminium salts for humic acid removal. Chemosphere 234, 478–487.

Speitel Jr., G. E., Wanielista, M. M., Symons, J. M. and Davids, J. M. eds. (1999). Advanced Oxidation and Biodegredation Processes for the Destruction of TOC and DBP Precursors. AwwaRF, Denver, Colorado.

Spicer, P. T., Pratsinis, S. E., Raper, J., Amal, R., Bushell, G. and Meesters, G. (1998). Effect of shear schedule on particle size, density, and structure during flocculation in stirred tanks. Powder Technology, 97, 26-34.

Stevenson, F. J. (1994). Humus chemistry: genesis, composition, reactions. New york: Wiley/Interscience.

Suffet, I. H. and MacCarthy, P. (1989). Aquatic humic substances influence on fate and treatment of pollutants. Washington, DC: America Chemical Society.

Swiderska-Bróz, M. and Rak, M. (2002). On the importance of aluminium coagulant basicity in organic matter removal. in Hahn, H. H., Hoffmann, E., Ødegaard, H. (Eds.). Chemical Water and Wastewater Treatment VII, IWA Publishing, London, 153-162.

Şam, S. and Yükselen, M. A. (2006). Kimyasal çamur floklarının özellikleri ve susuzlaştırma uygulamaları. Çevre Kirlenmesi Öncelikleri Sempozyumu V (ÇEVKOS V), Gebze Yüksek Teknoloji Enstitüsü.

Tang, H. X. and Stumm, W. (1987). The coagulating behaviors of Fe (III) polymeric species - I. Preformed polymers by base addition. Water Research, 21, 115-121.

Tate, C. H. and Arnold, K. F. (1990). Health and aesthetic aspects of water quality. Water Quality and Treatment (F. W. Pontius, editor). McGraw Hill, Toronto.

Tenny, A. M. and Derka, J. (1992). Hydroxylated ferric sulphate-an aluminum salt alternative. Water Supply, 10, 167-174.

Thurman, E. M. (1985). Humic substances in soil, sediment and water. Geochemistry, isolation and characterisation. John Wiley and Sons, New York, USA.

Thurman, E. M. (1985). Organic geochemistry of natural water. Boston, Martinus Nijhoff/Dr W. Junk Publishers.

Tobiason, J. E., Edzwald, J. K., Reckhow, D. A. and Switzenbaum, M. S. (1993). Effect of pre-ozonation on organics removal by in-line direct-filtration. Water Science and Technology, 27 (11), 81-90.

Van Geluwe, S., Braeken, L., Van der Bruggen, B. (2011). Ozone oxidation for the alleviation of membrane fouling by natural organic matter: A review. Water Research, 45 (12), 3551-3570.

Vik, E. A. and Eikebrokk, B. (1989). Coagulation process for removal of humic substances from drinking water. Aquatic Humic Substances (I. H. Suffet and P. MacCarthy, editors). American Chemical Society, Washington.

Visser, S. A. (1985). Viscosimetric studies on molecular weight fractions of fulvic and humic acids of aquatic, terrestrial and microbial origin. Plant and Soil, 87, 209-221.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G. and Lechevallier, M. (2000) Impact of enhanced and optimised coagulation on removal of organic matter and its biodegradable fraction in drinking water. Water Research, 34, 3247-3257.

Wall, N. A. and Choppin, G. R. (2003). Humic acids coagulation: influence of divalent cations. Applied Geochemistry, 18, 1573-1582.

Wahlroos, G. (1991). The realization of activated carbon filtration in a water purification process for a highly humic water by prior two-stage iron (III) salt coagulation. Journal of Water Supply: Research and Technology, AQUA, 40, 211-216.

White, M. C., Thompson, J. D., Harrington, G. W. and Singer, P. C. (1997). Evaluating criteria for enhanced coagulation compliance. Journal of AWWA, 89 (5), 64-77.

Woelki, G., Friedrich, S., Hanschmann, G. and Salzer, R. (1997). HPLC fractionation and structural dynamics of humic acids. Fresenius Journal of Analytical Chemistry, 357, 548-552.

Xie, P., Chen, Y., Ma, J., Zhang, X., Zou, J. and Wang, Z. (2016). A mini review of preoxidation to improve coagulation. Chemosphere, 155, 550-563.

Yan, M., Wang, D., Shi, B., Wang, M., Yan, Y., 2007. Effect of Pre-ozonation on Optimized Coagulation of a Typical North-China Source Water. Chemosphere 69 (11), 1695–1702.

Yao, C. and O'Melia, C. R. (1989). Required coagulant dosage, Journal of Water Supply: Research and Technology, AQUA, 38, 339-344.

Yu, J., Sun, D. D. and Tay, J. H. (2002). Characteristics of coagulation-flocculation of humic acid with effective performance of polymeric flocculant and inorganic coagulant. Water Science and Technology, 47 (1), 89-95.

Yukselen, M. A. and Gregory, J. (2002a). Breakage and reformation of alum flocs. Environmental Engineering Science, 19, p. 229–236.

Yukselen, M. A. and Gregory, J. (2002b). Properties of flocs formed using different coagulants. Water Science and Technology: Water Supply, 2, p. 95-101.

Yukselen, M. A. and Gregory, J. (2004a). The reversibility of floc breakage. International Journal of Mineral Processing, 73, p. 251–259.

Yukselen, M. A. and Gregory, J. (2004b). The effect of rapid mixing on the break-up and re-formation of flocs. Journal of Chemical Technology and Biotechnology, 79, p. 782-788.

Yukselen, M. A., Sam, S., Dede, A. and Gregory, J. (2007). Impact of ozonation on the floc reversibility in waters with high organic content. International Water Association-International Conference on Particle Separation (IWA-PS 2007), Toulouse, France.

