

152437

**EFFECTS OF OZONATION, PHOTOCATALYTIC OXIDATION, AND
SEQUENTIAL OXIDATION ON COAGULATION OF HUMIC ACIDS**

by

SİBEL ŞEN

B.S. in Env. Eng. İstanbul Technical University, 2000

152437

**Submitted to the Institute of Environmental Sciences in partial fulfillment of the
requirements of Master Science
in
Environmental Technology**

Boğaziçi University

2004

**EFFECTS OF OZONATION, PHOTOCATALYTIC OXIDATION, AND
SEQUENTIAL OXIDATION ON COAGULATION OF HUMIC ACIDS**

APPROVED BY:

Prof. Dr. Miray BEKBÖLET..... *M. Bekebolet*
(Thesis Supervisor)

Prof. Dr. Cumali KINACI..... *Cumali Kinaci*

Assoc. Prof. Dr. Işıl BALCIOĞLU..... *Işıl Balcioğlu*

DATE OF APPROVAL... *29.01.2004*.....



Dedicated to my family...

ACKNOWLEDGMENT

I express my gratitude to my thesis supervisor Prof. Miray Bekbölet for her guidance, support, patience, encouragement and help throughout my thesis. I would also like to express my appreciation to the other members of my thesis committee Prof. Cumali Kınacı and Assoc. Prof. Işıl Balcıoğlu for their valuable time and comments.

The experiments in this study were conducted in Boğaziçi University of Environmental Sciences Laboratory. I want to thank all the laboratory staff for their help. Special thanks are extended to my all friends in Boğaziçi University for their support.

I am thankful to Umut Kavurmacı for his encouragements during my studies and generous helps.

Lastly, I am grateful to my family for providing me support and help that I needed throughout my work.

ABSTRACT

EFFECTS OF OZONATION, PHOTOCATALYTIC OXIDATION, AND SEQUENTIAL OXIDATION ON COAGULATION OF HUMIC ACIDS

In this study, coagulation behavior of untreated and treated humic acids with two different types of metal coagulant and two types of polyelectrolyte as coagulant aid were investigated. The aim of this study was to understand the coagulation efficiencies of different type of coagulant and the mechanisms underlying the contribution of pretreatments to coagulation. Pretreatment were done by ozonation, photocatalytic oxidation and sequential oxidation in which ozonation was applied as pretreatment stage for partial oxidation of humic acids prior to photocatalytic oxidation using TiO_2 .

The coagulation properties of humic acid were evaluated according to Color_{436} and UV_{254} values. These parameters were calculated for treated and untreated humic acid samples as well as for alum, ferric chloride, and combination of metal coagulant with anionic and nonionic polyelectrolyte. Coagulation efficiencies decreased with pretreatments regardless of the type of the coagulants used. However, anionic and nonionic polyelectrolytes were effective coagulant aids for the coagulation of humic acid. Especially, polyelectrolytes were more effective for untreated humic acid than treated humic acid. Removal percentages of UV_{254} and Color_{436} values increased with using metal salts combining with anionic and nonionic polyelectrolyte. Nevertheless, applied high dosage of primary coagulant combining with low synthetic polyelectrolyte led to higher removal percentages of humic acid than applied low dosage of primary coagulant combining with high dosage of synthetic polyelectrolyte. Furthermore, using metal salts combining with anionic and nonionic polyelectrolyte lead to decrease in used primary coagulant.

ÖZET

OZONLAMANNIN, FOTOKATALİTİK OKSİDASYONUN VE BİRLEŞTİRİLMİŞ OKSİDASYONUN HÜMİK ASİTLERİN KOAGÜLASYONU ÜZERİNE ETKİLERİ

Bu çalışmada, arıtılmamış ve ön arıtma yapılmış hümik asitlerin iki farklı tipteki koagülant ve iki farklı koagülant yardımcısı anyonik ve noniyonik polielektrotlarla sağlanan koagülasyon verimleri araştırılmıştır. Bu çalışmanın amacı, farklı koagülantların koagülasyon verimleri üzerine etkilerini ve önarıtmaların koagülasyon mekanizması üzerine etkilerinin anlaşılmasıdır. Ön arıtma işlemleri, ozonlama, fotokatalitik oksidasyon ve ozonlamanın TiO_2 kullanılan fotokatalitik oksidasyonu öncesinde hümik asitlerin kısmen oksidasyonu için ön arıtma olarak kullanıldığı ardışık bir sistemde uygulanmıştır.

Hümik asitlerin koagülasyon özellikleri $Color_{436}$ ve UV_{254} değerlerine göre incelenmiştir. Bu parametreler önartılmış ve önartılmamış hümik asitlerin alum, demir (III) klorür ve bunların anyonik ve noniyonik polielektrolitlerle birlikte kullanıldıkları durumlar için ölçülmüştür. Koagülasyon verimlerinin koagülant tipine bağlı olmaksızın ön arıtma ile düştüğü gözlenmiştir. Koagülant yardımcısı olarak anyonik ve noniyonik polielektrolit kullanılması ön arıtma uygulanmamış hümik asit giderim verimleri önartma uygulanmış hümik asitlerin giderim verimlerinden daha yüksektir. Fakat yüksek dozlardaki koagülant ile düşük dozlarda polielektrolit kullanılması, düşük dozlarda koagülant ile yüksek dozlarda polielektrolit kullanılmasına göre daha iyi sonuç vermektedir. Ayrıca koagülant yardımcısı olarak anyonik ve noniyonik polielektrolitlerin kullanılması gereken alum ve demir (III) klorür miktarını da azaltmaktadır.

TABLE OF CONTENTS

ACKNOWLEDGMENT	iv
ABSTRACT	v
ÖZET	vi
LIST OF FIGURES	xii
LIST OF TABLES	xvi
1. INTRODUCTION	1
2. THEORETICAL BACKGROUND	
2.1. Humic Substances	3
2.1.1. Formation of Humic Substances	4
2.1.2. Composition and Structure of Humic Substances	4
2.1.3. Interactions of Humic Substances with Environmental Chemicals	6
2.1.3.1. Sorptive Effects	6
2.1.3.2. Solubilizing Effects	7
2.1.3.3. Catalytic Effects on Hydrolysis	7
2.1.3.4. Photosensitizing and Quenching Effects	8
2.1.4. The Environmental Effect of Humic Substances	8
2.1.5. Removal of Humic Substances	9
2.2. Oxidative Removal of Humic Substances	10
2.2.1. Ozonation	11
2.2.1.1. Oxidation of Humic Substances with Ozone	12
2.2.2. Photocatalysis	16
2.2.2.1. Kinetics of Photocatalytic Degradation	16
2.2.2.2. Removal of Humic Substances by TiO ₂ /UV Process	17
2.3. Coagulation	19
2.3.1. Colloidal Systems	20
2.3.2. The Stability of Colloids	22
2.3.2.1. Electrostatic Stabilization	22
2.3.2.2. Steric Stabilization	24
2.3.3. Destabilization	24
2.3.3.1. Double Layer Compression	25

4.2.2.2. Coagulation Profiles for Photocatalytically Treated Humic Acid with Ferric Chloride	54
4.2.2.3. Coagulation Profiles for Sequentially Treated Humic Acid with Ferric Chloride	55
4.3. Coagulation of Humic Acid with Combination of Alum and Polymer	56
4.3.1. Coagulation of Untreated Humic Acid with Combinations of Alum and Anionic Polymer	56
4.3.2. Coagulation of Treated Humic Acid with Combinations of Alum and Anionic Polymer	59
4.3.2.1. Coagulation of Ozonated Humic Acid with Combinations of Alum and Anionic Polymer	59
4.3.2.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Alum and Anionic Polymer	61
4.3.2.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Alum and Anionic Polymer	63
4.3.3. Coagulation of Untreated Humic Acid with Combinations of Alum and Nonionic Polymer	65
4.3.4. Coagulation of Treated Humic Acid with Combinations of Alum and Nonionic Polymer	67
4.3.4.1. Coagulation of Ozonated Humic Acid with Combinations of Alum and Nonionic Polymer	67
4.3.4.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Alum and Nonionic Polymer	68
4.3.4.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Alum and Nonionic Polymer	71
4.4. Coagulation of Humic Acid with Combinations of Ferric Chloride and Polymer	73
4.4.1. Coagulation of Untreated Humic Acid with Combinations of Ferric Chloride and Anionic Polymer	73
4.4.2. Coagulation of Treated Humic Acid with Combinations of Ferric chloride and Anionic Polymer	76
4.4.2.1. Coagulation of Ozonated Humic Acid with Combinations of Ferric Chloride and Anionic Polymer	76

4.4.2.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Ferric Chloride and Anionic Polymer	78
4.4.2.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Ferric Chloride and Anionic Polymer	80
4.4.3. Coagulation of Untreated Humic Acid with Combinations of Ferric Chloride and Nonionic Polymer	82
4.4.4. Coagulation of Treated Humic Acid with Combinations of Ferric chloride and Nonionic Polymer	84
4.4.4.1. Coagulation of Ozonated Humic Acid with Combinations of Ferric chloride and Nonionic Polymer	84
4.4.4.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Ferric Chloride and Nonionic Polymer	86
4.4.4.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Ferric Chloride and Nonionic Polymer	88
4.5. Evaluation of Humic Acid Coagulation Properties	90
4.5.1. Coagulation Properties of Humic Acid with Alum	90
4.5.1.1. Coagulation Properties of Untreated Humic Acid with Alum	90
4.5.1.2. Coagulation Properties of Treated Humic Acid with Alum	91
4.5.2. Coagulation Properties of Humic Acid with Ferric Chloride	93
4.5.2.1. Coagulation Properties of Untreated Humic Acid with Ferric Chloride	93
4.5.2.2. Coagulation Properties of Treated Humic Acid with Ferric Chloride	94
4.5.3. Coagulation Properties of Combinations with Alum and Polymer	95
4.5.3.1. Coagulation of Humic Substances Combining with Alum and Anionic Polymer	95
4.5.3.2. Coagulation of Humic Substances Combining with Alum and Nonionic Polymer	98
4.5.4. Coagulation Properties of Combinations with Ferric Chloride and Polymer	101
4.5.4.1. Coagulation of Humic Substances Combining with Ferric Chloride and Anionic Polymer	101

4.5.4.2. Coagulation of Humic Substances Combining with Ferric Chloride and Nonionic Polymer	105
4.5.5. Comparison of Coagulation Properties of Alum and Ferric Chloride	108
CONCLUSIONS	109
REFERENCES	111