APPENDIX

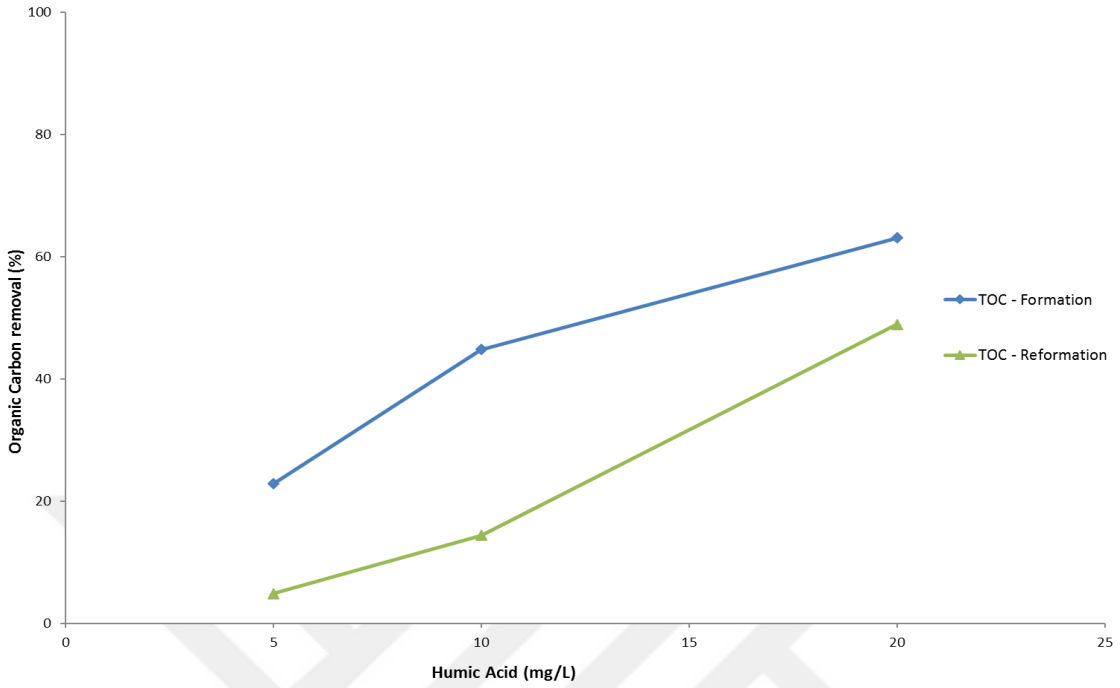

Figure 1. TOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

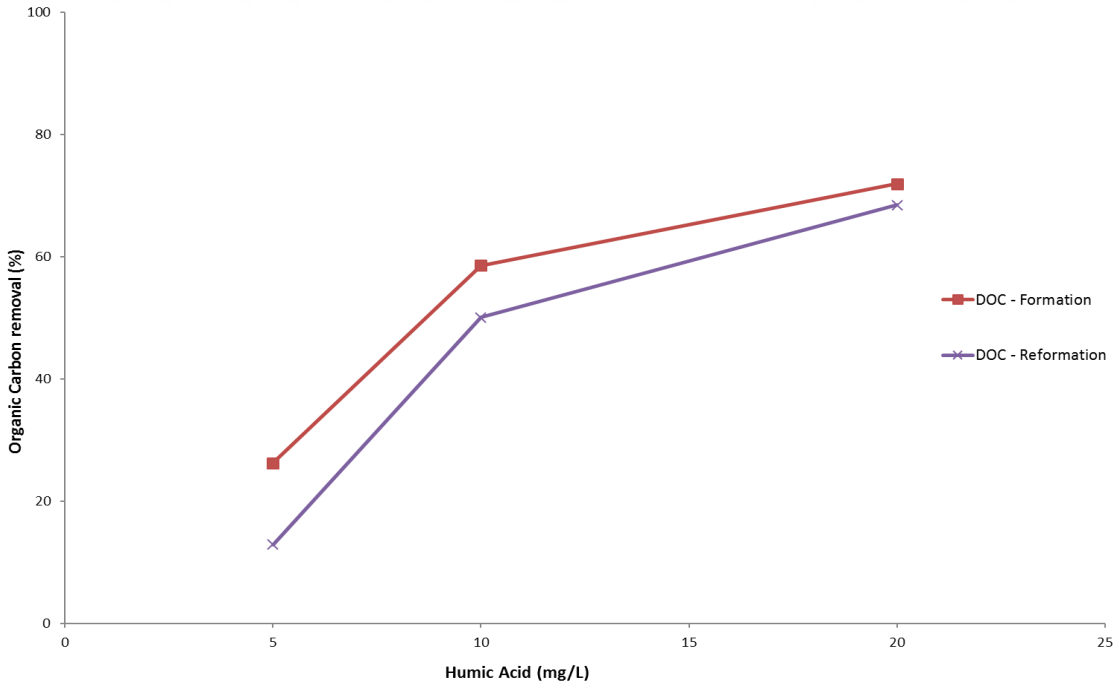

Figure 2. DOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

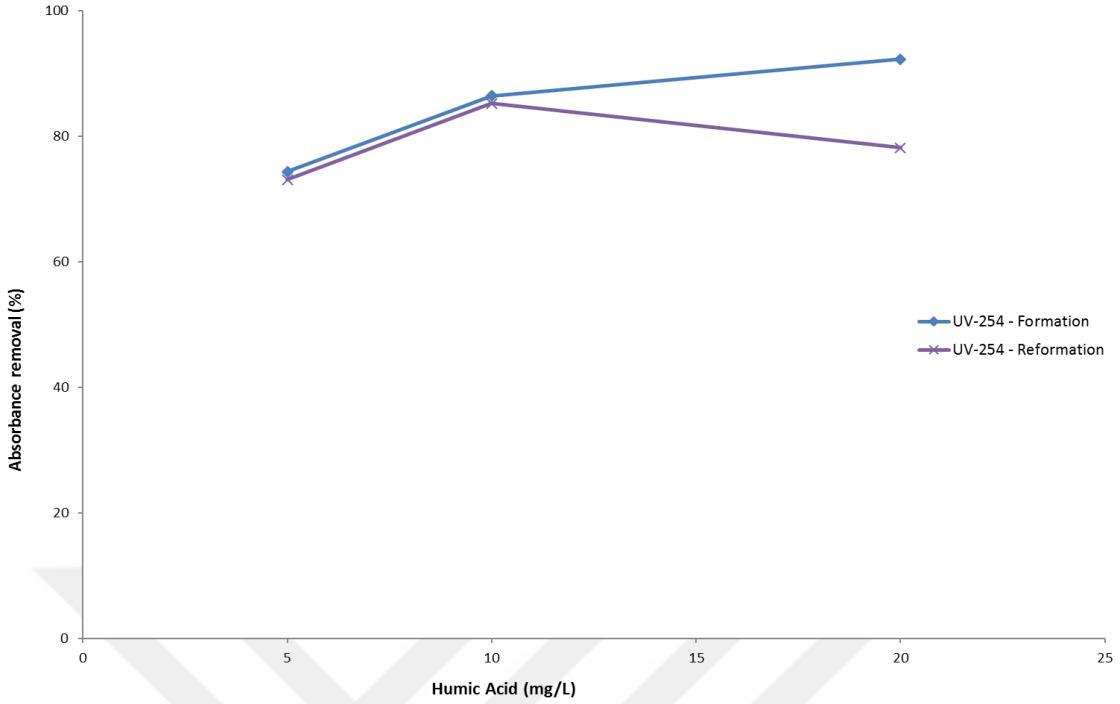

Figure 3. UV_{254} removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

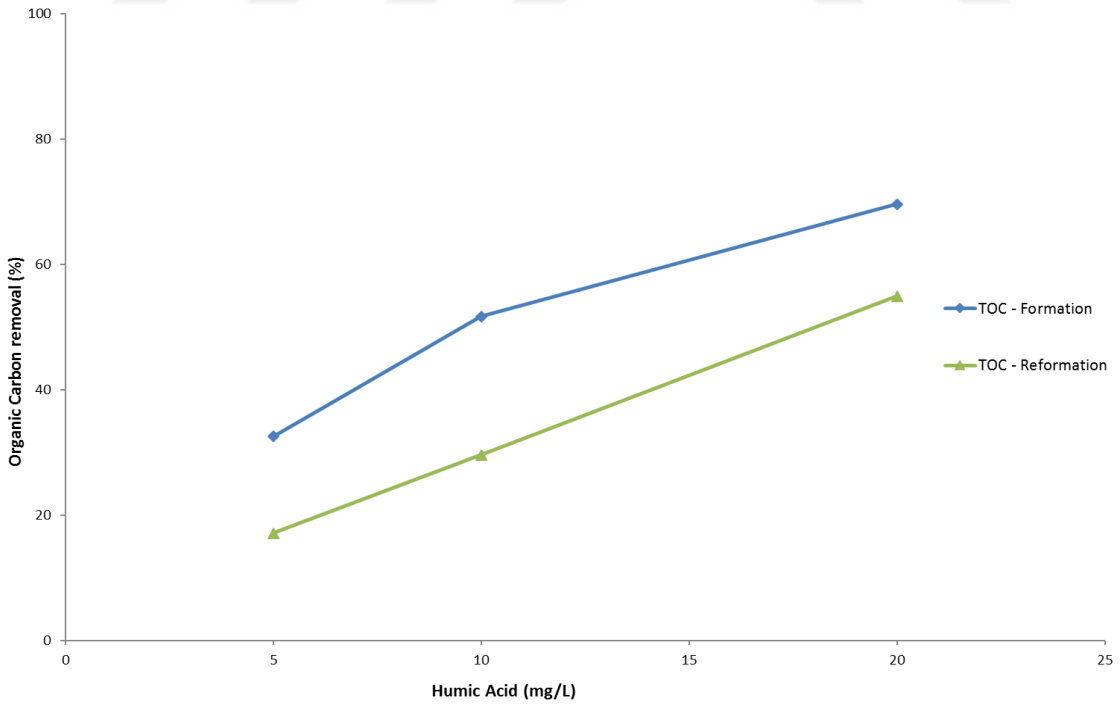

Figure 4. TOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

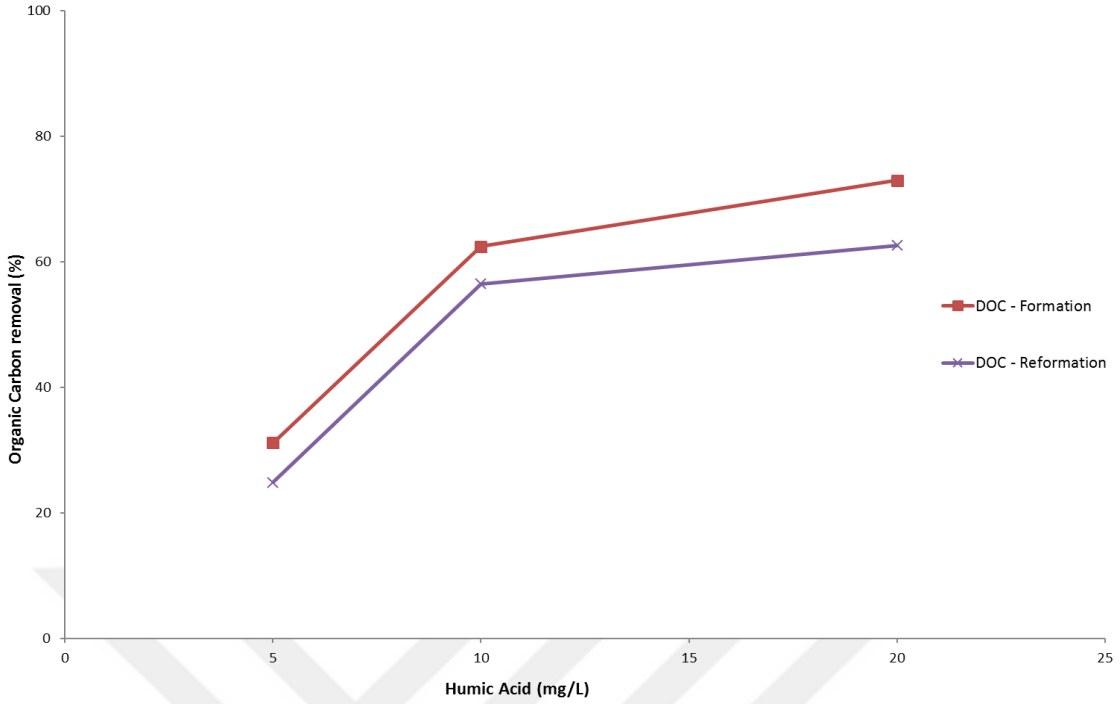

Figure 5. DOC removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

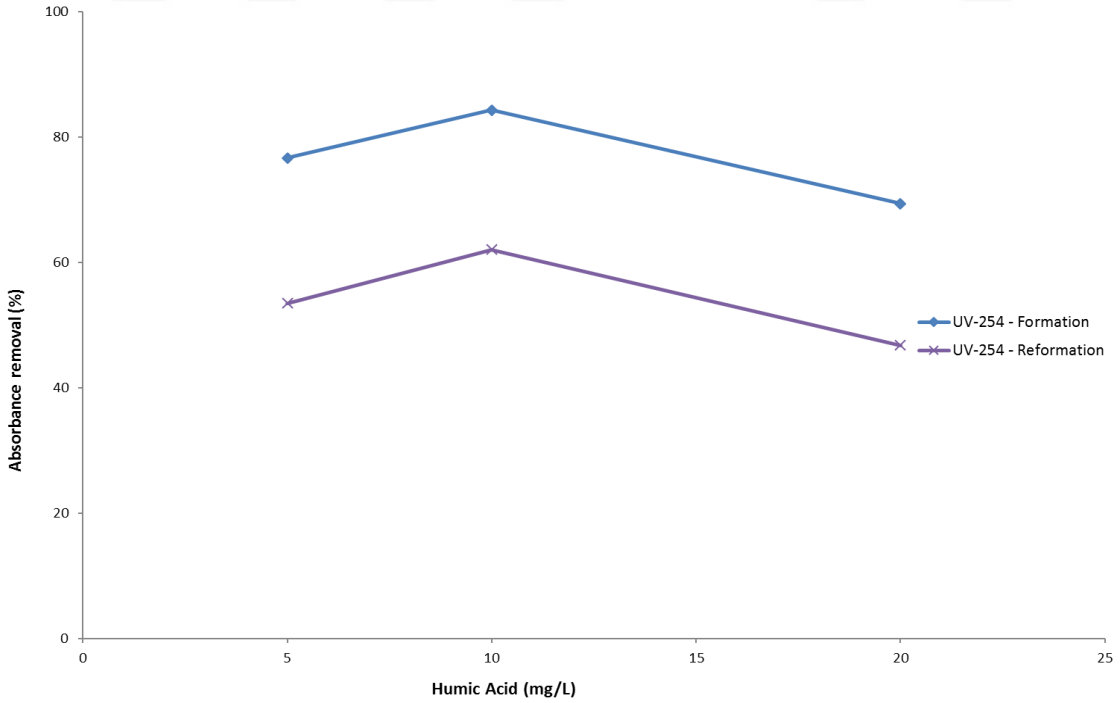

Figure 6. UV_{254} removal efficiency after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