LIST OF FIGURES

Figure 2.1 The pathways for the formation of soil humic substances	4
Figure 2.2 Hypothetical molecular structure of humic acid, showing important functional groups	5
Figure 2.3 Ozone action on humic substances	14
Figure 2.4 Size spectrum of waterborne particles and filter pores	21
Figure 2.5 Negatively charged particles and the diffuse double layer	23
Figure 2.6 Schematic diagrams showing the interaction of aluminum species with initially negatively charged particles in water	29
Figure 2.7 Schematic of reactions between colloidal particles and polyelectrolyte	30
Figure 3.1 Molecular formula of anionic polymer	39
Figure 3.2 Molecular formula of nonionic polymer	40
Figure 3.3 Experimental set-up for ozonation experiments	42
Figure 4.1 Comparison of the coagulation profiles based on UV ₂₅₄ for treated humic acid	46
Figure 4.2 Comparison of the coagulation profiles based on Color ₄₃₆ for treated humic acid	46
Figure 4.3 Comparison of the coagulation profiles based on TOC for untreated humic acid	47
Figure 4.4 Comparison of the coagulation profiles based on UV ₂₅₄ for untreated, ozonated and sequentially treated humic acid	50
Figure 4.5 Comparison of the coagulation profiles based on Color ₄₃₆ for untreated, ozonated and sequentially treated humic acid	50
Figure 4.6 Comparison of the coagulation profiles based on UV ₂₅₄ for untreated humic acid	52
Figure 4.7 Comparison of the coagulation profiles based on Color ₄₃₆ for untreated humic acid	53
Figure 4.8 Comparison of the coagulation profiles based on TOC for untreated humic acid	53
Figure 4.9 Comparison of the coagulation profiles based on UV ₂₅₄ for untreated and treated humic acid	55

Figure 4.10 Comparison of the coagulation profiles based on Color ₄₃₆ for untreated and treated humic acid	56
Figure 4.11 UV ₂₅₄ functions of anionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	57
Figure 4.12 Color ₄₃₆ functions of anionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	58
Figure 4.13 TOC functions of anionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	58
Figure 4.14 UV ₂₅₄ functions of anionic polymer dosage for ozonated humic acid	60
Figure 4.15 Color ₄₃₆ functions of anionic polymer dosage for ozonated humic acid	60
Figure 4.16 UV ₂₅₄ functions of anionic polymer dosage for photocatalytically treated humic acid	62
Figure 4.17 Color ₄₃₆ functions of anionic polymer dosage for photocatalytically treated humic acid that contain 30mgL ⁻¹ alum	62
Figure 4.18 UV ₂₅₄ functions of anionic polymer dosage for sequentially oxidized humic acid	64
Figure 4.19 Color ₄₃₆ functions of anionic polymer dosage for sequentially oxidized humic acid	64
Figure 4.20 UV ₂₅₄ functions of nonionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	66
Figure 4.21 Color ₄₃₆ functions of nonionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	66
Figure 4.22 TOC functions of nonionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	67
Figure 4.23 UV ₂₅₄ functions of nonionic polymer dosage for ozonated humic acid	68
Figure 4.24 Color ₄₃₆ functions of nonionic polymer dosage for ozonated humic acid	69
Figure 4.25 UV ₂₅₄ functions of nonionic polymer dosage for photocatalytically treated humic acid	70

Figure 4.26 Color ₄₃₆ functions of nonionic polymer dosage for photocatalytically treated humic acid	71
Figure 4.27 UV ₂₅₄ functions of nonionic polymer dosage for sequentially oxidized humic acid	72
Figure 4.28 Color ₄₃₆ functions of nonionic polymer dosage for sequentially oxidized humic acid	73
Figure 4.29 UV ₂₅₄ functions of anionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	74
Figure 4.30 Color ₄₃₆ functions of anionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	74
Figure 4.31 TOC functions of anionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	75
Figure 4.32 UV ₂₅₄ functions of anionic polymer dosage for ozonated humic acid	77
Figure 4.33 Color ₄₃₆ functions of anionic polymer dosage for ozonated humic acid	77
Figure 4.34 UV ₂₅₄ functions of anionic polymer dosage for photocatalytically treated humic acid	79
Figure 4.35 Color ₄₃₆ functions of anionic polymer dosage for photocatalytically treated humic acid	79
Figure 4.36 UV ₂₅₄ functions of anionic polymer dosage for sequentially oxidized humic acid	81
Figure 4.37 Color ₄₃₆ functions of anionic polymer dosage for sequentially oxidized humic acid	81
Figure 4.38 UV ₂₅₄ functions of nonionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	82
Figure 4.39 Color ₄₃₆ functions of nonionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	83
Figure 4.40 TOC functions of nonionic polymer dosage for 50 mgL ⁻¹ untreated humic acid	83
Figure 4.41 UV ₂₅₄ functions of nonionic polymer dosage for ozonated humic acid	85

Figure 4.42 Color ₄₃₆ functions of nonionic polymer dosage for ozonated humic acid	86
Figure 4.43 UV ₂₅₄ functions of nonionic polymer dosage for photocatalytically treated humic acid	87
Figure 4.44 Color ₄₃₆ functions of nonionic polymer dosage for photocatalytically treated humic acid	88
Figure 4.45 UV ₂₅₄ functions of nonionic polymer dosage for sequentially oxidized humic acid	89
Figure 4.46 Color ₄₃₆ functions of nonionic polymer dosage for sequentially oxidized humic acid	90



LIST OF TABLE

Table 2.1. The elemental composition of humic substances from different origins	6
Table 2.2. Types of colloidal dispersions	20
Table 3.1 Characteristic of polymers	40
Table 4.1 Color ₄₃₆ and UV ₂₅₄ parameters for the untreated and treated humic acid samples	44
Table 4.2 The removal percentages of different concentration of humic acid for optimum alum dose	91
Table 4.3. Removal percentages of untreated and treated humic acid with alum	92
Table 4.4 The removal percentage of different concentration of humic acid at optimum ferric chloride dose	93
Table 4.5 Removal percentages of untreated and treated humic acid with ferric chloride	94
Table 4.6 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of untreated humic acid by combination with alum and anionic polymer	96
Table 4.7 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of ozonated humic acid by combination with alum and anionic polymer	96
Table 4.8 Removal percentages of color ₄₃₆ and UV ₂₅₄ values of photocatalytically treated humic acid by combination with alum and anionic polymer	97
Table 4.9 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of sequentially oxidized humic acid by combination with alum and anionic polymer	98
Table 4.10 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of untreated humic acid by combination with alum and nonionic polymer	99
Table 4.11 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of ozonated humic acid by combination with alum and nonionic polymer	100
Table 4.12 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of photocatalytically treated humic acid by combination with alum and nonionic polymer	100
Table 4.13 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of sequentially oxidized humic acid by combination with alum and nonionic polymer	101
Table 4.14 Removal percentage of Color ₄₃₆ and UV ₂₅₄ values of untreated humic acid by combination with ferric chloride and anionic polymer	103

Table 4.15 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of ozonated humic acid by combination with ferric chloride and anionic polymer	103
Table 4.16 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of photocatalytically treated humic acid by combination with ferric chloride and anionic polymer	104
Table 4.17 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of sequentially oxidized humic acid by combination with ferric chloride and anionic polymer	104
Table 4.18 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of untreated humic acid by combination with ferric chloride and nonionic polymer	106
Table 4.19 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of ozonated humic acid by combination with ferric chloride and nonionic polymer	106
Table 4.20 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of photocatalytically treated humic acid by combination with ferric chloride and nonionic polymer	107
Table 4.21 Removal percentages of Color ₄₃₆ and UV ₂₅₄ values of sequentially oxidized humic acid by combination with ferric chloride and nonionic polymer	107

1. INTRODUCTION

The common yellow to brown coloration of freshwaters is associated with dissolved organic matter (DOM) of the type commonly referred as humic substances. It is related to the organic matter of soil but is only partly of soil origin. Humic substances account for 40-80 per cent of the dissolved organic matter in water; they are an important and ubiquitous fraction. Typical freshwater concentrations may be in range of 1-25 mgL⁻¹ expressed as DOC. The term humic substances are defined as the product of a heteropolycondensation of carbohydrates, proteins, fatty acids, lignins, tannins and many other materials depending on their origin (Gjessing, 1976).

Humic acids, which are a subgroup of humic substances, are heterogeneous and polydisperse macromolecules comprise a wide area. They have an important role in binding and fate of inorganic and organic compounds in natural environment (VanLoon and Duffy, 2000). Another topic that makes humic acids weighty to examine is their interaction with halogens during drinking water treatment and these interactions result with the formation of halogenated carcinogens, like chloroform. When these chemical compounds are introduced in to the public drinking water directly, the outcome is undesired health consequences (Hayes, 1998). Therefore, the removal of humic acids from a water supply is essential, in order to prevent direct health effects and the problems that can be occur during water treatment processes. There are several methods for the removal of humic acids from water. The major ones are coagulation, adsorption, and advanced or chemical oxidation processes.

Coagulation is a widely used process for the removal of humic substances in water treatment and has been an area of interest for so many years (Hall and Packham, 1965; O'Melia, 1999). Various types of coagulants, mainly Fe (III) and Al (III) are used in the coagulation-flocculation of humic material (Hunt and O'Melia, 1988; Stephenson and Duff, 1996). In most studies, coagulation dosage and pH were found as the most important parameters in the coagulation of humic material (Gregor et al., 1997).

Ozonation is one of the oxidation methods of humic acids and has a great application in many water treatment plants. Recently, heterogeneous photocatalytic

oxidation process using irradiated dispersions of TiO_2 have been as an alternative treatment for the removal of humic acids.

In this study, coagulation efficiencies of untreated, ozonated, photocatalytically treated, and sequentially oxidized humic acids samples were examined. In order to investigate the effects of ozonation on coagulation properties of humic acid, humic acid samples 50 per cent ozonated in terms of Color_{436} . Humic acid samples were 50 per cent treated in terms of Color_{436} to obtain the effects of photocatalysis on humic acid. Ozonation and photocatalytic oxidation were combined in a sequential system in which ozone is applied for pretreatment of humic acids by partial oxidation.

Two different type of primary coagulant and two types of coagulant aids were used for coagulation of untreated and treated humic acid samples. Primary coagulants were alum and ferric chloride. Coagulant aids were anionic and nonionic polyelectrolyte. Coagulant aids were used with primary coagulant to enhance the coagulation efficiency and economize the dosage of the primary coagulant.

2. THEORETICAL BACKGROUND

2.1. Humic Substances

The term humic substance refers to the organic material in the environment those results from the decomposition of plant and animal residues. Humic substances are ubiquitous, being found in all soils, sediments, and waters (MacCarty and Suffet, 1989). Aquatic humic substances are the degradation products of polymers of natural origin involving depolymerization and oxidation reactions that are catalyzed by enzymes. They lead to yellow to brown color in water. In natural waters, 50-70 per cent of dissolved organic carbon (DOC) consists of humic substances.

Humic substances are mixed with, or chemically or physically associated with other classes of materials. In natural waters, humic acids are mixed with amino acids, sugars, various aliphatic and aromatic acids and other organic compounds. In soil and sediments, they are frequently bound to the mineral components.

Over the years many subfractions of humic substances have been isolated. Because of the complex nature of the humic substances, they have traditionally been classified according to the operational procedures needed to separate them. Oden's classification has been used since 1919.

1. Humic Acid: The fraction of humic substances that is not soluble in water under acidic conditions ($\text{pH} < 2.0$) but is soluble at higher pH values.
2. Fulvic Acid: The fraction of humic substances that is soluble in water under all pH conditions.
3. Humin: The fraction of humic substances that is not soluble in water at any pH value (McCarthy and Suffet, 1989).