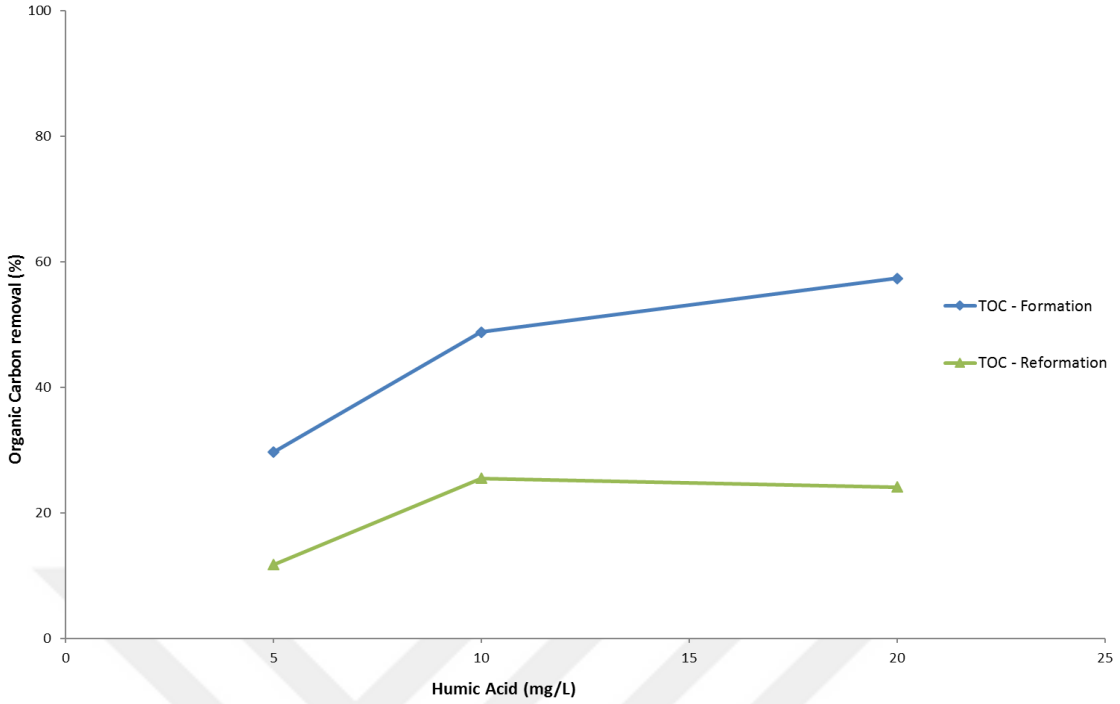

Figure 7. TOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

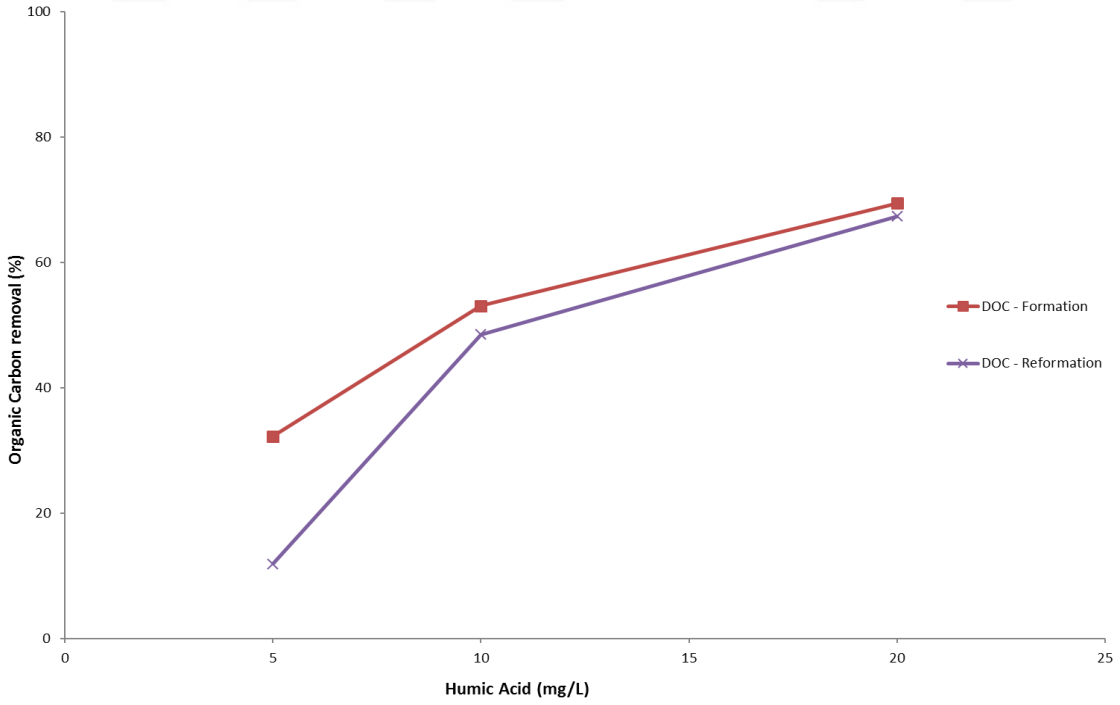

Figure 8. DOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

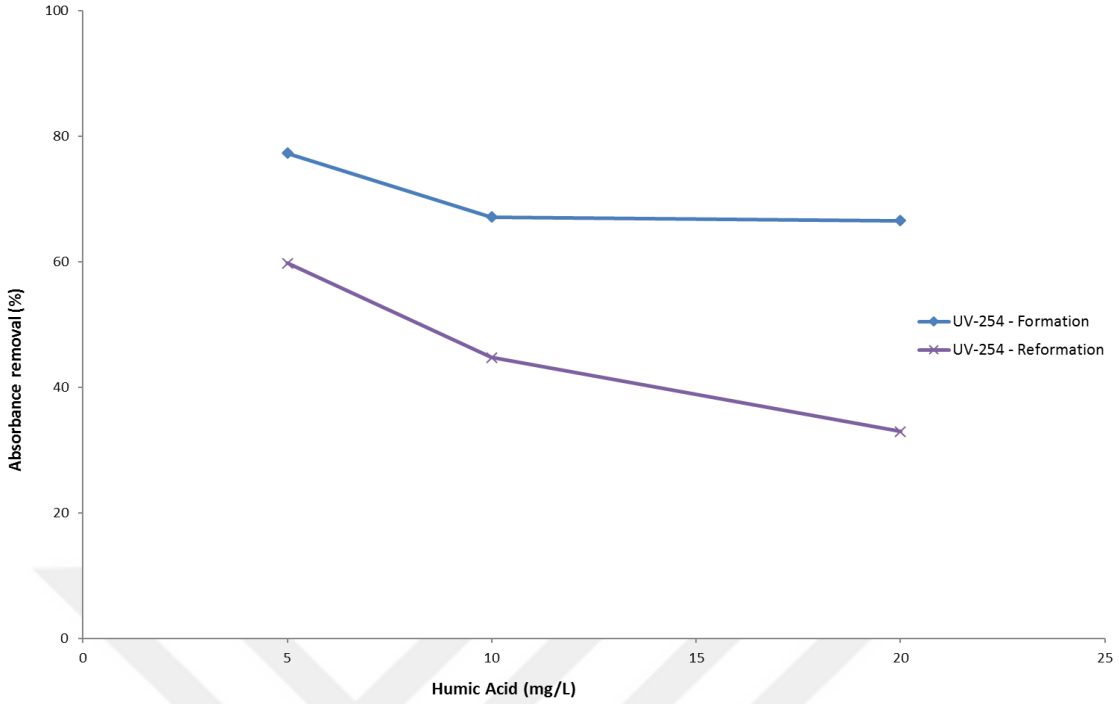

Figure 9. UV_{254} removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

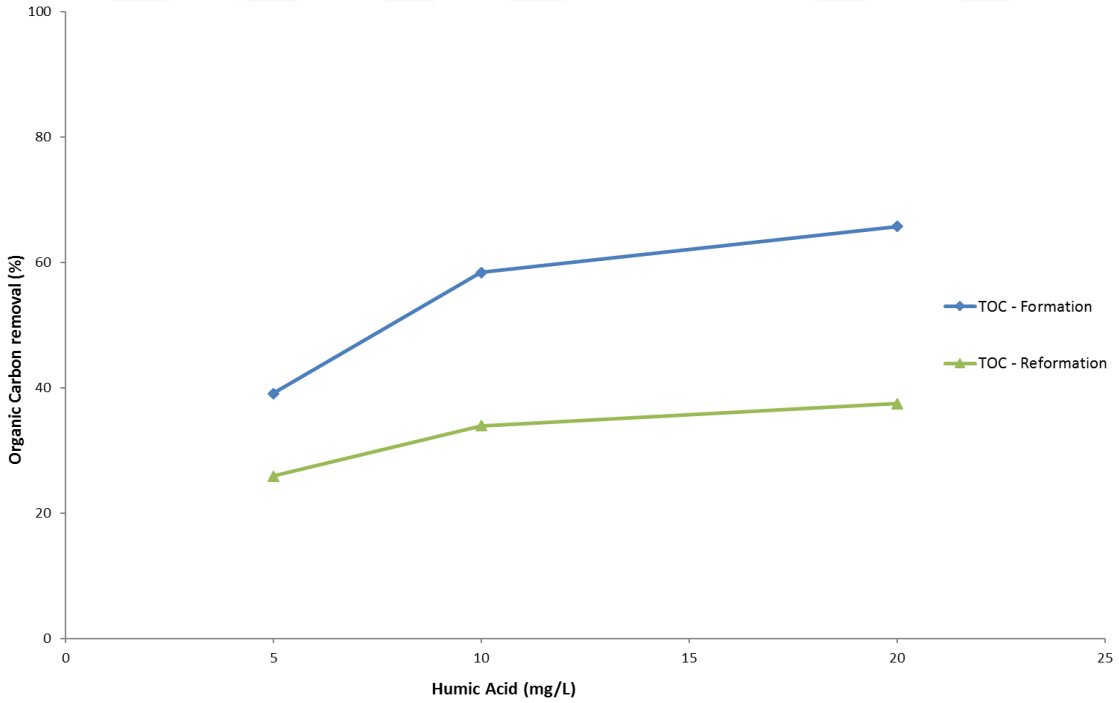

Figure 10. TOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

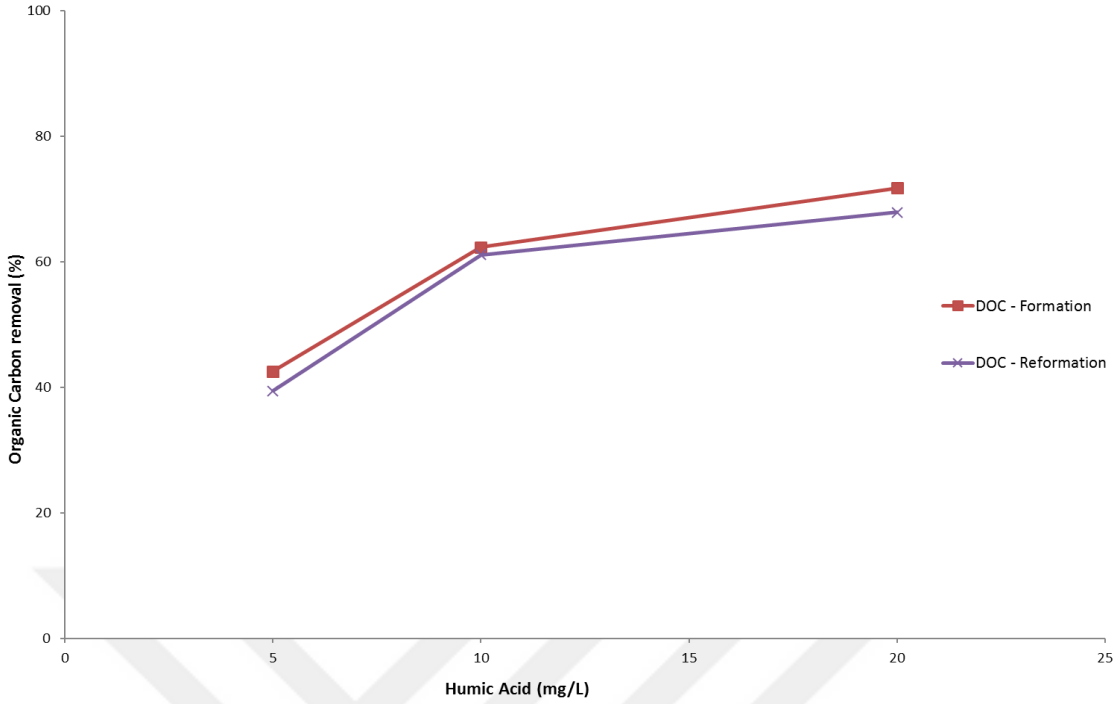

Figure 11. DOC removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

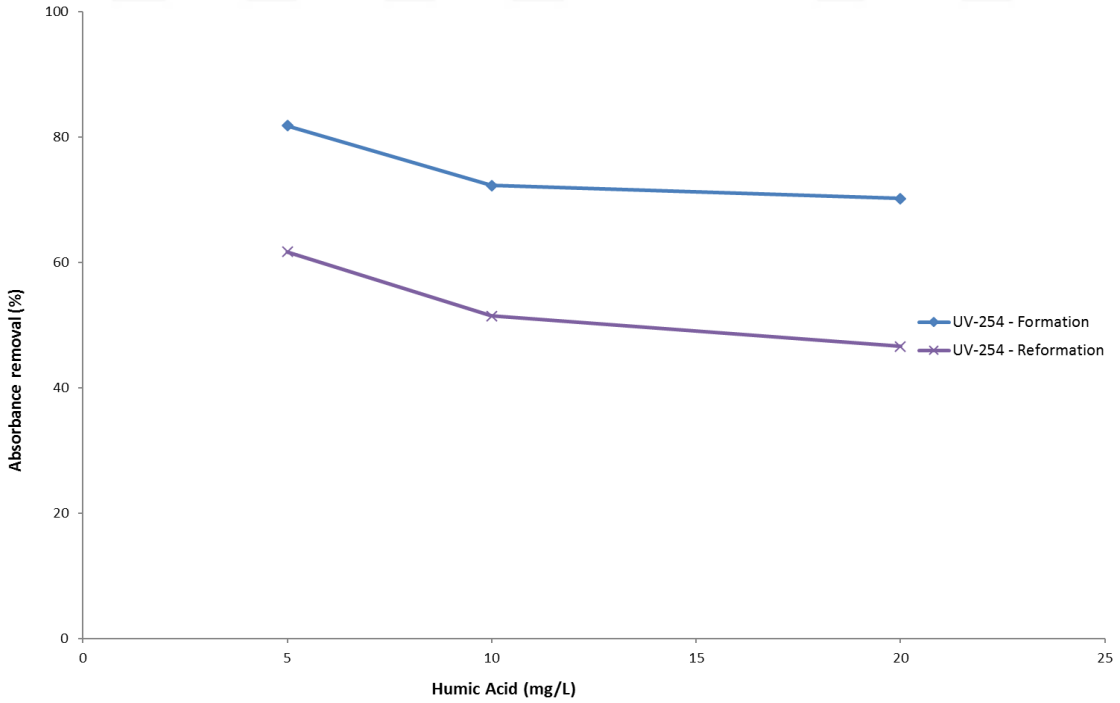

Figure 12. UV_{254} removal efficiency after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