Typically 90 per cent of the dissolved humic substances in natural waters consist of fulvic acid, and the remaining 10 per cent consist of humic acid. In contrast to this composition, humic substances from soils that humic acid is very large excess over the fulvic acid

The molecular weight of humic substances is ranging from 500 to 5000. Typical average molecular weights of aquatic fulvic acids are 800-1000, and those of aquatic humic acids are 2000-3000. In contrast, the molecular weights of soil humic acids are several hundred thousand.

2.1.1. Formation of Humic Substances

The formation of humus is depending on factors such as vegetation, population, and activity of microorganisms, and hydrothermal conditions. The physical and chemical properties of soil are very important, with regard to the rate of humification process and to the composition of humus products (Gjessing, 1976).

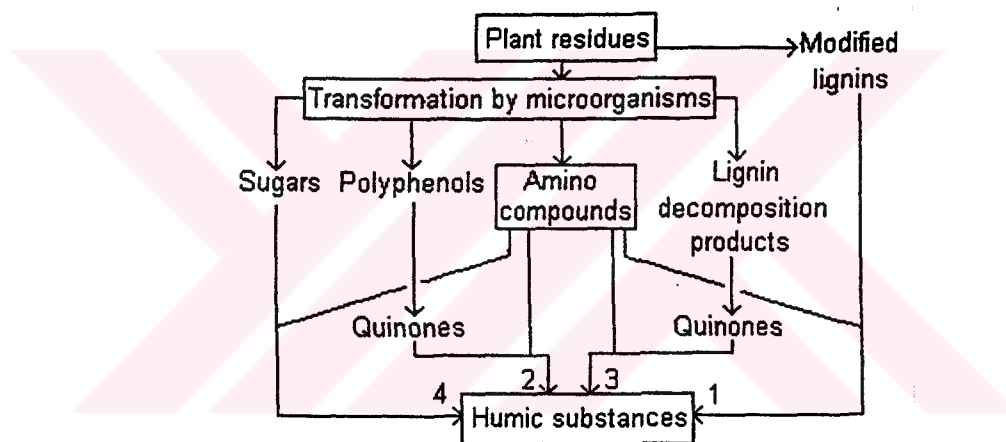


Figure 2.1 The pathways for the formation of soil humic substances (Stevenson, 1982).

The most important compounds in humus synthesis are carbohydrates (50-60 per cent), proteins (1-3 per cent), and lignins (10-30 per cent). Among these groups of organics, lignin is considered the most important, because carbohydrates and proteins are more available for soil organisms and a higher rate of chemical decomposition compared to lignin (Gjessing, 1982).

2.1.2. Composition and Structure of Humic Substances

Humic substances are generally described as yellow, acidic, chemically complex and polyelectrolyte like materials that range in molecular weight from a few hundred to several thousands (Kim et al., 1989). Besides, they are polar, amorphous, hydrophilic,

polydisperse substances (Choudry, 1982). They can be defined as polyelectrolyte with a various functional groups such as carboxylic and phenolic OH which are responsible for the acid-base, complexation and salt formation capabilities and aliphatic OH attached to the hydrocarbon skeleton (Manahan, 1989).

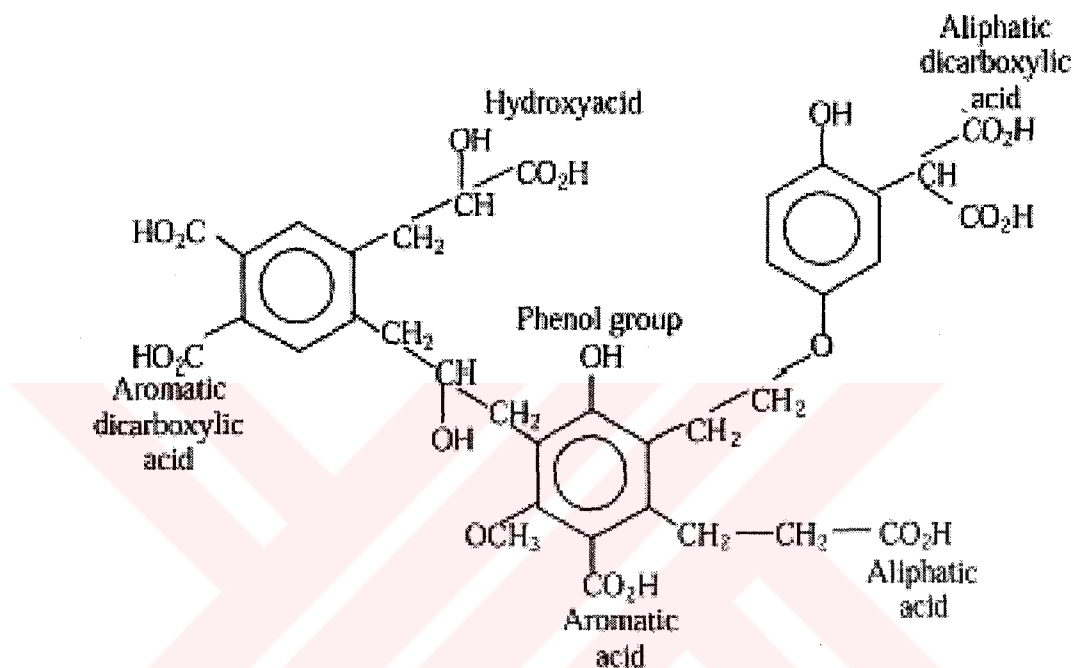


Figure 2.2 Hypothetical molecular structure of humic acid, showing important functional groups (Duan and Gregory, 2003).

Humic materials vary in composition depending on their source, location and method of extraction; however their similarities are more pronounced than their differences. The range of elemental composition of humic materials is relatively narrow, being approximately 40-50 per cent carbon, 30-50 per cent oxygen, 4-5 per cent hydrogen, 1-4 per cent nitrogen, 1-2 per cent sulfur, and 0-0.3 per cent phosphorus (MacCarty and Suffet, 1989).

Humic acids contain more hydrogen, carbon, nitrogen, and sulfur and less oxygen than fulvic acids. Studies on humins have shown that they are similar to humic acids except that they are strongly bound to metals and clays, rendering them insoluble (Schnitzer and Kahn, 1972).

Humic material contains high amount of radicals, probably of the semiquinone type, which are more prominent in humic acids than fulvic acids. These radicals can exist as permanent components or as transient species, generated by pH changes, chemical reduction, or solar irradiation. They generally play important roles in polymerization or oxidation-reduction reactions (Gaffney et al., 1996).

Table 2.1 The elemental composition of humic substances from different origins (Rice and MacCarty, 1991)

Element	Humic Acid				Fulvic Acid			
	Soil	Fresh-water	Marine	Peat	Soil	Fresh-water	Marine	Peat
C	55.4	51.2	56.3	57.1	45.3	46.7	45	54.2
H	4.8	4.7	5.8	5.0	5.0	4.2	5.9	5.3
N	3.6	2.6	3.8	2.8	2.6	2.3	4.1	2.0
S	0.8	1.9	3.1	0.4	1.3	1.2	2.1	0.8
O	36.0	40.4	31.7	35.2	46.2	45.9	45.1	37.8

2.1.3. Interactions of Humic Substances with Environmental Chemicals

Humic substances do not occur alone in the environment. They are mixed with other classes of materials. They are reactive substances and therefore undergo many interactions. These molecular interactions are controlled by the chemistry of water. Some of the interactions are controlled by the chemistry of water. Some of the interactions that will be described are:

- sorptive effects
- solubilizing effects
- catalytic effects
- photosensitizing effects

2.1.3.1. Sorptive Effects

Sorption is a process of adsorption or a substance on or in another substance. Adsorption can shortly be defined as a phenomenon in which molecules of a substance are

taken up and held on the surface of a material. It should be distinguished from absorption that refers to the taking up, usually, of a liquid or gas into the body of another material.

The molecules of humic substances can take up and increase the environmental distribution of inorganic and organic micropollutants. For example, PCB's, DDT and PAH's can attach themselves to molecules of humic materials in soil or water, especially to the water soluble portion of such molecules, and so be transported to, and in, water. Several mechanisms are involved in such interactions. Depending upon the nature of chemical and the surface of humic compound more than one mechanism can occur simultaneously (Gjessing, 1976). These mechanisms can be as follows:

- van der Waals attractions,
- hydrophobic bonding,
- hydrogen bonding,
- charge transfer,
- ion exchange and,
- ligand exchange.

2.1.3.2. Solubilizing Effects

Another property of humic substances that affect the mobility and transport of environmental chemicals is its solubilizing effect. Researches have shown that the association of slightly soluble or even insoluble chemical compounds with dissolved or suspended organic matter in the aquatic environment enhances the solubility of these compounds. It is known that factors, which control the enhancement of solubility, are polarity, size, and configuration of the humic substances and hydrophobicity of the solute.

2.1.3.3. Catalytic Effects on Hydrolysis

In aquatic systems, humic substances can influence the hydrolysis and cause to chemical changes in the present chemical compound. For example, due to some researches,

the hydrolysis of the propazine proceeds more rapidly in soil with higher organic matter content. The reason for this was the increased proton supply which was associated with the acidic surface (Nearpass, 1972). There was no correlation between the rate of hydrolysis and the number of effective groups but also on the arrangement of these groups on the humic acid molecules. Both humic acid and the acetate buffer-ion reduces the energy barrier (Li and Felbeck 1972).

2.1.3.4. Photosensitizing and Quenching Effects

Humic substances have the ability to absorb solar UV light, related to their ketonic and quinoid functional groups. They can transfer their excitational energy to chemicals and thus increase the rate of photodegradation of these compounds. The act of humic substances as photosensitizers is especially important for the photodegradation of chemicals which do not absorb UV light of wavelength $\lambda > 300\text{nm}$. An example for such groups could be the pesticides.

On the contrary, the aromatic polycyclic structure of humic substances leads to the quenching effects. Humic substances, which contain structures like anthracene, phenanthrene, pyrene, perlene, etc., accept the excitational energy of environmental chemicals and retard the photodegradation of these pollutants. The quenching effect can only occur when the energy of certain excited state of an environmental chemical.

2.1.4. The Environmental Effect of Humic Substances

Humic substances adversely affect the quality of drinking water in many ways. For instance, they impart color, serve as precursors to the formation of chlorinated compounds, possess ion exchange, and complexation properties that include association with toxic elements and micro pollutants, and precipitate in distribution systems (Vik and Eikebrokk, 1989).

The presence of humic substances in a water supply is undesirable not only for their environmental health effects, but also for their interferences with the water treatment processes. Primary influences of aquatic humic substances on treatment processes are as follows:

1. Humic substances produce aesthetically undesirable problems;
2. They serve as precursors of potentially hazardous chlorine containing organic compounds during chlorination process;
3. They serve as precursors of organic compounds during ozonation process, the biodegradable organic compounds produced in this step enhance regrowth of microorganisms within the distribution systems;
4. They stabilize dispersed and colloidal particles during coagulation process (McCarthy and Suffet, 1989).

2.1.5. Removal of Humic Substances

Removal of humic substances has long been of concern in water treatment because of their abundance in natural waters and their potential adverse effects on public health and aesthetics. There exist several methods for the removal of humic material from water. The major ones are coagulation, adsorption, and advanced or chemical oxidation processes.