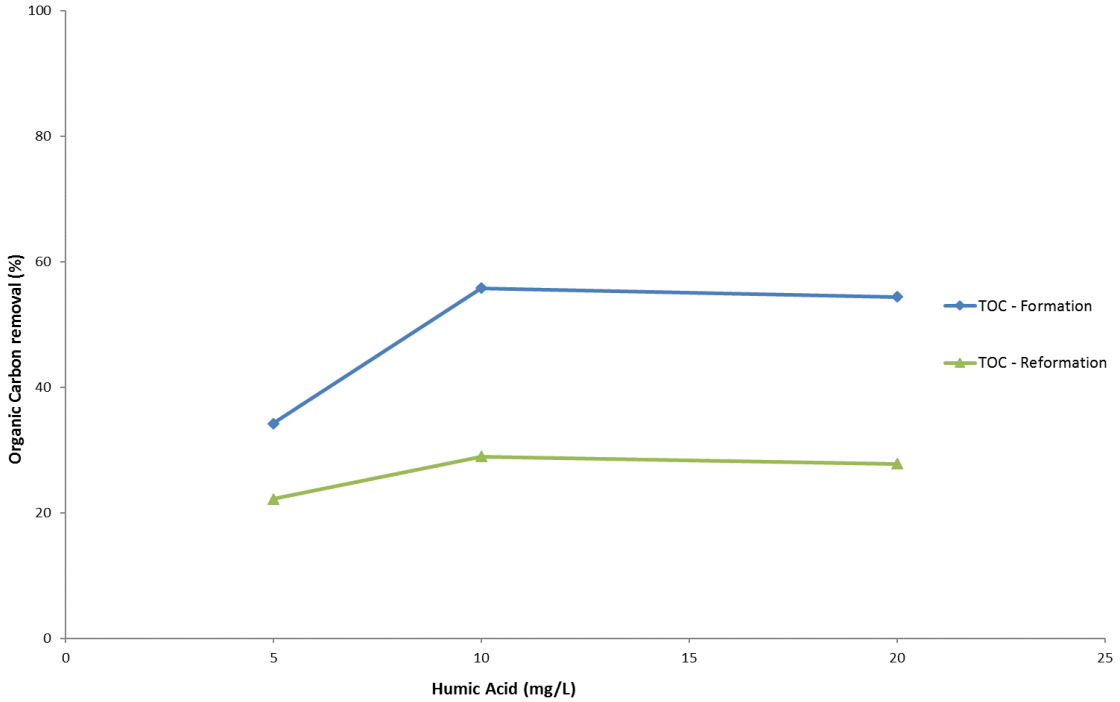

Figure 13. TOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

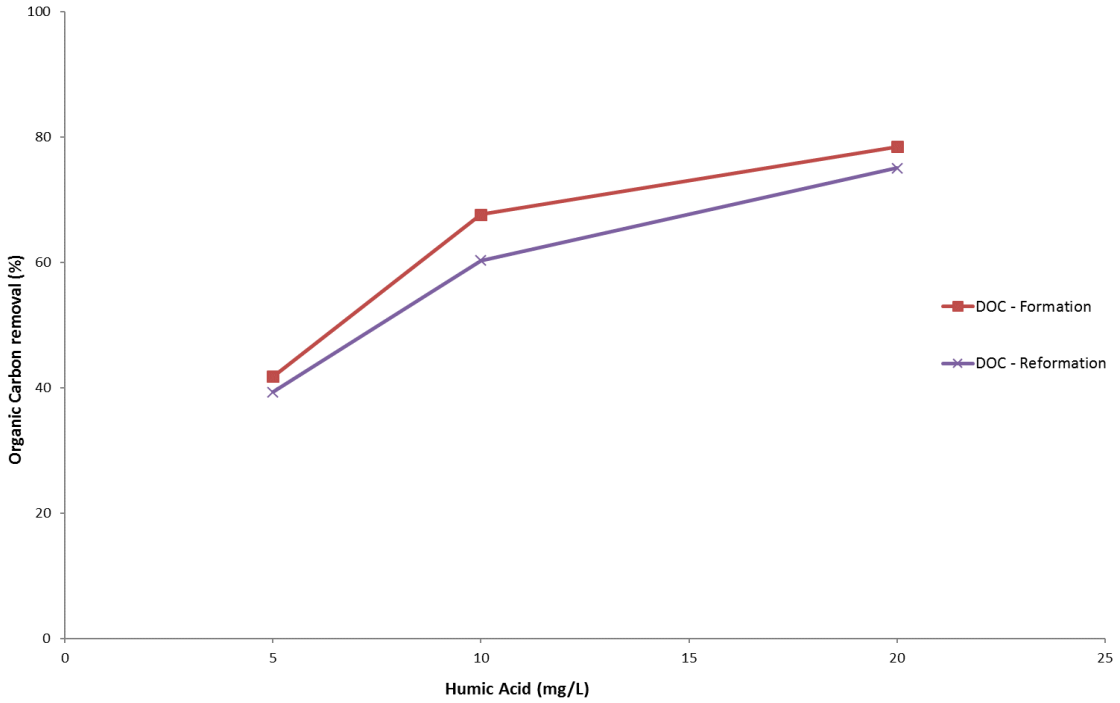

Figure 14. DOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

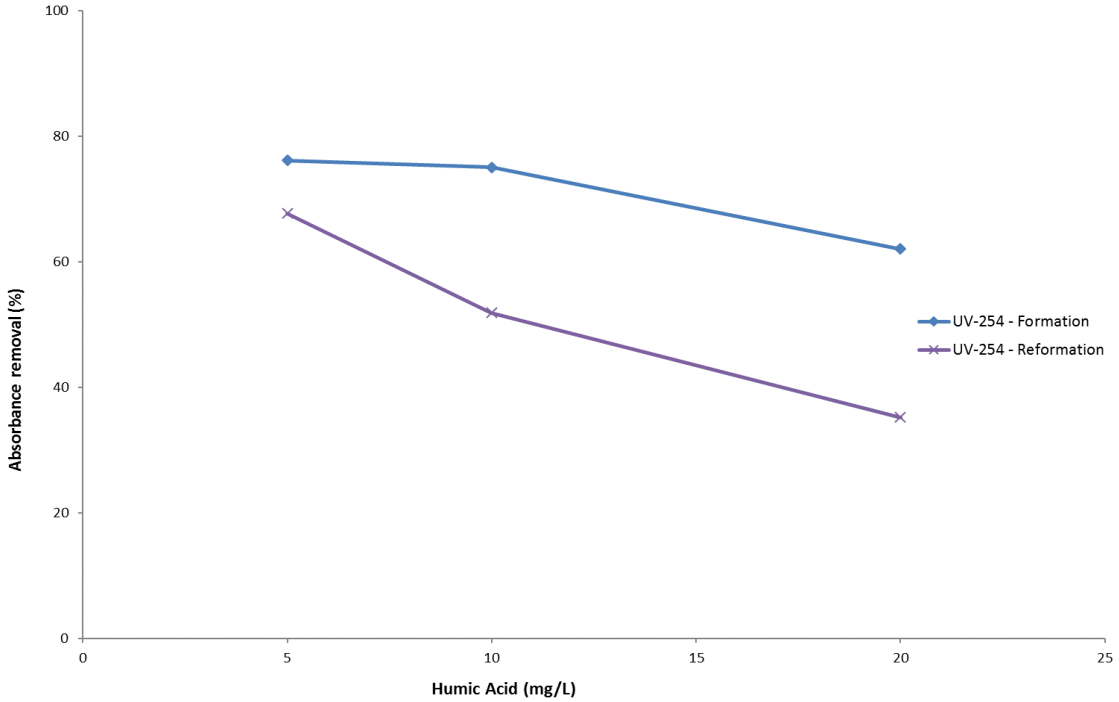

Figure 15. UV_{254} removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

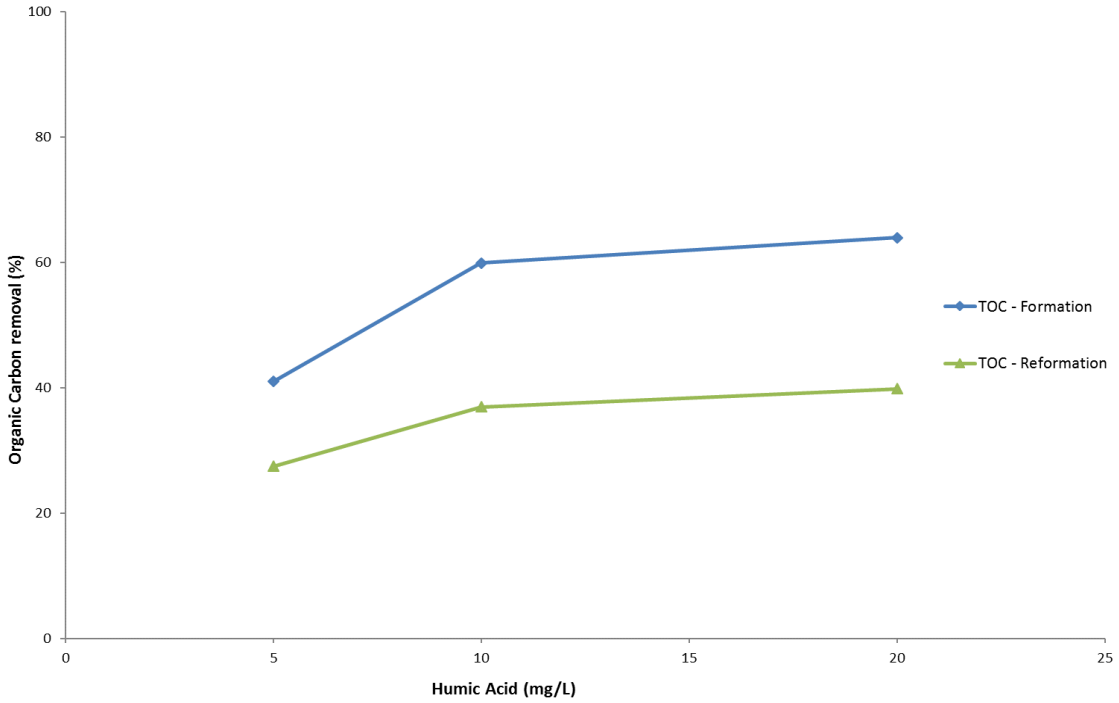

Figure 16. TOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

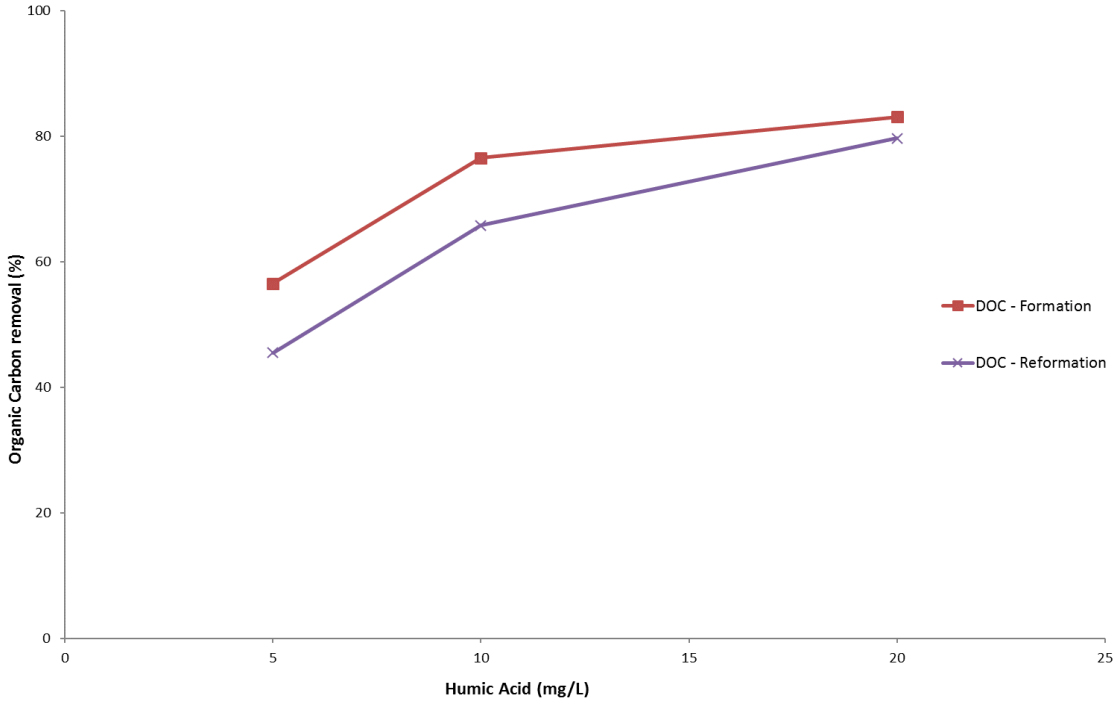

Figure 17. DOC removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

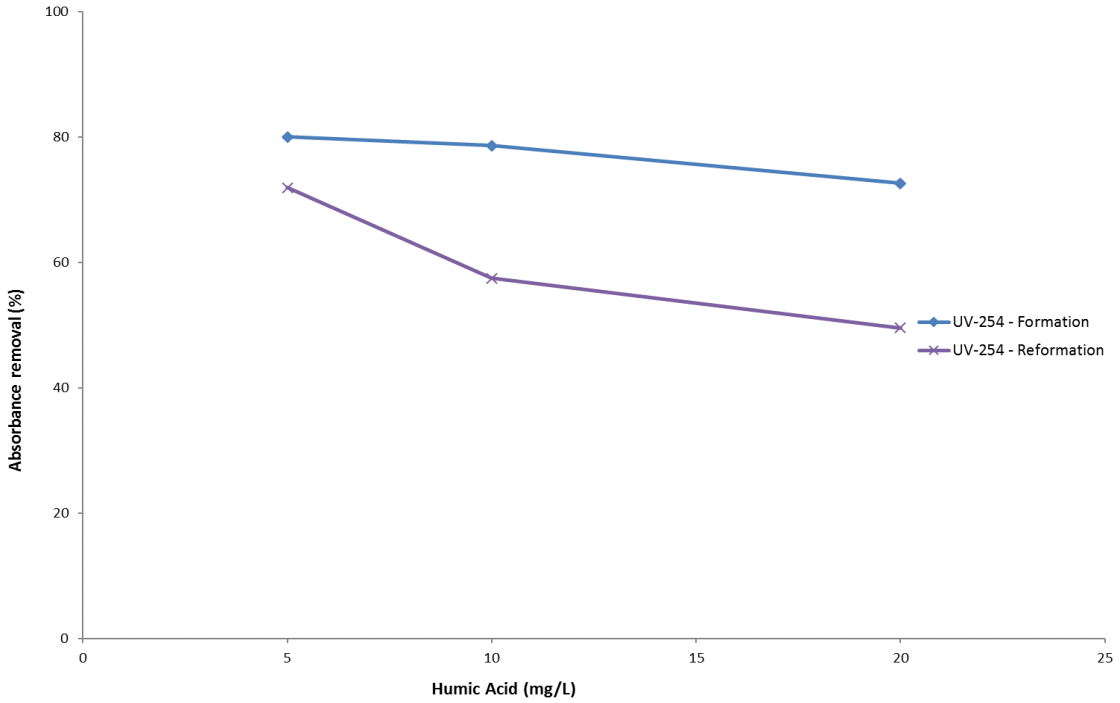

Figure 18. UV_{254} removal efficiency after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

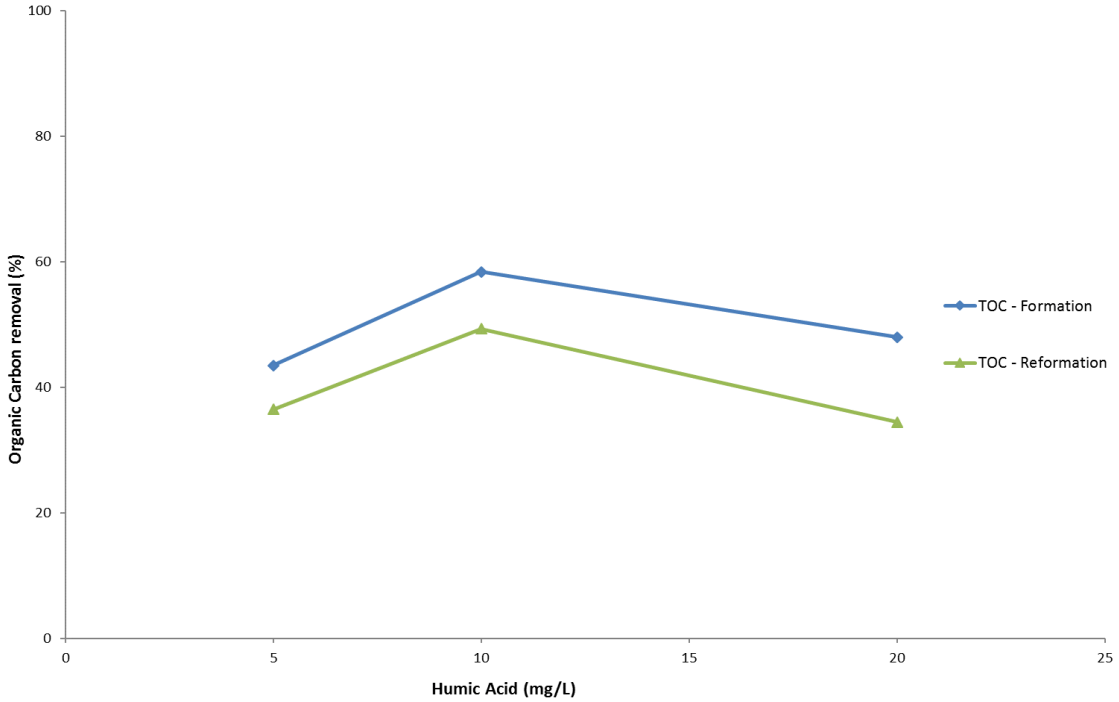

Figure 19. TOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

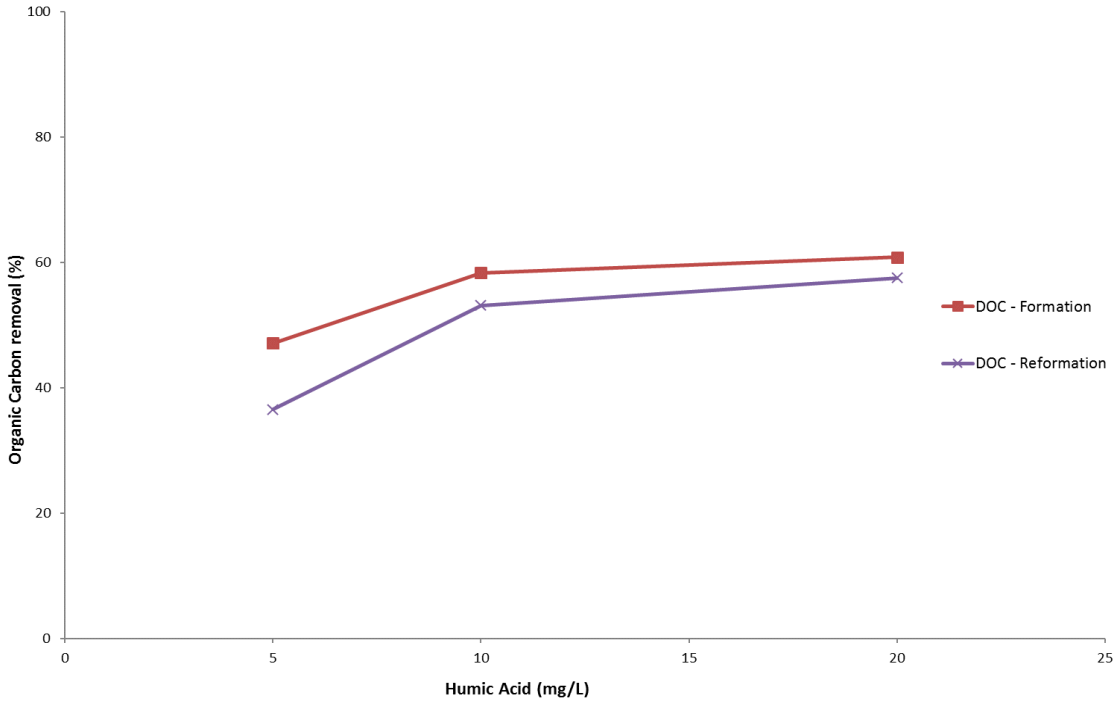

Figure 20. DOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

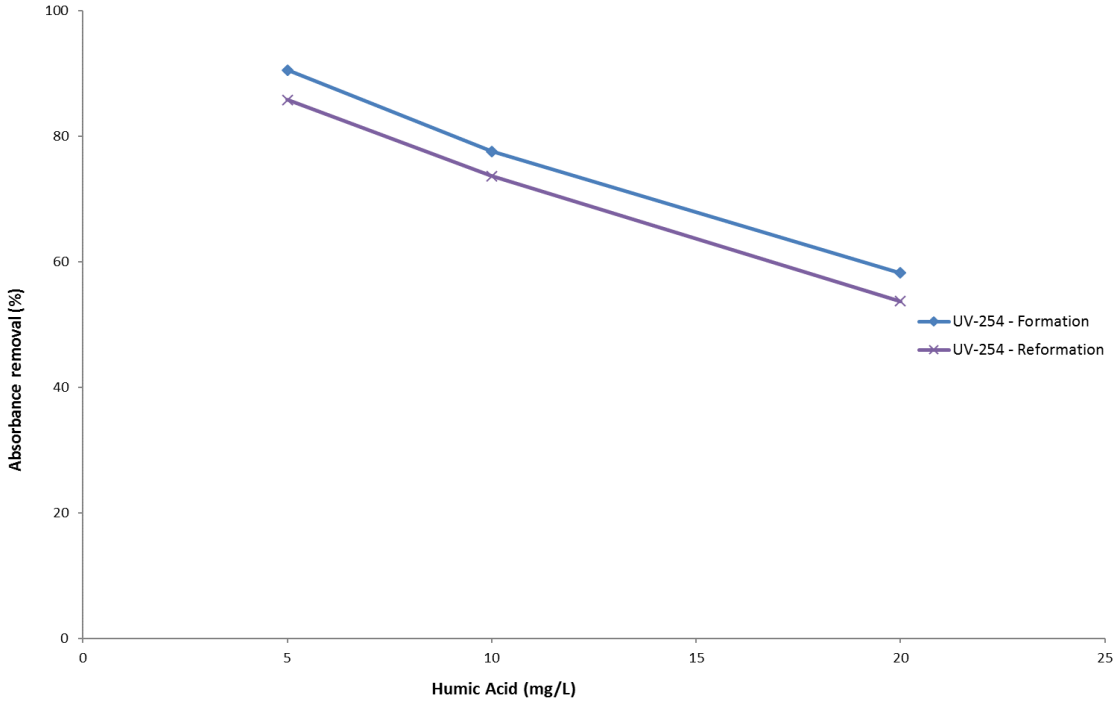

Figure 21. UV_{254} removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

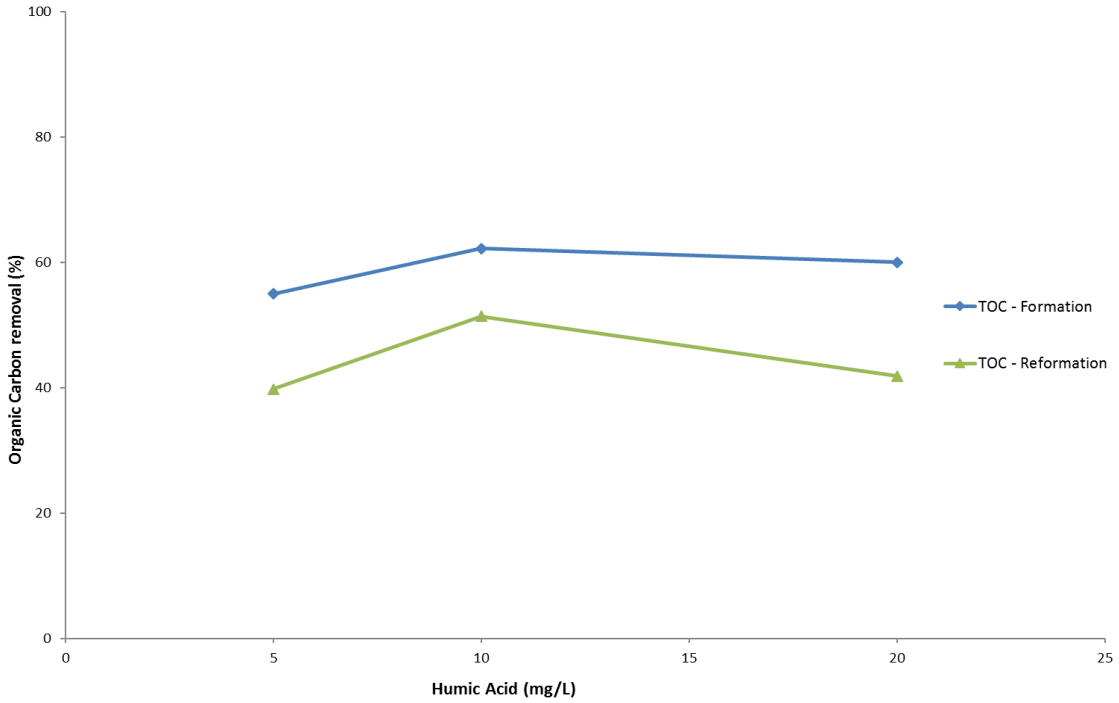

Figure 22. TOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

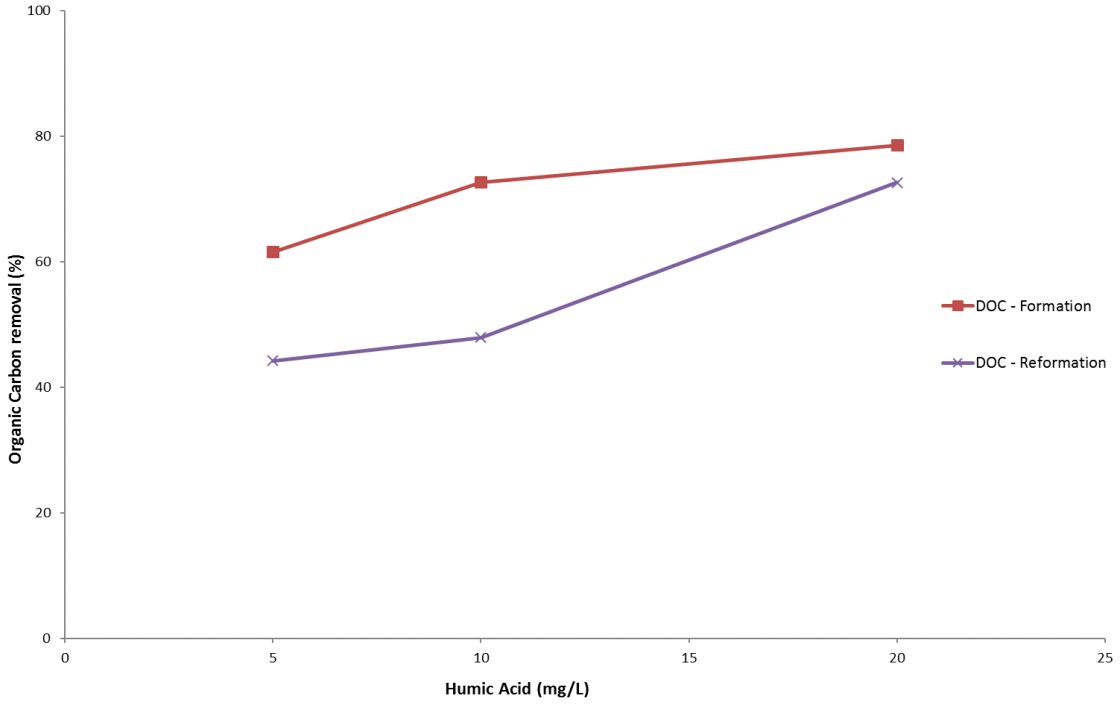

Figure 23. DOC removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

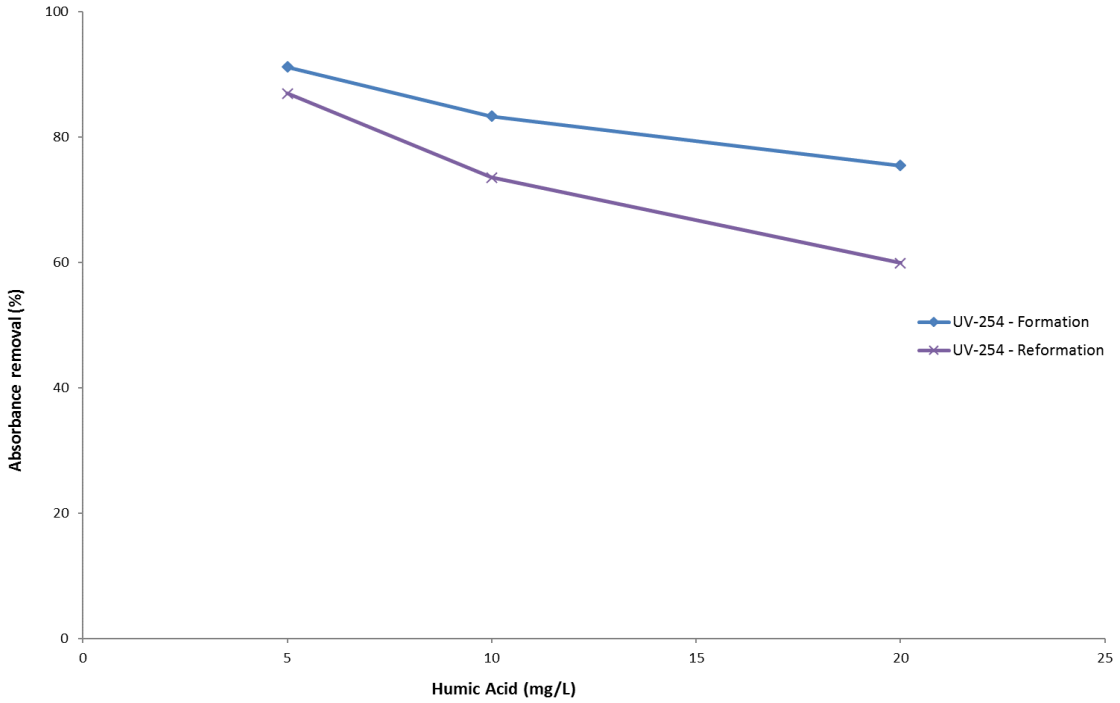

Figure 24. UV_{254} removal efficiency after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

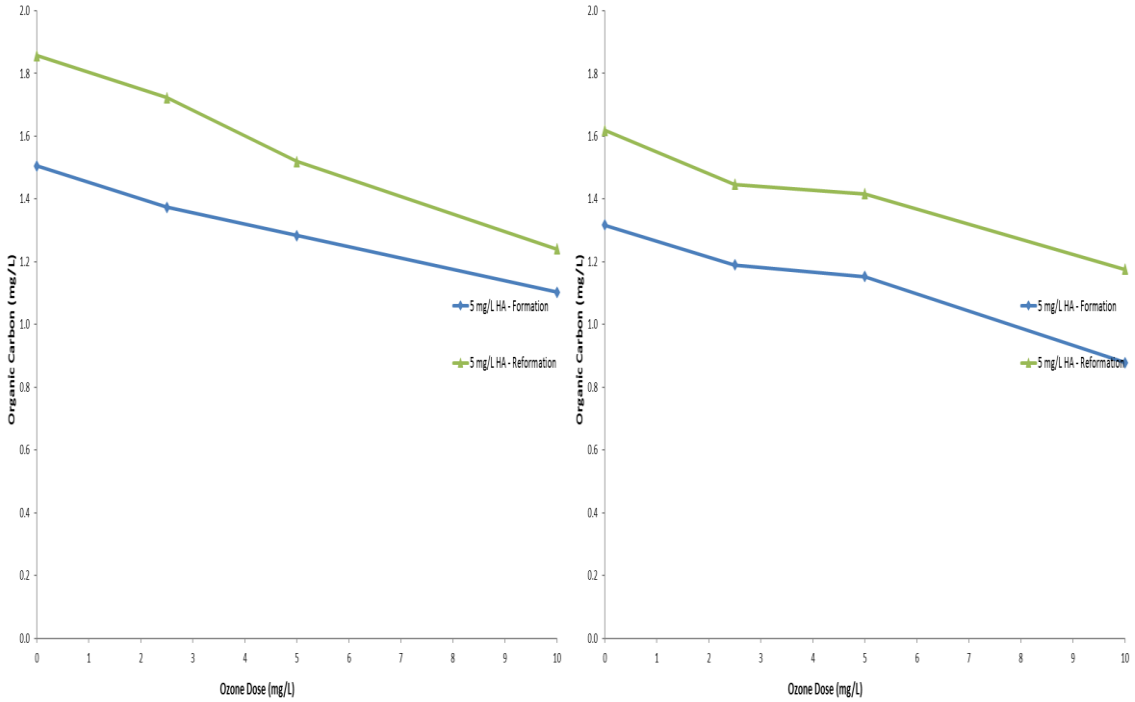

Figure 25. Residual TOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right)

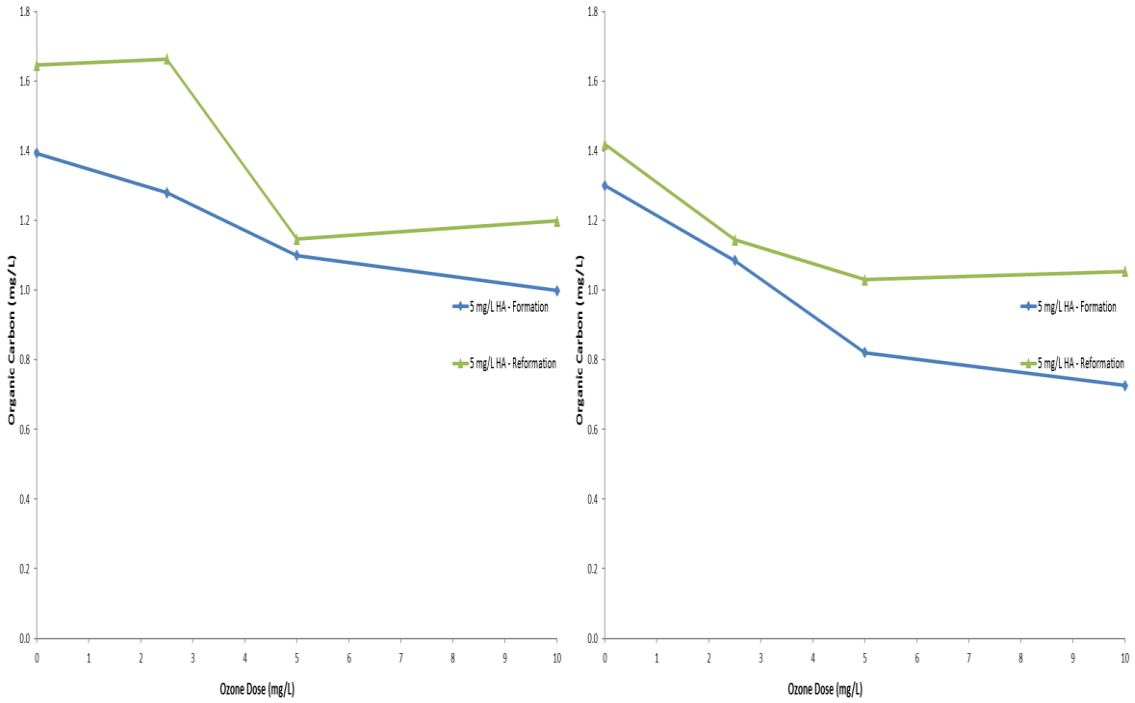

Figure 26. Residual DOC after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right)

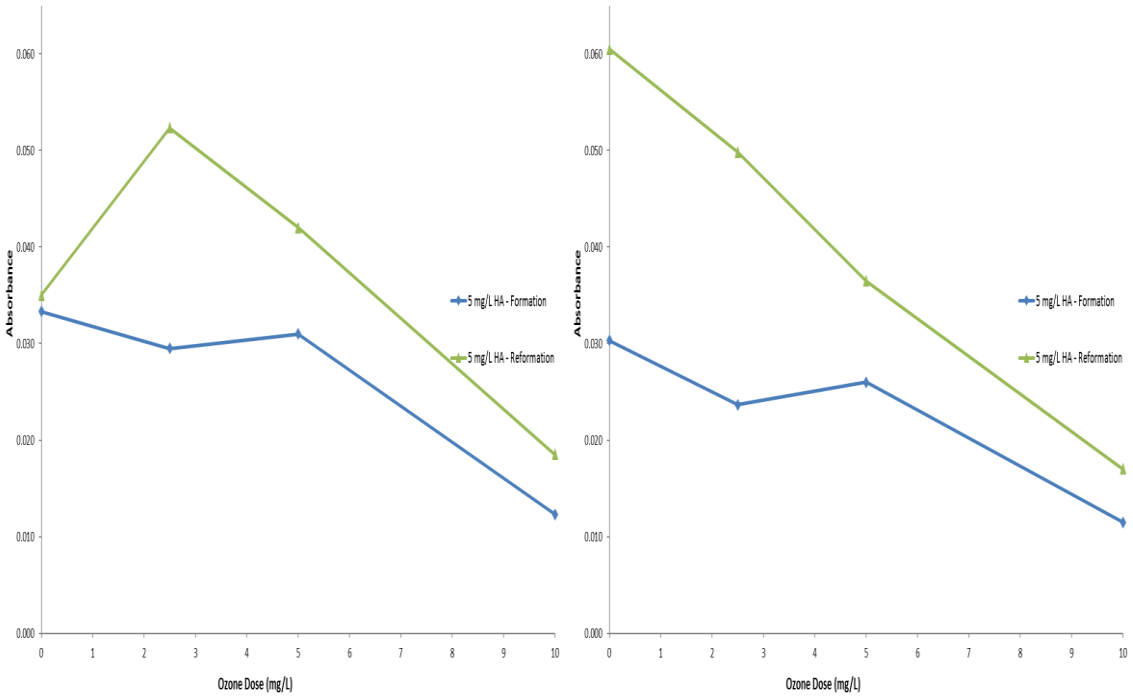

Figure 27. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right)