Coagulation is a widely used process for the removal of humic substances in water treatment and has been an area of interest for so many years (Black et al., 1963; Hall and Packham, 1965; Van Benschoten and Edzwald, 1990; O'Melia, 1999). Various types of coagulants, mainly Fe (III) and Al (III) are used in the coagulation-flocculation of humic material (Hunt and O'Melia, 1988; Stephenson and Duff, 1996; O'Melia et al., 1999; Vilge-Ritter et al., 1999). In most studies, coagulation dosage and pH were found as the most important parameters in the coagulation of humic material (Rebhun and Lurie, 1993; Gregor et al., 1997).

Most of organic compounds are removed from water by activated carbon adsorption. The adsorbability of individual compounds depends on a number of factors, such as polarity and molecular size and structure, and pH. Generally, relatively insoluble and soluble compounds are easily adsorbed. Size and structure may be limiting factors for too large molecules. Pore size distribution is the most important factor in the adsorbability of humic substances onto activated carbon. Carbons with high percentages of macrospores have the highest capacities for adsorption of humic substances, and capacities for the

smaller fulvic acid molecules are higher than for humic acids. Poor adsorbability is reflected in unfavorable adsorption isotherms, slow adsorption kinetics, and immediate breakthrough of color-imparting substances in adsorption columns (Kaastrup and Halmo, 1989).

Advanced oxidation process for the oxidative removal of aquatic humic substances is gaining importance in water treatment. Ozonation, photooxidation, and photocatalytic oxidation are all topics investigated under oxidative removal of humic material (Zhou and Smith, 2002).

Membrane filtration has not been used yet in full-scale waterworks for the prime objective of removing humic substances. However, laboratory and pilot-plant experiments have been carried out to evaluate the use of membrane processes for the removal of humic substances (Odegaard and Thorsen, 1989).

2.2. Oxidative Removal of Humic Substances

Oxidation is a chemical treatment method, whereby organic pollutants in water are converted to carbon dioxide and water by means of several oxidizing species such as chlorine, chlorine dioxide, ozone etc. In order to improve the oxidation process chemical reactants with relatively higher oxidizing potential are used. The advanced oxidation processes, which depend on the formation of hydroxyl radicals (OH \cdot), are applied for total elimination of organic compounds both in water and wastewater treatment. Highly reactive OH \cdot species are attack on non-selectively to almost all organics and result in rapid degradation. Hydroxyl radical is known to be the most powerful oxidizing species after fluorine and it has an oxidation potential of 2.80 V. (Backlund, 1992; Camel and Bermond, 1998; Kusakabe *et al.*, 1990). Combination of various oxidation techniques are applied in advanced oxidation processes. These processes include:

- ozone/UV radiation,
- ozone/TiO $_2$,
- ozone/TiO $_2$ /UV,
- ozone/H $_2$ O $_2$

2.2.1. Ozonation

Ozone (O_3), a colorless gas at room temperature, is an allotropic form of oxygen (O_2). Ozone is characterized by strong oxidizing properties. It is very unstable at ambient temperatures and pressures and decomposes very rapidly to oxygen.

Ozone has a characteristic odor, which can be detected by most humans at low concentrations (0.02 ppm by volume), far below the levels of acute toxicity. It is moderately soluble in water, with solubility depending on the temperature of the water and ozone concentration in the feed gas. As temperature increases, ozone becomes less soluble and less stable in water; however, the disinfection and chemical oxidation rates remain relatively stable (EPA, 1981).

The application of ozone in drinking-water treatment is widespread throughout the world the main reasons for the use of ozone are disinfection and oxidation (e.g. taste and odor control, decoloration, elimination of micropollutants, etc.) or a combination of both. Similar to other disinfectants for water treatment (e.g. chlorine or chlorine dioxide), ozone is unstable in water and undergoes reactions with some water matrix components. However, the unique feature of ozone is its decomposition into OH radicals ($\cdot OH$) which are the strongest oxidants in water. Therefore, the assessment of ozonation processes always involves the two species ozone and OH radicals. However, for different applications of ozone the two species are of differing importance. While disinfection occurs dominantly through ozone, oxidation processes may occur through oxidants, ozone, and OH radicals (Hoigne et al., 1985).

Ozonation applied for the removal of a variety of pollutants including potential carcinogens from drinking water, also is applied for tertiary treatment of municipal wastewater in combination with other treatment methods. Several inorganic substances can essentially change the properties of water such as smell, color, and taste. These include compounds of iron, manganese, arsenic sulfur and several others. Removal of these substances can be effected significantly by ozonation (Glaze, 1980).

2.2.1.1. Oxidation of Humic Substances with Ozone

Ozone is one of the strongest chemical oxidants known. It is used in water and wastewater treatment for disinfection, for decolorization, and as pretreatment for filtration and adsorption. The ozonation products are generally smaller, more polar, and hydrophilic than their precursor. Therefore, they are considered less adsorbable and more easily biodegradable. The decolorization of humic water occurs because ozone is a typical double-bond reagent. It reacts with double bonds in the conjugated chains of large, color-imparting molecules, and thereby reduces the color and size of the molecules (Kaastrup and Halmo, 1989). Aldehydes, alcohols, ketones and carboxylic acids, ethers, olefines, amines, aromatic compounds: benzene, polyaromatic compounds etc. are the organic groups, which can be oxidized by ozone (Von Gunten, 2002).

Ozone use in drinking water treatment is expanding as consumers demand a high level of water quality, and this has sparked several new studies to investigate ozone disinfection by-products (DPBs). The major DPBs occurring from ozone treatment of waters are lower molecular weight aliphatic aldehydes, in particular formaldehyde and acetaldehyde. Other partial oxidation by-products with carbonyl functionalities include glyoxylic, keto-malonic, and pyruvic acids. Ozone is bound to engage the raw water natural organics and some of the inorganic components in a series of reactions that ultimately produce a variety of by-products that are likely to be more polar (organics) and in higher oxidation states (organics and inorganics) than their precursors (Weinberg and Glaze, 1996).

Ozonation changes the character of humic substances strongly. UV absorbance of humic substances is greatly lowered, but there was not a significant decrease in the total organic carbon content. Instead, easily assimilable low-molecular weight organic compounds are formed, enhancing regrowth of bacteria in the distribution system. These negative side effects of ozonation must be considered in making decisions about the use of ozonation in a drinking water treatment plant (Kruithof et al., 1989).

Ozone is used in water and wastewater treatment for disinfection, for decolorization, and as pretreatment for filtration and adsorption processes. Carboxylic

acids, aromatics, hydrocarbons, aldehydes, ketones, aliphatic acids, esters, aliphatic alcohols, and aromatic esters are the by-products of ozonation process. Ozone reacts quickly with humic substances to produce oxidized by-products of low molecular weight that generally are more easily biodegradable, polar, and hydrophilic than their precursors (Gracia et al., 1996).

Humic substances react with ozone like a solution containing different concentrations of molecular ozone consumer sites, leading to the formation of radical or non-radical species, and different concentrations of hydroxyl radical consumer sites, possibly leading to a radical chain propagation. The action of ozone on humic substances leads to decrease of molecular weight, increase of the carboxylic functions, degradation of color and UV absorbance (Langlais *et al.*, 1991). Figure 2.3 represents the ozone action on humic substances.

The key variables that seem to determine ozone's effect are dose, pH, alkalinity, and, above all, the nature of the organic material. At low pH levels, precursor destruction by ozone is quite effective; however, above some critical pH, ozone actually is less effective and in fact sometimes increases the amount of chlorination byproduct precursors. For most humic substances, this critical pH is 7.5, which is the approximate level at which decomposition of ozone to hydroxyl free radicals increases rapidly, thus increasing organic oxidation rates. Therefore, the implications that at lower pH (approximately 6-7), at which molecular ozone predominates over the hydroxyl free radical, the initial trihalomethane precursor byproducts are different in nature than those formed by the hydroxyl free radicals oxidized at higher pH levels. This is logical in light of the greater oxidation potential of the hydroxyl free radical over that of ozone. As alkalinity increases, it has a beneficial effect on trihalomethane formation potential (THMFP) (Langlais et al., 1991).

Takahashi et al., (1995) investigated the reactivity of humic acid with ozone. Partial oxidation such as decolorization was observed, though the complete destruction represented by total organic carbon removal was not significantly caused. Decolorization was interpreted as a pseudo-first order reaction. It has also shown that, ozonation of natural

organic matter (NOM) results with a strong rapid decrease in color and UV-absorbance due to a loss of aromaticity and depolymerisation, increase in biodegradability, and reduction in THMFP (Camel and Bermond, 1998).

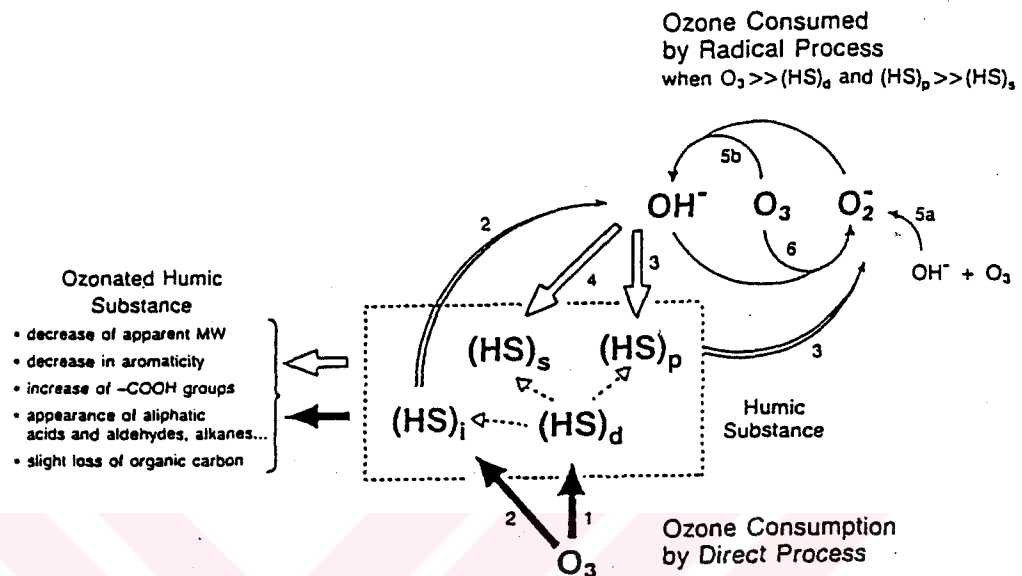


Figure 2.3 Ozone actions on humic substances (Langlais *et al.*, 1991).

Chang *et al.*, (2002) used ozonation as a pretreatment method to reduce the formation of disinfection by products (DBPs). They have shown that ozonation was useful for reducing DBPs, especially for THMFP. After ozonated pretreatment, 71 per cent and 53 per cent was reduced by ozonation, respectively, for the fulvic acid and humic acid. In raw water it is estimated that the structure of NOM includes aromatic hydrocarbons, C-H, C=C, C=O, and O-H functional groups. After ozonation, it was found that the structure of O-H and C-H is still present in water, but the strength of aromatic C=C double bond remarkably decreases. Similarly, Chiang *et al.*, (2002) showed that both pre-ozonation and post-ozonation processes could reduce some of the DBP precursors.

Two oxidation processes were applied in a sequential system in which ozonation was applied as a pretreatment stage for partial oxidation of humic acids prior to photocatalytic oxidation using TiO_2 (Kerç, 2002). The effect of preozonation was observed in the increased photocatalytic degradation rates as explained by pseudo first-order kinetic model. 50 per cent increase was reported in the pseudo first-order degradation rate

constants for the preozonated samples compared with unozonated humic samples for a TiO_2 loading of 0.5mgmL^{-1} . Pretreatment with ozonation affects the adsorption characteristics of the humic acids on the photocatalysis. In addition, THMFP analysis conducted on the sequentially oxidized humic acid samples have shown that 50 per cent THMFP reduction is achieved during the photocatalysis stage, irrespective of the ozone dose applied in the first stage for treatment purposes. Recently, Kerç et al., (2003) investigated the effects of pre-oxidation of humic acid by ozonation prior to photocatalysis. It was reported that photocatalytic oxidation rates were significantly affected by the degree of pre-oxidation by ozonation.

Nishijima et al., (2003) evaluated the dissolved organic carbon (DOC) removal by multi-stage ozonation-biological treatment to apply for drinking water treatment. Amount of DOC removed in biological treatment was defined as amount of biodegradable dissolved organic carbon (BDOC) in influent of biological treatment. DOC removal in the treatment with multi-stage ozonation-biological was higher than that in the conventional single-stage ozonation-biological treatment with the same total ozonation time for the reservoir water and humic substances solution. Moreover, three or four-stage ozonation for 5 min followed by biological treatment (total ozonation time 15 or 20 min) showed higher removal of DOC than the single-stage ozonation (60 min) and biological treatment. The higher DOC removal in multi-stage treatment is due to the production of BDOC by ozonation. The long-term ozonation was not effective to produce BDOC, because most of ozone was utilized to oxidize BDOC produced in the early stage of ozonation.

In the presence of bromide, ozonation of natural waters leads to the formation of hypobromous acid (HOBr), hypobromide ion (OBr^-), and brominated organic by-products and some of these inorganic and organic by-products are carcinogenic. Organic characteristics have significant influences on brominated organics and aldehydes formation. Generally, humic acid and fulvic acid proved to have higher aromatic content, phenolic acidity, and ultraviolet absorbance, and showed higher brominated organic formation. As far as pH effect is concerned, the bromoform (CHBr_3) formation of humic acid or fulvic acid was found to be decreased with increasing pH; the reverse was true for aldehydes (Huang et al., 2003).

2.2.2. Photocatalysis

Photocatalytic oxidation, which is an advanced oxidation method, has been applied in water, and wastewater treatment studies (Eggins et al., 1997). Photocatalysis relies on oxidative degradation reactions, where organic radicals are generated upon photolysis of the organic substrate or by reactions with generated hydroxyl radicals. These radicals are subsequently trapped by dissolved molecular oxygen and lead via peroxy radicals and peroxides to an enhancement of the overall degradation process and finally to complete mineralization (Legrini *et al.*, 1993). In photocatalysis, a suspension of a particulate metal oxide or other insoluble inorganic semiconductor powder is irradiated with natural or artificial UV light. This excitation promotes an electron from a bonding or no bonding level in the solid to a highly delocalized level, creating a localized oxidizing site (a hole) and a mobile reducing site (an electron). The holes react with the electron donors in the electrolyte to produce powerful oxidizing agents such as $\cdot\text{OH}$ (radicals) (Bahnemann *et al.*, 1994).

ZnO, TiO₂, and CdS are the examples of semiconductors used as photocatalysis. Because of its stability, non-toxicity, and low energy band-gap, TiO₂ is accepted to be one of the most suitable semiconducting materials for photocatalysis. The presence of natural organic matter, mainly humic substances in surface waters, constitutes the main route for the absorbance of solar energy in aquatic systems through which a series of photophysical and photochemical processes occur. Recently, the destruction of humic acids has become an important task and TiO₂ catalyzed photodegradation of humic acids has been subject to many projects utilizing artificial light sources as well as solar light (Bekbölet *et al.*, 2002).

2.2.2.1. Kinetics of Photocatalytic Degradation

The photocatalytic degradation of various organic solutes obeys pseudo first-order kinetics (Matthews, 1991).

$$-\frac{dS}{dt} = k[S] \quad (2.2)$$

Where k is the pseudo first-order decay constant and $[S]$ is the concentration of solute.

The half-life for the reaction is given as:

$$t_{1/2} = \frac{0.693}{k} \quad (2.3)$$

2.2.2.2. Removal of Humic Substances by TiO₂/UV Process

Eggin et al., (1997) investigated semiconductor photocatalysis for the degradation of aquatic humic substances. They have shown that, the absorbance at 254/400 nm of a humic acid test solution was reduced by 50 per cent after 12 min irradiation. However, only 50 per cent mineralization to carbon dioxide and water occurs after 1 hour. In the absence of oxygen, light or TiO₂ no significant degradation occurred. Recently, Wiszniowski et al., (2002) investigated the photocatalytic decomposition of humic acids on TiO₂, and reported that adsorption plays a prominent role in photocatalytic degradation of humic acids. It was presented that 88 per cent TOC removal was achieved with optimum TiO₂ loading of 1.0 gL⁻¹ after 6 hour of irradiation.

Bekbölet and Balcıoğlu (1996) examined the influence of hydrogen peroxide and bicarbonate ion on the photocatalytic degradation of humic acid in aqueous TiO₂ dispersions. The degradation rate constants were found to increase in the presence of hydrogen peroxide, also they explained that bicarbonate ions slowed down the degradation rate by scavenging the hydroxide radicals.

Özkaraova (1996) investigated the influence of nitrate and chloride ions on the photocatalytic degradation of humic acid in aqueous medium. It has shown that, nitrate ions and chlorine ions caused 40 per cent and 45 per cent adsorption respectively, following the adsorption photocatalytic, degradation took place, and the degradation rate was decreased. Later, Bekbölet et al., (1998) investigated the influence of common inorganic ions, namely, chloride, nitrate, sulfate, and phosphate ions on the photocatalytic removal of color from humic acid solutions. The presence of chloride, nitrate, and sulfate ions are showed different trends when the rate is expressed as pseudo first-order reaction kinetics. The presence of phosphate ion strongly inhibited the color removal rate.

Boyacıoğlu (1997) studied the influence of pH dependent on phosphate species on the photocatalytic degradation of 10 mgL^{-1} humic acid in aqueous media. Boyacıoğlu reported that, at low pH values, irradiation with 0.25 mgmL^{-1} TiO_2 for 1 hour resulted in 95 per cent Color_{436} and 62 per cent removal TOC removal. Karabacakoğlu (1998) investigated the influence of hardness cations such as calcium and magnesium on the photocatalytic degradation of humic acid. It was reported that, Color_{436} and UV_{254} removal rates increased in the presence of 50 mgmL^{-1} calcium and 5 mgmL^{-1} magnesium hardness. The increase in the removal rate was due to the changes in the humic acid structure due to the presence of divalent cations.

Recently, Li et al., (2002) studied the photocatalytic oxidation of humic acid in TiO_2 suspensions at neutral pH in presence of calcium and magnesium ions. They have reported that the degradation of humic acid significantly enhanced by adding calcium and magnesium ions. The increase of cation strength in aqueous solution could provide a favorable condition for adsorption of humic acid on the TiO_2 surface, therefore enhances the photooxidation rate.

Uyguner (1999) investigated the effects of the trace metal ions, namely chromium and manganese, on the adsorptive properties of TiO_2 as the photocatalysis and the photocatalytic oxidation rate of humic acid. Hunca (1999) studied the impact of copper and zinc ions on the photocatalytic degradation of humic acid. Color_{436} and UV_{254} removal rates were found to increase in the presence of zinc ion, on the other hand, the presence of copper ion caused a decrease in the removal rates.

Dincer (1998) studied the photocatalytic efficiency comparison of two crystal forms of TiO_2 that were anatase and rutile. Higher removal rates were observed with Degussa P-25 photocatalysis. Süphandağ (1998) studied the adsorption capacity of humic acid on three different semiconductor powders, namely Degussa P-25 (70 per cent anatase and 30 per cent rutile), Merck (100 per cent rutile), and Hombikat UV100 (100 per cent anatase). Hombikat UV100 was proven the most effective TiO_2 by means of adsorption efficiency. Recently, Baş (2001) investigated the adsorption and desorption behavior of humic acid

onto two structurally different TiO₂ powders as a contributor to the photocatalytic degradation of humic acids. For adsorption, Degussa P-25 was reported to be more effective. Likewise, Millennium PC500 was more effective in desorption.

Bekbölet et al., (2002) investigated the photocatalytic efficiencies of TiO₂ powders on the decolorization of humic acids. Decolorization rate of humic acid by photocatalytic oxidation in terms of pseudo first-order kinetics in the presence of Degussa P-25 was found to be more efficient than in the presence of Hombikat UV100 specimen. The results of the adsorption experiments for Degussa P-25 indicated higher adsorption capacity for humic acid at pH 6.7.

2.3. Coagulation

Surface waters generally contain a wide variety of colloidal impurities that may cause the water to appear turbid or may impart color. Turbidity is most often caused by colloidal clay particles produced by soil erosion. Color may result from colloidal forms of iron and manganese or, more commonly, from organic compounds contribute by decaying vegetation. The removal of larger particles with the dimension of 10⁻² cm or more is accomplished by sedimentation (O'Melia, 1972).

Colloidal particles that cause color and turbidity are difficult to separate from water because the particles will not settle by gravity and are so small that they pass through the pores of most common filtration media. For this reason, those colloidal particles should be aggregated into large, more readily settleable collision in order to achieve a successful sedimentation process (Benefied et al., 1982).

This aggregation of colloidal particles can be considered as involving two separate and distinct steps:

1. The repulsive forces must be reduced (the particle must be destabilized)
2. Particle transport must be achieved o provide contact between the destabilized particles (Stumm and O'Melia, 1968).

Chemical agents (coagulants) can be used to promote colloidal aggregation by destroying the forces that stabilize colloidal particles. Mechanisms responsible for destabilization of inorganic clay colloids have been identified through extensive research studies and are well understood. The process of destroying the stabilizing forces and causing aggregation of clay colloids is referred to the chemical coagulation (AWWA, 1971).

Coagulation refers to the overall process of particle aggregation, including both particle destabilization and particle transport. Flocculation is the physical process of producing interparticle contacts. Chemicals used to destabilize colloids would be referred to as coagulants or flocculants (O'Melia, 1972).

2.3.1. Colloidal Systems

A colloidal system is defined as a system in which particles, in a finely divided state, are dispersed in a continuous medium. The particles are called the dispersed phase, and the medium in which they exist is called the dispersing phase.

Table 2.2 Types of colloidal dispersions (Shaw, 1970).

Dispersed Phase	Dispersion Medium	Name	Example
Liquid	Gas	Liquid aerosol	Fog, liquid sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Foam on soap solutions, fire extinguisher foam
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Solid colloidal suspension: Paste (high solid concentration)	Au sol, AgI sol: toothpaste
Gas	Solid	Solid foam	Expanded Polystyrene
Liquid	Solid	Solid emulsion	Opal, pearl
Solid	Solid	Solid suspension	Pigmented plastics

Either colloidal systems may exist in which the dispersed phase or the dispersing phase is a solid, liquid, or gas. Since gases always form true solutions, either type of colloidal systems is possible as shown in Table 2.2.