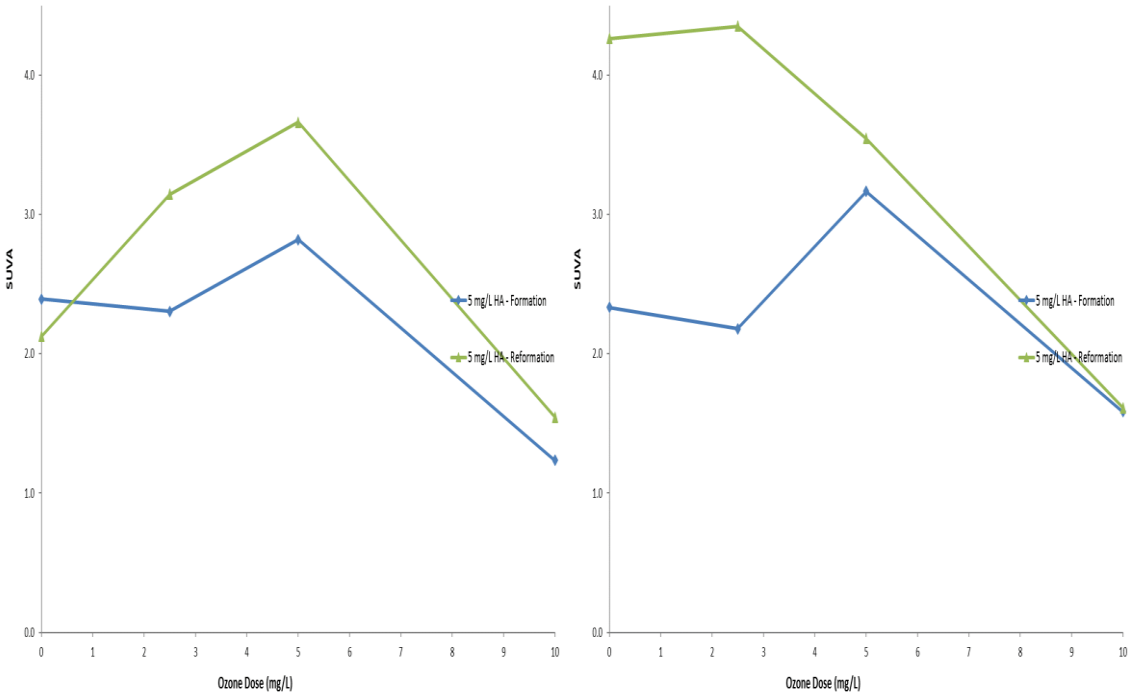

Figure 28. SUVA after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right)

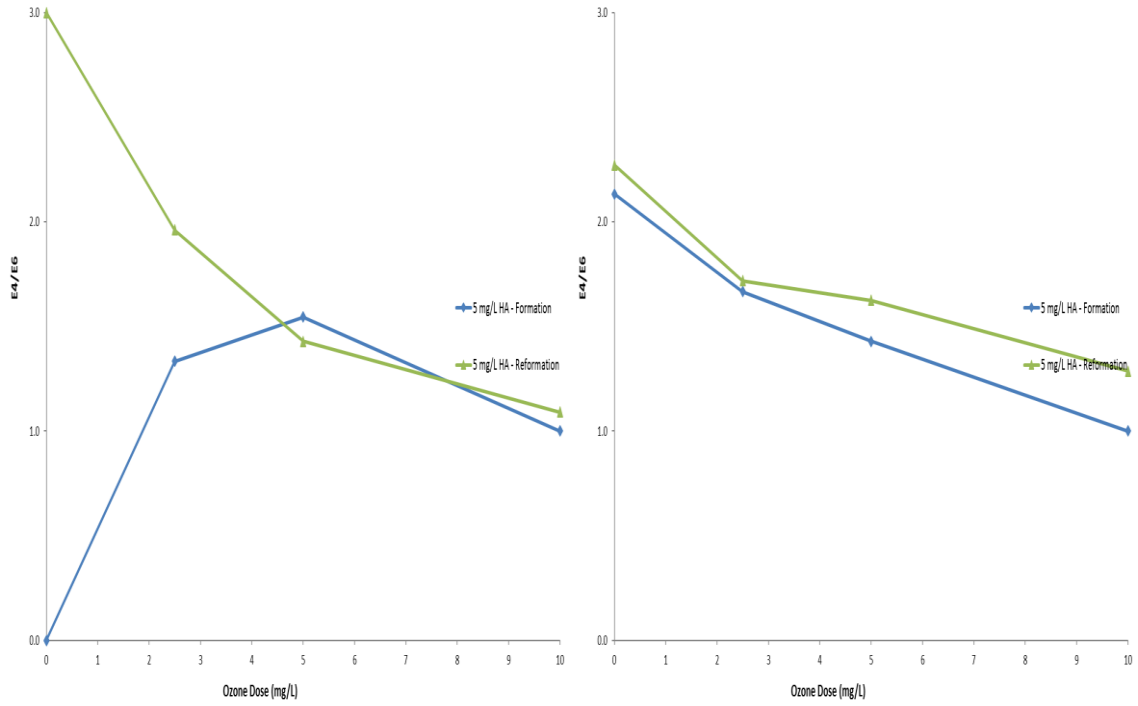

Figure 29. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 5 mg/L humic acid with alum (left) and with PACl (right)

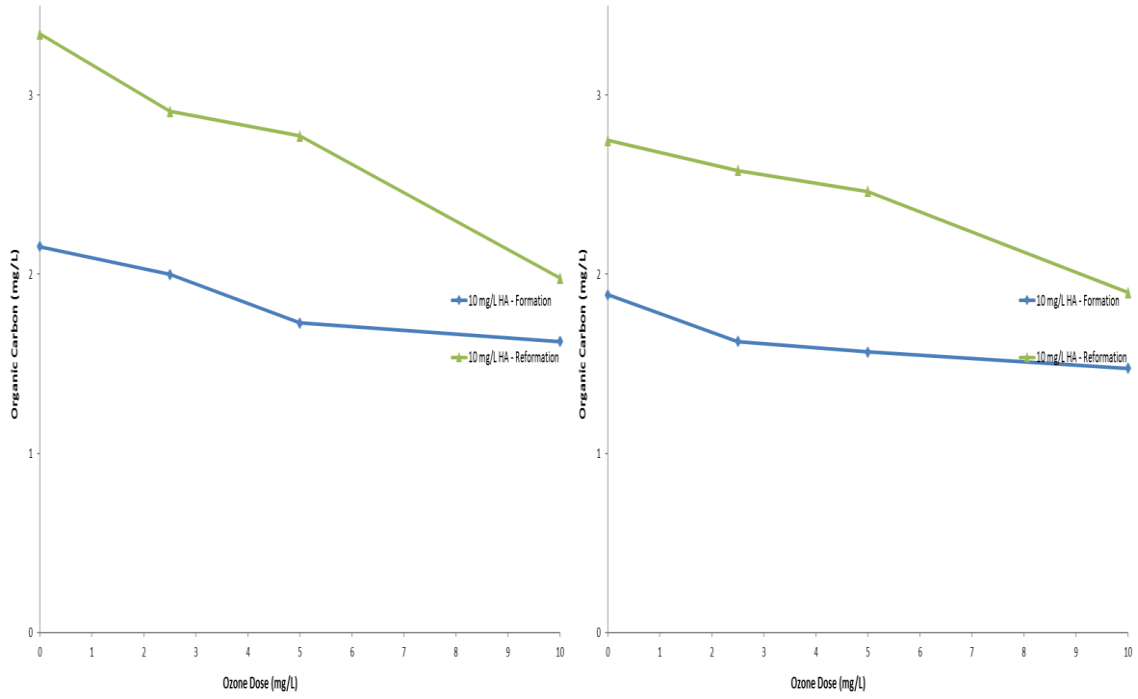

Figure 30. Residual TOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right)

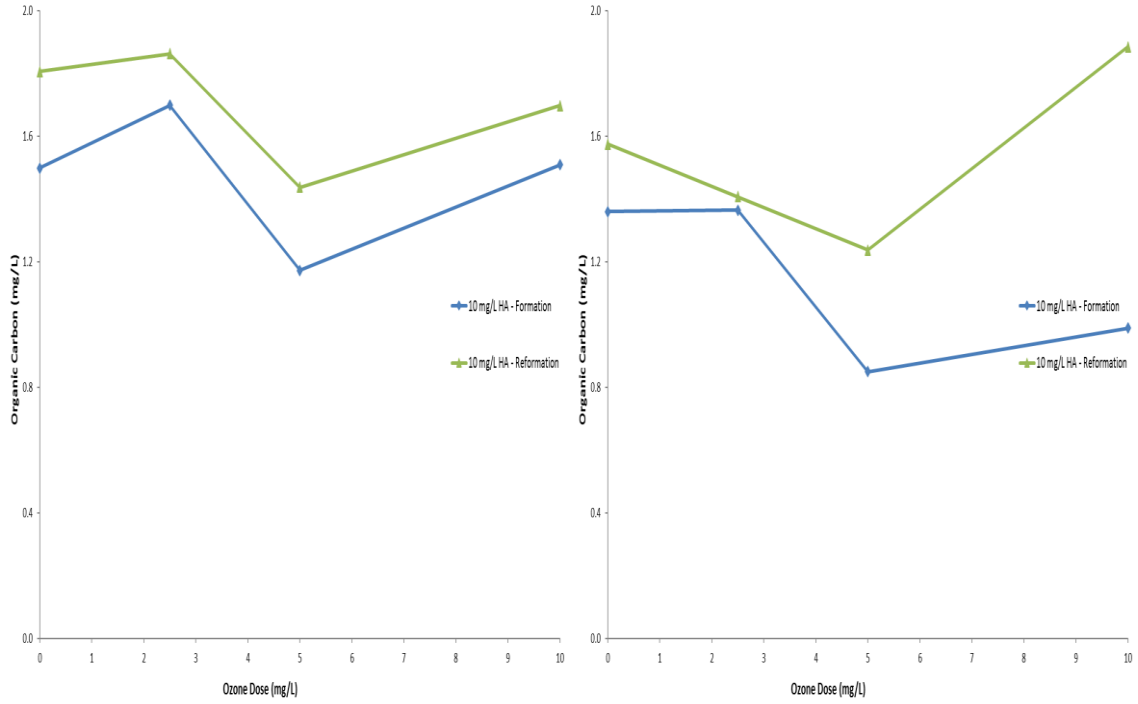

Figure 31. Residual DOC after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right)

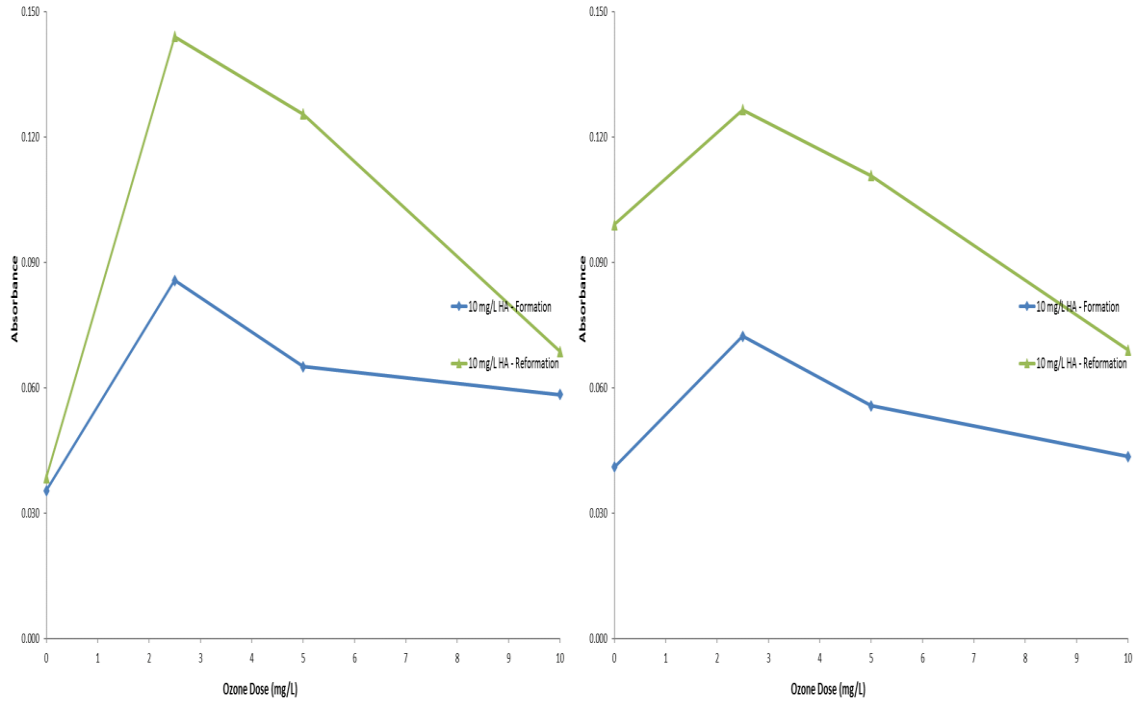

Figure 32. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right)

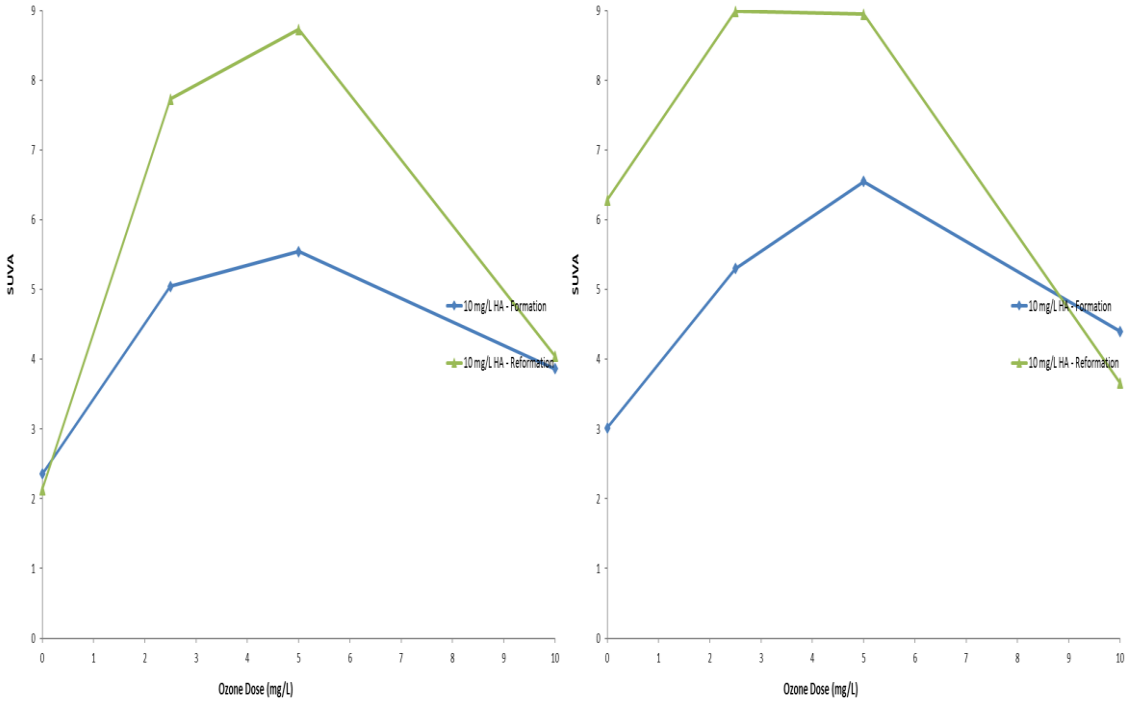

Figure 33. SUVA after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right)