The particles that form a colloidal dispersion are sufficiently large for a definite surface of separation, or interface, to exist between them and the medium in which they are contained. At this interface there is no sharp transition between one bulk phase and the other, but a transition region exist which shows properties differing from either of the two bulk phases. The transition region is very thin but plays an important role in determining of such systems (Benefield et al., 1982).

Colloidal particles are not limited to any particular group of substances but are defined by size. The colloidal size range is generally regarded to extend from 1 nanometer (nm) to 1 micrometer (μm) although some authors consider the colloidal range to extend up to a size of 10 μm . It is frequently quite difficult to distinguish between colloids and solution at the lower end off the scale and colloids and suspensions at the upper end (Benefield et al., 1982).

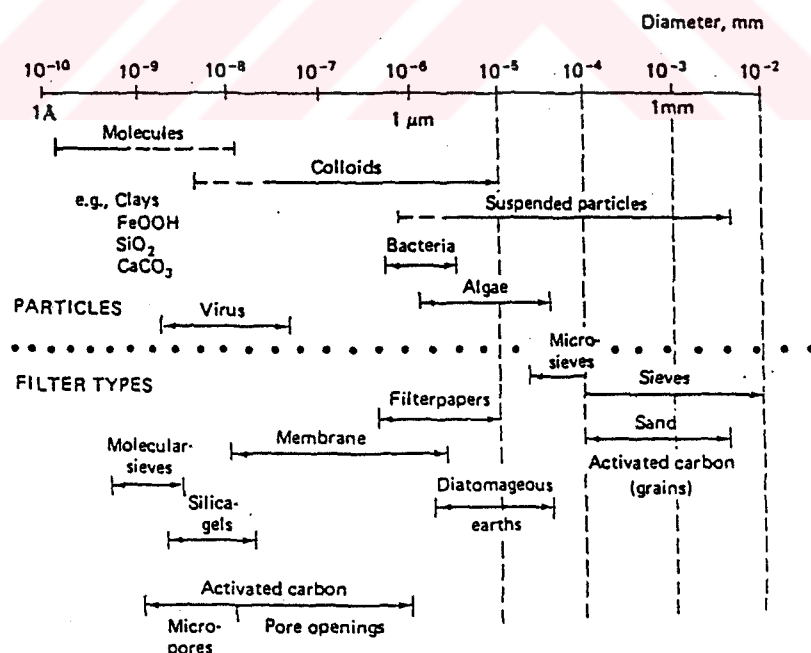


Figure 2.4 Size spectrum of waterborne particles and filter pores (Stumm and O'Melia, 1968).

Colloidal dispersions commonly encountered in environmental engineering include emulsified (liquid-in-liquid dispersion), which are found in many industrial wastes, and foams (gas-in-liquid dispersion), which frequently develop during wastewater aeration. The colloidal system that is perhaps most often encountered in environmental engineering is the solid-in-liquid dispersion formed by clay particles present in surface waters.

Colloidal system may be classified by the affinity of the dispersed phase for the dispersing medium. Systems are referred to as hydrophobic when a weak affinity exists as hydrophilic when there is a strong affinity. The terms hydrophobic and hydrophilic are used when water is the dispersing medium. Hydrophobic colloids include such things as clay, gold and other metals, whereas proteins, soaps, and synthetic detergents characterize hydrophilic colloids.

2.3.2. The Stability of Colloids

Two aspects can explain the causes of particle stability:

1. Electrostatic stabilization
2. Steric stabilization

2.3.2.1. Electrostatic Stabilization

Solid colloidal particles in an aqueous dispersion will move in an electrical field, indicating that these particles carry an electric charge. Colloidal particles can develop such an electric charge in many ways. The sign of this primary charge can be either positive or negative, although most colloids in water and wastewater develop a negative primary charge. The sign and the magnitude of the primary charge are frequently affected by the pH and ionic content of the aqueous phase (O'melia, 1968).

A colloidal dispersion does not have a net electrical charge, and the primary charge on the particle must be counterbalanced in the system. Because the particle is negatively charged, an excess of ions of opposite charge (positive) accumulate in the interfacial region. As a result, an electrical double layer exists at every interface between a solid and water. An electrical double layer surrounding a solid particle in aqueous solution is given in Figure 2.5, where Ψ_0 and Ψ_d are surface and diffuse layer potentials, and n_+ and n_- are cation and anion concentration respectively.

The electrostatic attraction of ions of opposite charge to the particle, electrostatic repulsion of ions of the same charge as the particle, and thermal or molecular diffusion that acts against the concentration gradients produced by the electrostatic effects from a cloud of ions around the particles which is termed the diffuse layer. The competing processes (diffusion and electrostatic attraction) spread the charge in the water over a diffuse layer, within which the excess concentration of counter ions is highest adjacent to the surface of the particle and decreases with increasing distance from solid-water interface. The electric potential surrounding the particle has a maximum value at the particle surface and decreases with distance from surface. This decrease is affected by the characteristics of the diffuse layer and by the type and concentration of ions in the bulk solution (Amirtharajah and O'Melia, 1990).

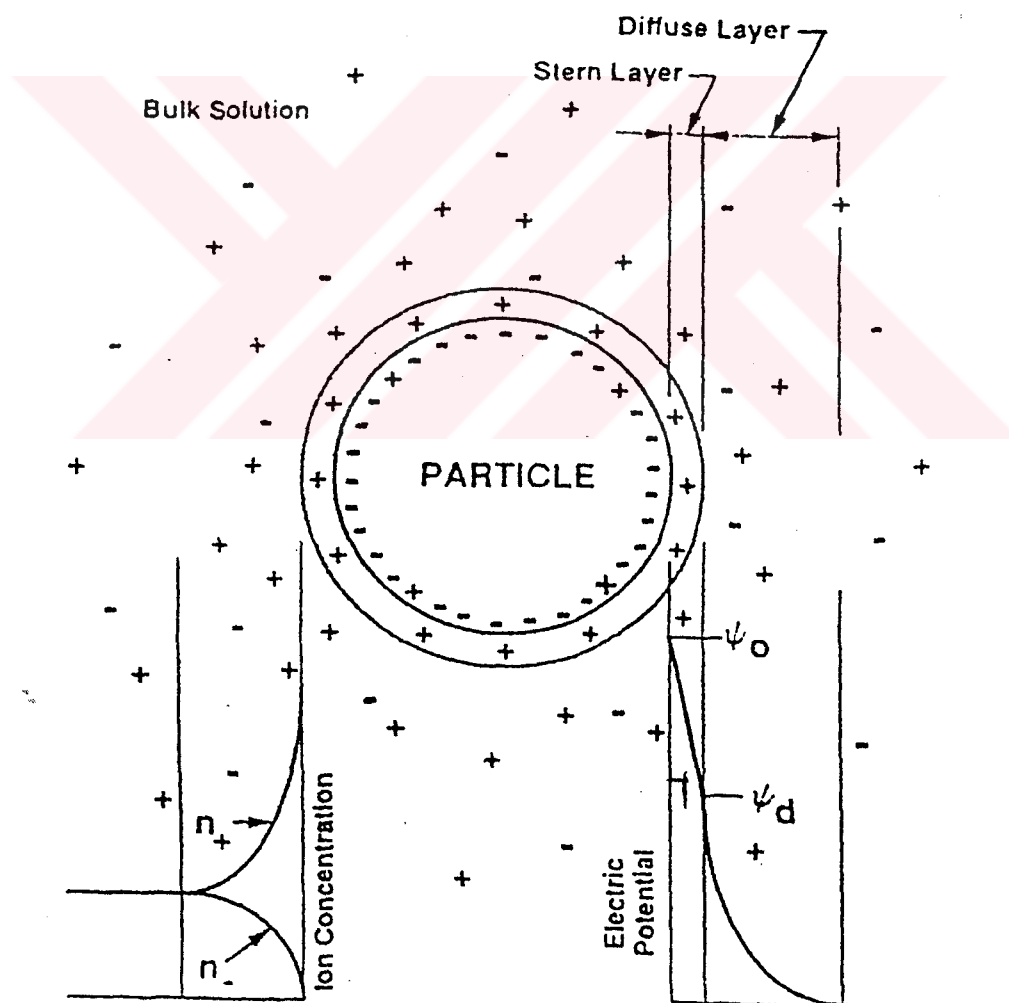


Figure 2.5 Negatively charged particle and the diffuse double layer (O'Melia, 1990).

When an electrical potential is applied across a suspension of negatively charged particles, they move toward the positive electrode. This motion is caused by the zeta potential, which is the potential drop across the mobile part of the electrical double layer. The zeta potential reflects the potential difference between plane of shear and the bulk phase. The distance between the surface and the plane of shear cannot be defined rigorously (Stumm and Morgan, 1996).

2.3.2.2. Steric Stabilization

Steric stabilization can result from the adsorption of polymers at solid-water interfaces. Large polymers can form adsorbed segments on a solid surface with loops and tails extending into solution. The stabilizing or destabilizing effects of adsorbed polymers depend on the relative amounts of polymer or solid particles, the affinities of the polymer for the solid and for water, electrolyte type and concentration, and other factors. A stabilizing polymer may contain two types of group; one with a high affinity for the solid surface and a hydrophilic group that is left suspended in water (O'Melia, 1987).

2.3.3. Destabilization

Different chemical coagulants can bring about the destabilization of colloids in different ways. Moreover, depending upon the conditions under which they are used, some materials can function as coagulants or as coagulant aids, and some coagulants can achieve colloidal destabilization by more than one method (O'Melia, 1972).

Two distinct steps must occur in order to accomplish the aggregation of colloidal particle. First, particle transport to provide contacts and secondly, particle destabilization to permit attachment when contact occurs (Stumm and Morgan, 1968).

Particle destabilization can be achieved by four mechanisms:

1. Compression of the double layer.
2. Adsorption to produce charge neutralization
3. Enmeshment in a precipitate
4. Adsorption to permit interparticle bridging

2.3.3.1. Double Layer Compression

It has been known that colloidal systems could be destabilized by the addition of ions having a charge opposite to that of the colloid. Schulze, in 1882, noted that the coagulation power of cations increased in the ratio of 1:10:100 as the valence of the ions increased from 1 to 2 to 3. Hardy (1900), who formulated the Schulze-Hardy rule (Benefied et al., 1982), noted a similar observation for anions. This rule states that a colloid is destabilized by an indifferent electrolyte by ions of opposite charge to that of the colloid (counterions) and that the coagulation effectiveness of these ions increases markedly with charge. For example, the concentration of Na^+ , Ca^{2+} , Al^{3+} required to destabilize a negatively charged colloids are observed to vary approximately in the ratio of $1:10^{-2}:10^{-3}$ (O'Melia, 1972).

Destabilization by counterions occurs by compression of the diffuse layer surrounding the particles. High concentrations of electrolyte in solution produce high concentrations of counterions in the diffuse layer. The volume of the diffuse layer necessary to maintain electroneutrality is lowered and the effective thickness of the diffuse layer is reduced (O'Melia, 1972). The repulsive forces between similar colloidal particles decrease, the van der Waals attractive forces become more dominant, the activation energy barrier can disappear, and electrostatic stabilization can be eliminated. Double layer compression also cause a decrease in zeta potential and it has been suggested that coagulation by double layer compression is usually optimum when the value of zeta potential is near zero (Amirtharajah and O'Melia, 1990).

2.3.3.2. Adsorption and Charge Neutralization

Some chemical species are capable of being adsorbed at the surface of colloidal particle. If the adsorbed species carry a charge opposite to that of the colloids, such adsorption causes a reduction of surface potential and a resulting destabilization of the colloidal particle.

Destabilization by adsorption differs from destabilization by double layer compression in three very important ways. First, sorbable species are capable of

destabilizing colloids at much lower dosages than nonsorbable, “double layer compression” ions. Secondly, destabilization by adsorption is stoichiometric. As the concentration of colloids increases, the required dosage of coagulant increases. Thirdly, it is possible to overdose a system with adsorbable species and cause a charge reversal on the colloidal particle which results in restabilization. Hydrolyzed species of Al(III) and Fe(III) can cause coagulation by adsorption (Benefield et al., 1982).

2.3.3.3. Enmeshment in a Precipitate

When a metal salt such as $\text{Al}_2(\text{SO}_4)_3$ or FeCl_3 is added to water in sufficiently high concentration to cause precipitation of metal hydroxide, colloidal particles can be enmeshed in these precipitates as they are formed and also colloid with them afterwards. This is termed “sweep-floc coagulation” by Packham (1965). The colloidal particles themselves can also serve as nuclei for the formation of precipitate, so that the rate of precipitation increases with increasing concentration of colloidal particles to be removed. This can result in an inverse relationship between the optimum coagulant dose and the concentration of colloidal material (Packham, 1965).

2.3.3.4. Adsorption and Interparticle Bridging

Both positive and negative polymers are capable of destabilizing negatively charged colloidal particles. The chemical bridging theory used to explain these results. This theory developed by Ruehrwein and Ward (1952) and LaMer and Healy (1963) to observed behavior of polymeric compounds (Benefield et al., 1982).

The chemical bridging theory proposes that a polymer molecule will become attached to a colloidal particle at one or more sites. Attachment may result from coulombic attraction if the polymer and particle are of opposite charge, or from ion exchange, hydrogen bonding, or van der Waals' forces if they are of similar charge (O'Melia, 1968). The tail of the adsorbed polymer will extend out into the bulk of the solution and can become attached to vacant sites on the surface of another particle to form a chemical bridge this bridging action results in the formation of a floc particle having favorable settling characteristics. If the extend segment fails to contact another particle, it may fold

back and attach to other sites on the original surface, thus restabilizing the particle. (Benefied et al., 1982).

2.3.4. Particle Transport Processes

After destabilization of the colloidal particles, they should be brought into contact with one another in order to provide an aggregation. Interparticle contact, like particle destabilization, can be accomplished in three separate mechanisms.

Firstly, contacts by thermal motion often termed Brownian motion or Brownian diffusion. When such Brownian motion the transport process produces interparticle contacts is sometimes termed perikinetic flocculation (Overbeek, 1952). Such random motion of colloidal particles results from the rapid and random bombardment of the colloidal particles by molecules of the fluids (O'Melia, 1968).

Secondly, contacts resulting from bulk motion as, for example, from transport induced stirring. When contacts between particle are caused by fluid motion the process is sometimes termed orthokinetic flocculation (Overbeek, 1952).

Thirdly, contacts resulting from settling of the particles. Differential settling produces vertical transport of particles resulting in collisions. The driving force for differential settling is gravity, and the parameter controlling mechanism is the settling velocity of the particle (Amirtharajah and O'Melia, 1990).

2.3.5. Coagulants

Hydrolyzing metal salts, based on aluminum or iron, are very widely used as coagulants in water treatment. These additives can also remove dissolved natural organic matter (NOM), either by charge neutralization to give insoluble forms, or by adsorption on precipitated metal hydroxide. As well as simple hydrolyzing salts, a range of commercial pre-hydrolyzed coagulants is available. These contain cationic hydrolysis products and are often more effective than aluminum or iron salts (Duan and Gregory, 2003).

2.3.5.1. Coagulation with Al(III) and Fe(III) Salts

There are two likely mechanisms for the removal of humic substances by hydrolyzing metal coagulants:

- Binding of metal species to anionic sites, thus neutralizing their charge and giving a reduced solubility. For large molecules, this can lead to precipitation of the metal-humic complex, to form particles that can be removed by sedimentation or filtration.
- Adsorption of humic substances on amorphous metal hydroxide precipitate. At pH values approximately 5–6, the humic substances are negatively charged and Al and Fe hydroxides are positively charged, which give strong adsorption and some would charge neutralization. Pre-formed ferric floc has been shown to be a good adsorbent for humic substances (Cathalifaud et al., 1993).

In practice it is often quite difficult to distinguish between surface precipitation and the deposition of colloidal hydroxide particles which have been precipitated in bulk solution. A combination of these effects is included in the Precipitation Charge Neutralization (PCN) model explain coagulation by hydrolyzing metal salts in water treatment (Dentel and Crit, 1991). According to the PCN model, coagulation with aluminum or iron salts involves three steps:

1. Destabilization begins after addition of a dose of coagulant that exceeds the operational solubility limit of aluminum (or iron) hydroxide.
2. Aluminum or iron hydroxide species are then deposited onto colloidal surfaces.
3. Under typical conditions, metal hydroxide is positively charged, while the original colloidal particles are negatively charged.

So the deposition process can result in charge neutralization or charge reversal of the colloidal particles at certain doses, as shown in a simplified manner sweep flocculation generally gives considerably improved particle removal than when particles are destabilized just by charge neutralization. At least part of the reason is the greatly improved rate of aggregation, because of the increased solids concentration. Hydroxide

precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and, hence, a high probability of capturing other particles. It is also possible that binding ('bridging') of particles by precipitated hydroxide will give stronger aggregates. Increasing the coagulant dose in the sweep region gives progressively larger volumes of sediment (Gregory and Dupont, 2001). However, beyond the operational optimum dosage, there is little further improvement in particle removal.

Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), Ferric chloride (FeCl_3), Ferric Sulfate ($\text{Fe}_2(\text{SO}_4)_3$) are commonly used Al(III) and Fe(III) salts as coagulants. Compared with Al_2SO_4 (alum), ferric chloride coagulates effectively over a broader pH range, forms a stronger, heavier floc and does not contribute to aluminum residual in the effluent. The continuous usage of aluminum salts is questioned due to chemical cost, impact of residual aluminum upon receiving waters, and a possible link between aluminum and Alzheimer's disease. A disadvantage of adding alum is the high concentration of sulphate ions, which remain in solution, posing downstream treatment difficulties and leading to increased total dissolved solids levels.

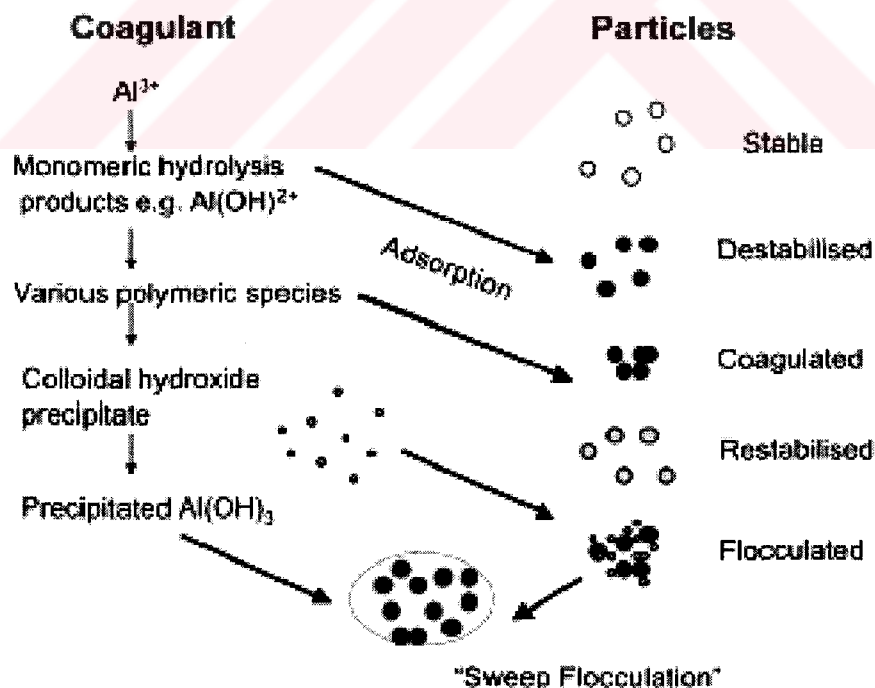


Figure 2.6 Schematic diagrams showing the interaction of aluminum species with initially negatively charged particles in water (Duan and Gregory, 2003).

2.3.5.2. Coagulation with Polymers

A polymer is a chain of small subunits or monomers. Synthetic polymers contain only one kind of monomer; some contain two or three different types of subunits. The total number of subunits in a synthetic polymer can be varied, producing material of different molecular weight. Polymer chains may be linear, or may be branched to vary degrees.

If a monomeric unit in a polymer contains ionizable groups (e.g., carboxyl, amino, sulfonic groups), the polymer is termed a polyelectrolyte. Depending upon the type of ionizable groups on the monomeric unit, a polyelectrolyte may be termed cationic, anionic, or amphoteric (contain both positive and negative groups, e.g., proteins). Polymers without ionizable groups are termed nonionic (O'Melia, 1968).

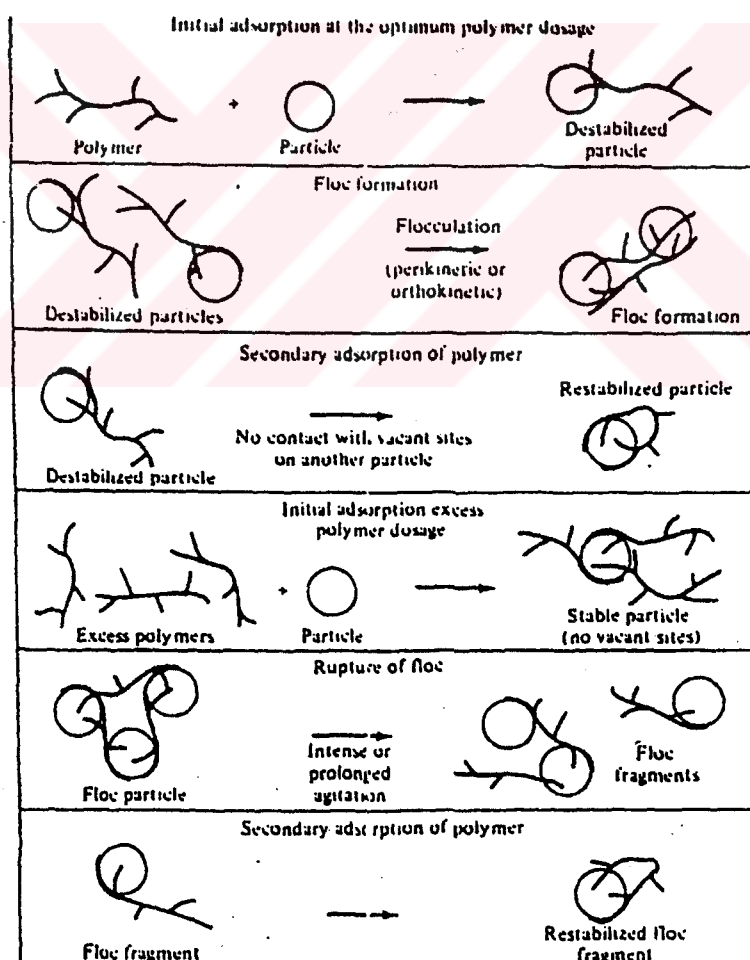


Figure 2.7 Schematic of reactions between colloidal particles and polyelectrolyte (O'Melia, 1968).