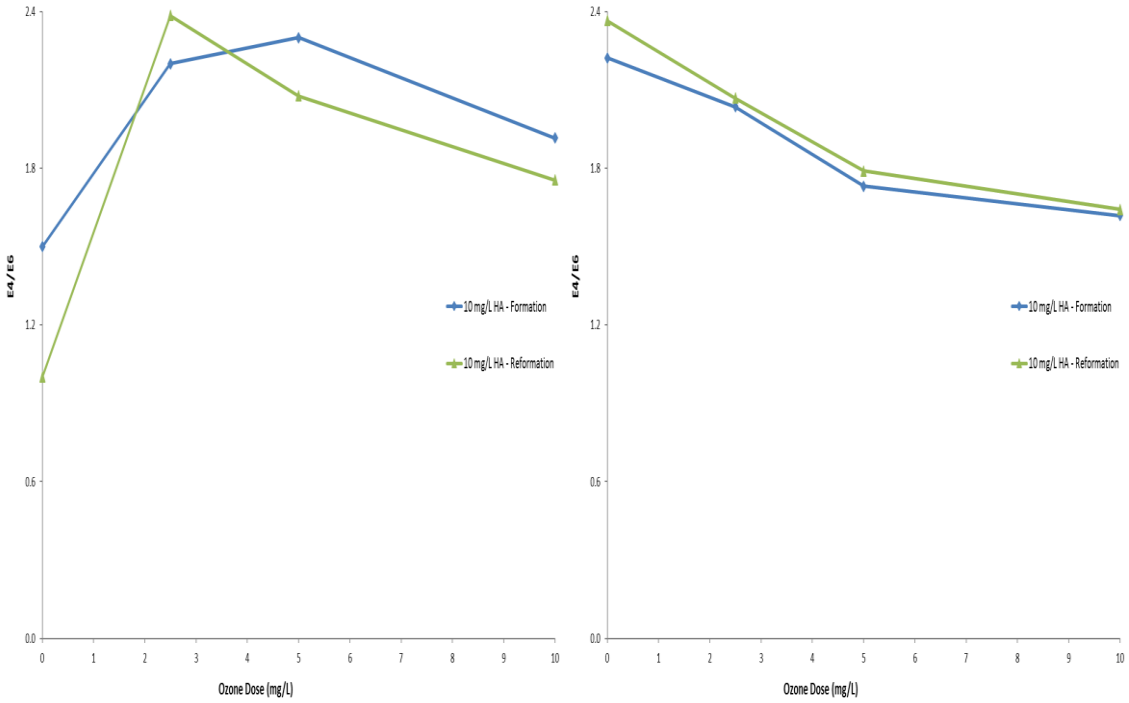

Figure 34. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid with alum (left) and with PACl (right)

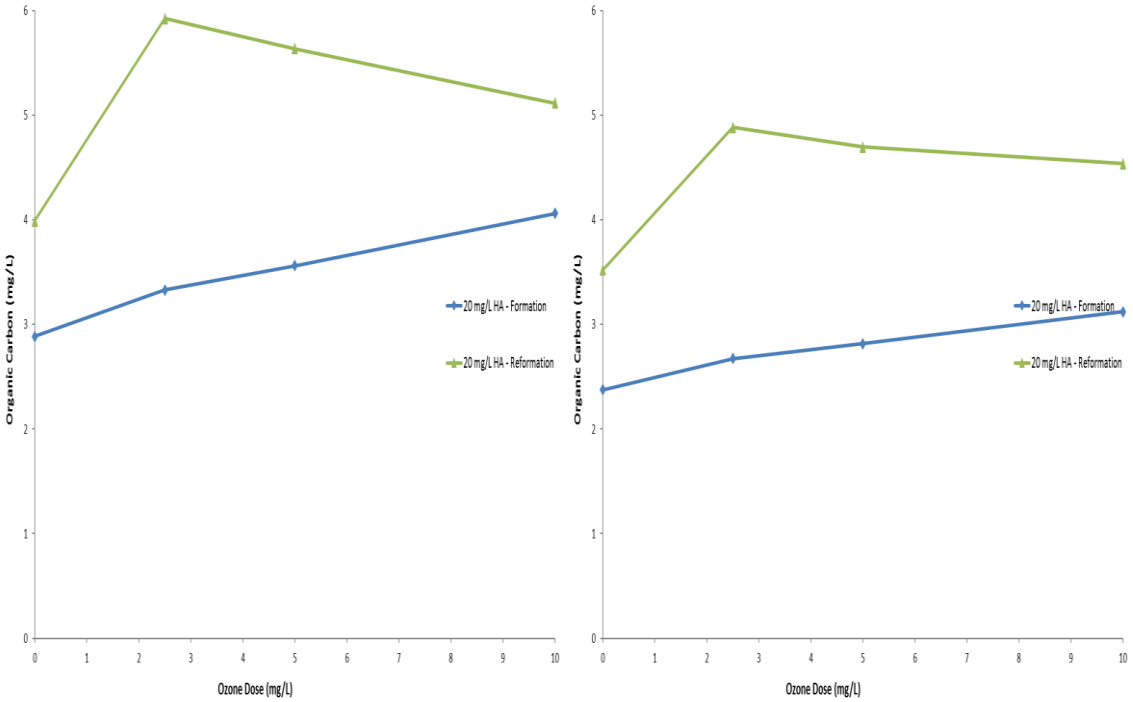

Figure 35. Residual TOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right)

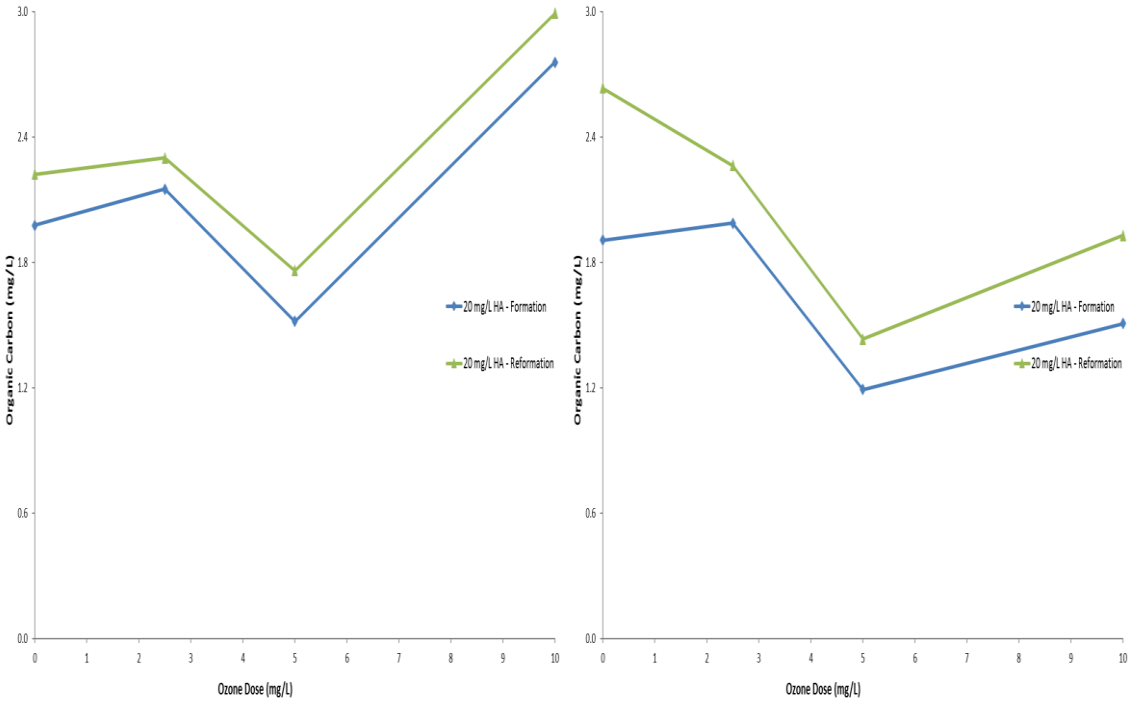

Figure 36. Residual DOC after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right)

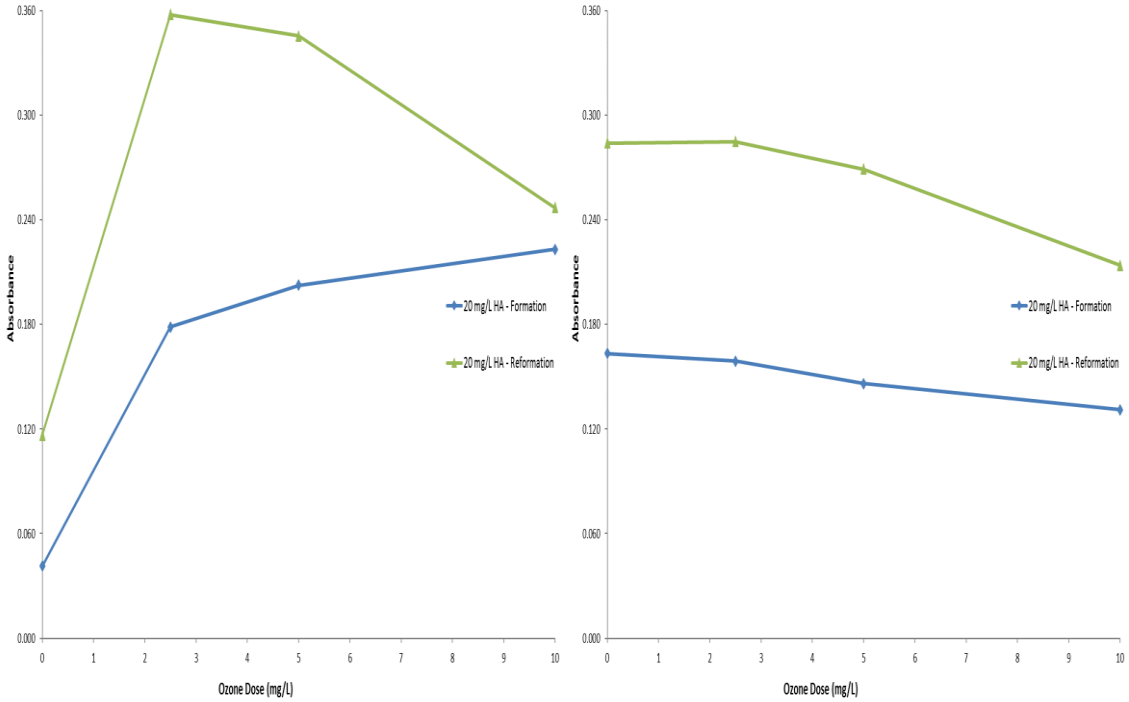

Figure 37. Residual absorbance at 254 nm after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right)

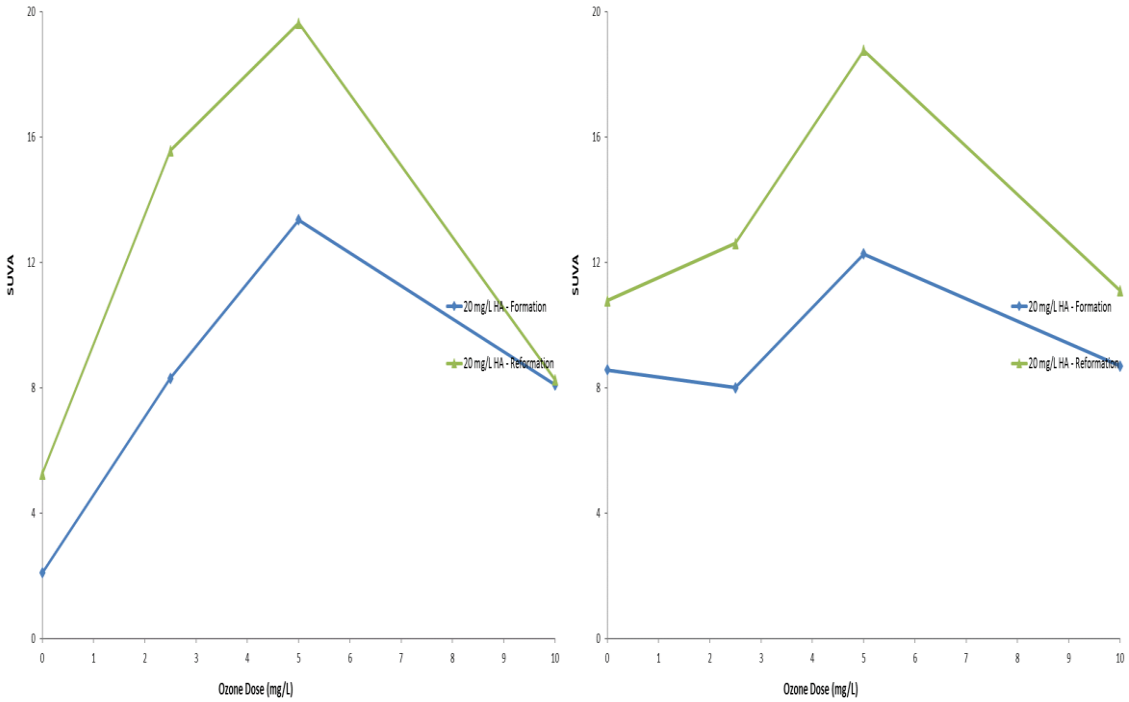

Figure 38. SUVA after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right)

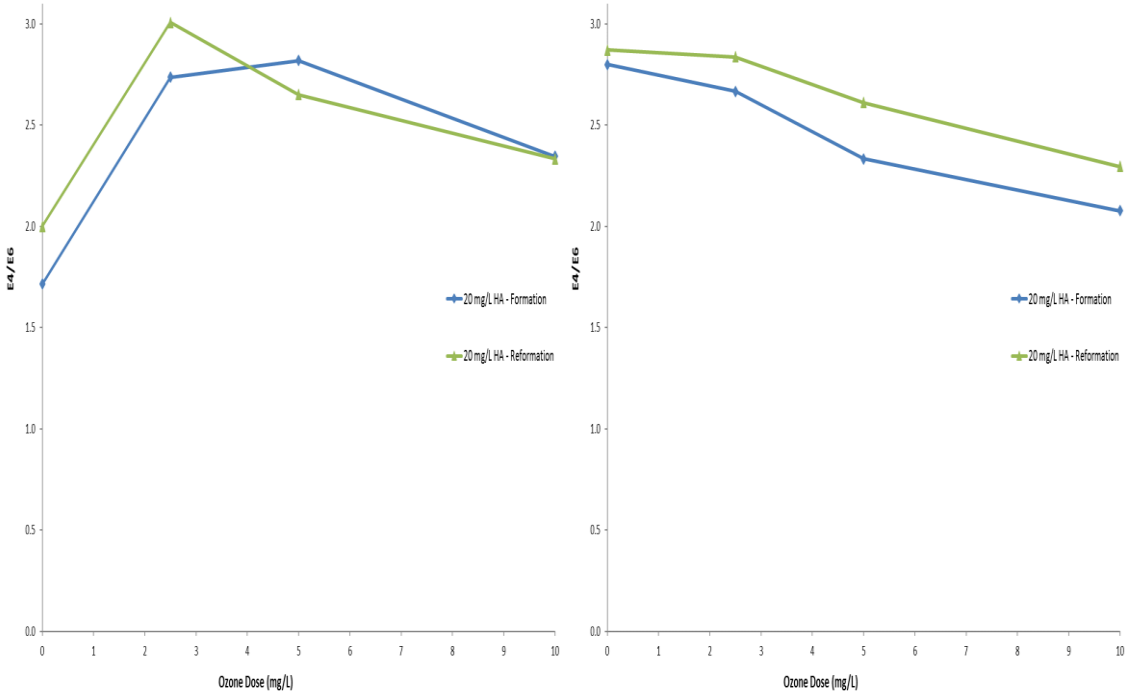

Figure 39. E_4/E_6 ratio after flocculation of pre-ozonated synthetic waters containing 20 mg/L humic acid with alum (left) and with PACl (right)

Table 1. Parameters measured in raw water

TOC (mg/L)	DOC (mg/L)	UV_{254} (cm^{-1})	UV_{465} (cm^{-1})	UV_{656} (cm^{-1})	SUVA (L/mg.m)	E_4/E_6
1.95	1.89	0.130	0.024	0.008	6.88	3.06
3.88	3.62	0.261	0.048	0.017	7.20	2.91
7.79	7.04	0.533	0.099	0.033	7.58	2.96

Table 2. Removal efficiencies after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

	Removal Efficiency (%)					
Humic acid	Formation			Reformation		
conc. (mg/L)	TOC	DOC	UV_{254}	TOC	DOC	UV_{254}
5	22.85	26.26	74.36	4.86	12.85	73.08
10	44.82	58.57	86.44	14.38	50.08	85.22
20	63.05	71.93	92.25	48.90	68.43	78.16

Table 3. Removal efficiencies after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

	Removal Efficiency (%)					
Humic acid	Formation			Reformation		
conc. (mg/L)	TOC	DOC	UV_{254}	TOC	DOC	UV_{254}
5	29.65	32.23	77.31	11.70	11.89	59.74
10	48.76	53.06	67.11	25.46	48.52	44.72
20	57.36	69.45	66.53	24.12	67.35	32.94

Table 4. Removal efficiencies after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

	Removal Efficiency (%)					
Humic acid	Formation			Reformation		
conc. (mg/L)	TOC	DOC	UV_{254}	TOC	DOC	UV_{254}
5	34.22	41.79	76.15	22.16	39.27	67.69
10	55.75	67.62	75.05	28.98	60.27	51.82
20	54.37	78.45	62.03	27.78	75.01	35.22

Table 5. Removal efficiencies after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with alum

	Removal Efficiency (%)					
Humic acid	Formation			Reformation		
conc. (mg/L)	TOC	DOC	UV_{254}	TOC	DOC	UV_{254}
5	43.46	47.09	90.51	36.44	36.55	85.77
10	58.37	58.30	77.61	49.32	53.09	73.64
20	47.95	60.83	58.19	34.44	57.50	53.69

Table 6. Removal efficiencies after flocculation of unozonated (0 mg/L O_3) synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

	Removal Efficiency (%)					
Humic acid	**Formation**			**Reformation**		
conc. (mg/L)	**TOC**	**DOC**	**UV_{254}**	**TOC**	**DOC**	**UV_{254}**
5	32.52	31.14	76.67	17.07	24.86	53.46
10	51.69	62.41	84.26	29.61	56.46	62.00
20	69.59	72.93	69.38	54.91	62.58	46.75

Table 7. Removal efficiencies after flocculation of 2.5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

	Removal Efficiency (%)					
Humic acid	**Formation**			**Reformation**		
conc. (mg/L)	**TOC**	**DOC**	**UV_{254}**	**TOC**	**DOC**	**UV_{254}**
5	39.06	42.54	81.79	25.87	39.40	61.67
10	58.40	62.29	72.23	33.91	61.12	51.44
20	65.73	71.77	70.19	37.44	67.86	46.56

Table 8. Removal efficiencies after flocculation of 5 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

	Removal Efficiency (%)					
Humic acid	**Formation**			**Reformation**		
conc. (mg/L)	**TOC**	**DOC**	**UV_{254}**	**TOC**	**DOC**	**UV_{254}**
5	40.96	56.52	80.00	27.42	45.48	71.92
10	59.89	76.52	78.63	36.90	65.81	57.49
20	63.91	83.09	72.63	39.84	79.64	49.56

Table 9. Removal efficiencies after flocculation of 10 mg/L pre-ozonated synthetic waters containing 5, 10 and 20 mg/L humic acid with PACl

	Removal Efficiency (%)					
Humic acid	**Formation**			**Reformation**		
conc. (mg/L)	**TOC**	**DOC**	**UV_{254}**	**TOC**	**DOC**	**UV_{254}**
5	54.99	61.54	91.15	39.74	44.20	86.92
10	62.22	72.68	83.30	51.38	47.91	73.51
20	60.02	78.59	75.44	41.87	72.60	59.88

Curriculum Vitae

Biography

Environmental Engineering, Marmara University (BSc)

Environmental Engineering, Marmara University (MSc)

Environmental Engineering, Marmara University (PhD)

Research Fields:

- Particle aggregation
- Chemical treatment
- Treatment & ozonation of NOM
- Sludge dewatering

Foreign Languages

English, C1 Advanced

Research Areas

Environmental Engineering, Environmental Sciences, Environmental Technology

Academic Titles / Tasks

Research Assistant, Marmara University, Faculty of Engineering, Environmental Engineering, 2011 - Continues

Published journal articles indexed by SCI, SSCI, and AHCI

I. **Flocculating performances of exopolysaccharides produced by a halophilic bacterial strain cultivated on agro-industrial waste**
ŞAM S., Kucukasik F., Yenigun O., Nicolaus B., Oner E., Yukselen M. A.
BIORESOURCE TECHNOLOGY, vol.102, no.2, pp.1788-1794, 2011 (SCI-Expanded)

II. **The Effect of Ozone on the Reversibility of Floc Breakage: Suspensions with High Humic Acid Content**
Sam S., Yukselen M. A., Zorba M., Gregory J.
OZONE-SCIENCE & ENGINEERING, vol.32, no.6, pp.435-443, 2010 (SCI-Expanded)

Refereed Congress / Symposium Publications in Proceedings

I. **Pharmaceuticals removal by adsorption with functionalized cellulose based foam**
Kalule S., Can Z. S., Haciosmanoğlu G. G., Şam S., Deghles A., Hamed O. A.
İTÜ 2nd INTERNATIONAL GRADUATE RESEARCH SYMPOSIUM IGRS'23, İstanbul, Turkey, 16 - 18 May 2023

II. **EVALUATION OF HEAVY METAL SORPTION CAPACITIES OF CELLULOSE BASED ADSORBENTS WITH IONIC FUNCTIONAL GROUPS – AQUEOUS COBALT (II) ION REMOVAL –**
Hashi A. A., Erdoğan B., Kuzucu Y., Şam S., Hacıosmanoğlu G. G., Deghles A., Hamed O. A., Can Z. S.
IWA DIPCON 2022, İstanbul, Turkey, 24 - 28 October 2022, no.92, pp.217-223

III. **Study on Adsorption Performance of MIL-101(Cr) for Ibuprofen Uptake from Aqueous Media**
Faisal M., Engel H. B., Hacıosmanoğlu G. G., Şam S., Kıran Yıldırım B., Genç S., Can Z. S.
1 st International Conference on Advances in Engineering, Architecture, Science and Technology, Turkey, 15 - 17 December 2021

IV. **Synthesis and Characterization of Magnetic Metal Organic Framework (MOF) for Methyl Orange Removal from Aqueous Solutions**
Karakaya B., Kıran Yıldırım B., Can Z. S., Hacıosmanoğlu G. G., Şam S., Genç S.
1 st International Conference on Advances in Engineering, Architecture, Science and Technology, Erzurum, Turkey, 15 - 17 December 2021, vol.1, no.67, pp.642

V. **Investigation of the Effect of Pre-ozonation on Organic Matter Removal via Flocculation**
ŞAM S., YÜKSELEN M. A., CAN Z. S.
THE 11TH EASTERN EUROPEAN YOUNG WATER PROFESSIONALS CONFERENCE - Water for All - Water for Nature, Reliable Water Supply, Wastewater Treatment and Reuse, 1 - 05 October 2019

VI. **Halofil kaynaklı ekzopolisakkaritlerin flokülasyon performanslarının incelenmesi**
ŞAM S., Küçükaşık F., YENİGÜN O., TOKSOY ÖNER E., YÜKSELEN M. A.
II. UlusalEkoloji ve Çevre Öğrenci Kongresi, Çanakkale, Turkey, 23 - 25 September 2010

VII. **Ekstremofil kaynaklı ekzopolisakkaritlerin biyoflokülant özellikleri**
ŞAM S., Küçükaşık F., YENİGÜN O., TOKSOY ÖNER E., YÜKSELEN M. A.
12. EndüstriyelKirlenme Kontrolü Sempozyumu, İstanbul, Turkey, 16 - 18 June 2010

VIII. **Comparison of coagulation performances of monomeric and polymeric hydrolysing coagulants under increasing humic acid and pre-ozonation conditions**
ŞAM S., YÜKSELEN M. A., Gregory J.
4th IWA Specialist Conference - NaturalOrganic Matter: from Source to Tap, Bath, United Kingdom, 2 - 04

IX. **Impact of ozonation on thefloc reversibility in waters with high organic content**
YÜKSELEN M. A., ŞAM S., Dede A., Gregory J.
IWA - International Conference onParticle Separation (IWA-PS 2007), Toulouse, France, 9 - 11 July 2007

X. **Kimyasal çamur floklarının özellikleri ve hızlı karıştırma süresinin susuzlaştırmaya etkisi**
ŞAM S., YÜKSELEN M. A.
Ulusal Çevre Sempozyumu, Mersin, Turkey, 01 May 2007

XI. **Reversibility of floc breakage: Importance for sludge dewatering properties**
ŞAM S., YÜKSELEN M. A.
Environment: Survival and Sustainability Symposium, Lefkoşa, Cyprus (Kktc), 19 - 24 February 2007

XII. **Importance of rapid mixing time on sludge dewatering properties**
ŞAM S., YÜKSELEN M. A.
Environment: Survival and Sustainability Symposium, Lefkoşa, Cyprus (Kktc), 19 - 24 February 2007

XIII. **Aggregation and breakage of activated sludge flocs: implication for dewatering**
YÜKSELEN M. A., Salpar G. D., ŞAM S., Saatçı A. M.
IWA SpecializedConference - Sustainable Sludge Management: state of the art, challenges andperspectives, Moskva, Russia, 29 - 31 May 2006

XIV. **Kimyasal çamur floklarının özellikleri ve susuzlaştırma uygulamaları**
ŞAM S., YÜKSELEN M. A.
Çevre Kirlenmesi Öncelikleri Sempozyumu V (ÇEVKOS V), Kocaeli, Turkey, 01 May 2006

Supported Projects

Genç, S., TUBITAK Project, Tekstil Endüstrisi Atık Sularında Zr-MOF Bazlı Membranlar ile Boyar Madde Gideriminin Incelenmesi, 2023

Akkoyunlu B. O., TUBITAK Project, Yağış Alt olay Örneklemesi ve Analizi ile Bulut Altı Temizleme Mekanizmasının İncelenmesi, 2010 - 2012

Toksoy Öner E., TUBITAK Project, Bioethanol - A Source of Renewable Energy from Extremophiles, 2009 - 2011

Tayanç M., TUBITAK Project, Türkiye'de İklim Değişkenliği: İstanbul'da Yeni Bir Gözlem Ağı ve Tarihsel Veriler, 2007 - 2009

Can Z. S., Yükselen M. A., Gökyay O., TUBITAK Project, Yüksek Çözünmüş Organik Madde İçeren Sularda Flok Yapılarının İncelenmesi , 2005 - 2008

Yükselen M. A., TUBITAK Project, Yüksek organik madde içeren sularda flok yapısının incelenmesi, 2005 - 2007

Şam S., Yükselen M. A., Project Supported by Higher Education Institutions, Kimyasal çamur floklarının özellikleri ve bunların susuzlaştırmaya etkisi, 2005 - 2007

Metrics

Publication: 16

Citation (WoS): 78

Citation (Scopus): 96

H-Index (WoS): 2

H-Index (Scopus): 2

Congress and Symposium Activities

Investigation of the Effect of Pre-ozonation on Organic Matter Removal via Flocculation, Working Group, Praha, Czech Republic, 2019

Halofil kaynaklı ekzopolisakkaritlerin flokülasyon performanslarının incelenmesi, Working Group, Çanakkale, Turkey, 2010

Ekstremofil kaynaklı ekzopolisakkaritlerin biyoflokülant özellikleri, Working Group, İstanbul, Turkey, 2010

Comparison of coagulation performances of monomeric and polymeric hydrolysing coagulants under increasing humic acid and pre-ozonation conditions, Working Group, London, United Kingdom, 2008

Impact of ozonation on the floc reversibility in waters with high organic content, Working Group, Toulouse, France, 2007

Kimyasal çamur floklarının özellikleri ve hızlı karıştırma süresinin susuzlaştırmaya etkisi, Working Group, Mersin, Turkey, 2007

Reversibility of floc breakage: Importance for sludge dewatering properties, Working Group, Lefkoşa, Cyprus (Kktc), 2007

Importance of rapid mixing time on sludge dewatering properties, Working Group, Lefkoşa, Cyprus (Kktc), 2007

Kimyasal çamur floklarının özellikleri ve susuzlaştırma uygulamaları, Working Group, Kocaeli, Turkey, 2006

Aggregation and breakage of activated sludge flocs: implication for dewatering, Working Group, Moscow, Russia, 2006