2.3.6. Removal of Humic Substances by Coagulation

Humic substance colloids retain a dispersed or dissolved (stable) state in surface water. The coagulation process is used to overcome the factors promoting the stability of humic-substance molecules in water. Flocculation is the process whereby destabilized particles formed during coagulation are induced to come together and thereby form larger agglomerates. The removal of humic substances is achieved by means of a probable adsorption of some organic materials on suspended particles (turbidity) and a direct interaction of the natural humic material with the coagulants themselves. The conventional water treatment process includes coagulation, flocculation, sedimentation, and final filtration. Iron salts and alum are widely used as a coagulant. Up to 90 per cent removal of the humic acids fraction has been achieved with both Al (III) and Fe (III). Direct filtration is another option at which synthetic organic cationic polyelectrolyte is used as a primary coagulant. A dose required depends on both the amount of humic material present and the pH. Removal of organics by coagulation is best under slightly acidic conditions, pH 4 to 6 (Vik and Eikebrokk, 1989).

Aluminum and iron salts are widely used as coagulants in water and wastewater treatment. They are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances. Their mode of action is generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate ('sweep flocculation'). The relative importance of these mechanisms depends on factors such as pH and coagulant dosage. Alternative coagulants, based on prehydrolysed forms of aluminum and iron, are more effective than the traditional additives in many cases, but their mode of action is not completely understood, especially with regard to the role of charge neutralization and hydroxide precipitation. Although the results can be reasonably well explained in terms of established ideas, a detailed understanding of the 'sweep flocculation' mechanism is not yet available. There are also still some uncertainties regarding the action of pre-hydrolyzed coagulants (Duan and Gregory, 2002).

Effective removal of soluble natural organic matter (NOM) from low turbidity waters can be achieved by aluminum coagulation provided due attention is paid to

coagulation and flocculation. To obtain maximum NOM removal studied with different pH influencing chemicals such as acid, alum, and lime. For low turbidity waters, essential floc nucleating sites can be provided by the lime that is used for pH and alkalinity adjustment, provided that the lime is added in sufficient quantity and at a point where it retains some of its particulate nature, i.e. immediately after coagulant addition. Adjusting the pH downwards to between 4 and 5 prior to the coagulant addition allows to the formation of soluble NOM-aluminum complexes that link to each other, thereby forming large insoluble bridges complexes that also act as nuclei for flocculation (Gregor et al., 1997). At lower pH < 4.5, humic substances formed soluble complexes with Al^{3+} and the amount of these HS-Al complexes increased with increasing concentration of the humic substances. Maximum removal of humic substances was found to occur in the pH range from 5.0 to 7.0 due to the adsorption of humic substances on the surface of $Al(OH)_3(s)$ crystal. High molecular weight humic substances containing carboxylic groups play an important role in the molecular self assembling processes that lead to the immobility of macromolecular substances on the surface of the $Al(OH)_3(s)$ crystal (Lu et al., 1999).

Similarly, Stephenson and Duff, (1996) examined the effect of metal coagulant concentration, effluent dilution and pH on the removal of total carbon, color and turbidity from mechanical pulping effluent. Both chloride and sulphate salts of iron and aluminum were effective in treating the mechanical pulping effluent in batch jar screening test. pH had a pronounced affect on precipitation. In terms of minimizing the total carbon (TC), color and turbidity levels, the optimum adjusted pH ranges were: 4.0-6.5 for ferric chloride, above 7.4 ferrous sulphate, 5.0-6.0 for aluminum chloride and 5.8 to 6.8 for aluminum sulphate. Removal of TC, color and turbidity of up to 88, 90 and 98 per cent, respectively, were observed. The precipitation yielded a supernatant that was virtually clear and colorless.

Mineral and organic particles may be stable in water due to electrostatic charge interactions, hydrophilic effects, or to steric interactions from adsorbed macromolecules. NOM rather than particles initially in water supplies can control coagulant dosages and selection. NOM consist of a mixture of various organic compounds hydrophobic and hydrophilic fractions. The negative charge and chemical structure of the hydrophobic acids affect chemical reactions with coagulants, particularly metal-based coagulants. The

removal of NOM with Al coagulants can involve hydrolysis, complexation, and precipitation and adsorption reactions. Preozonation of water supplies containing algae may lead to microfloculation or impair coagulation depending on algae type, concentration and molecular weight of extracellular organic matter, and ozone dose (Edzwald, 1993).

The presence of biodegradable organic matter (BOM) can affect drinking water quality. Studies of enhanced coagulation that is optimized for removal of dissolved organic material as well as particles showed that removal of DOC could be improved from the current average of 29 per cent (plant condition termed baseline coagulation) to an average of 43 per cent for optimized coagulation. Similarly, removal of biodegradable dissolved organic carbon (BDOC) could be improved from the current baseline level of 30 per cent to 38 per cent through the application of optimized coagulation. In most of the cases, assimilable organic carbon (AOC) was not affected by coagulation, because the AOC fraction was composed of small molecular weight, non-humic compounds that are not appropriate for coagulation (Volk et al., 2000).

The effectiveness of water treatment processes in the removing natural organic matter varies with the nature of the natural organic matter (NOM), its molecular size, polarity and charge density, and with properties of the raw water such as turbidity and hardness. In some cases conventional treatment is inefficient. For this reason, jar tests were conducted with the isolated NOM compared to coagulation with polyelectrolyte, alum, clays, and metal oxides, with each of the inorganic being in conjunction with a polyelectrolyte. Bolto et al., (1999) investigated that coagulation with alum and cationic polyelectrolyte show synergistic benefits from combinations of the two. The more hydrophobic NOM fractions were the most easily removed by polymer. The performance of cationic polymers improved significantly with increasing charge density and molecular weight. An alum/polymer combination is the most attractive treatment option.

Bolto et al. (2001) investigated that cationic polymer and clay or metal oxide combinations for natural organic matter removal. The effect of adding suspended matter in the form of clay or metal oxide when a cationic polymer was employed as the primary coagulant was found to be beneficial. The solids provide both an adsorbent for natural

organic matter (NOM) and a nucleating species for precipitating the NOM polymer complex. Metal oxides in conjunction with a cationic polymer were more promising than clay, with effectiveness in the order of $\text{Fe}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{Al}_2\text{O}_3 > \text{MnO}_2$. Magnesium oxide at a much lower dose was nearly as effective as ferric oxide, but of course raised the pH level significantly. A simpler and more convenient way of having reactive solids present was to add alum to form flocs; for one of the waters studied the alum dose could be reduced by 67 per cent by adding 1 mgL^{-1} of polymer, to give equal or better performance than alum alone at the optimum dose.

Another study of Bolto et al., (2002) is the removal of natural organic matter (NOM) from drinking water by coagulation and adsorption. Synthetic waters made from concentrates of humic substances from reservoir and river waters were tested in the laboratory for ease of removal of NOM by coagulation with cationic organic polymers and with alum, and by adsorption on anion exchangers. For polymers such as high molecular weight polydiallyldimethylammonium chloride (polyDADMAC) and cationic polyacrylamides of high charge, performance was nearly as effective as alum, with color removals 86-100 per cent of those obtained from alum. The NOM was separated into four fractions based on hydrophobic and hydrophilic properties. Alum was not as effective as ion exchange for the elimination of individual ionic NOM fractions. It was better than cationic polymers for removal of humic and fulvic acids, although polyDADMAC was as good for one water. For the removal of charged compounds, alum then polyDADMAC was the best performers for that water. A combination of coagulation with a cationic polymer and adsorption by an anion exchanger removed essentially all of the NOM.

Recently, Kam and Gregorty (2001) investigated that the humic acid interactions with a series of synthetic cationic polyelectrolytes. These covered a range of charge densities and molecular weight. The techniques used were colloid titration by spectrophotometry and streaming current detection, and flocculation determined by color removal by an optimal monitoring method. For a given cationic polyelectrolyte, all four methods gave charge densities for humic substances which were in good agreement. However, schematic differences in the apparent humic charge density were found, depending on the charge density of the cationic polyelectrolyte used. With low charge density polyelectrolyte, the apparent anionic charge of the humic substances was found to

be low. With higher charge density polyelectrolyte, the apparent humic substances charge density increases and reaches a limiting value when the polyelectrolyte charge is greater than three meqg⁻¹. This indicates a non-stoichiometric interaction between the anionic sites of the humic substances and the cationic charge of the low charge polyelectrolytes. Optimum flocculation of humics occurred with less cationic charge in the case of low charge polyelectrolytes than those with higher charge density. However, the degree of removal was considerably better in the latter case. In all cases, the molecular weight of the cationic polyelectrolytes appeared to have no effect on the results.

In addition, Walker and Bob (2000) examined the influence of two natural organic polymers (polysaccharide and humic acid) on the stability of colloidal aggregates. The primary objective of research was to determine whether addition of organic matter to floc suspensions results in the fragmentation or stabilization of aggregates. A second objective was to determine how the size of aggregates and the composition of organic matter influence the floc breakup or stabilization process. They were found that the stability of aggregates depended on the type of organic material present as well as floc size. They were also found that the addition of humic acid or polysaccharide generally decreased the rate of coagulation of small aggregates but had less influence on large aggregates. The existence of strong interparticle forces within flocs prevented aggregate breakup upon adsorption of natural organic polymers.

Preozonated altered removal of organic matter during water treatment through two main effects. First, preozonation directly removed organic matter by mineralization, volatilization, and stripping reactions, improving removal in comparison to unozonated systems. On the other hand, preozonation decreased the surface charge of floc formed after coagulation with hydrolysable metal salts, hindering adsorptive removal of the anionic organic molecules by floc surfaces and inducing the stabilized floc formation; changes that decrease removal in comparison to unozonated systems. The relative importance of the two effects determined whether preozonation enhanced or hindered removal of organic matter. In most water, treatment plants preozone doses above 0.7 mgO₃mg⁻¹ TOC, while enhanced removal may occur if relatively high concentrations volatile organic matter is present. As a result, preozonation hindered turbidity removal and increased the concentration of coagulant metal residuals in finished drinking water at low coagulant doses (Edwards et al., 1993).

O'Melia et al., (1999) examined removal of humic substances by coagulation. Firstly, the adsorption of NOM on oxide surfaces is investigated. Agreement is good and supports the view that the adsorption of NOM on oxides depends significantly on complex formation reactions between specific sites on oxide surfaces and functional groups on the NOM. Frequently there is a stoichiometric relationship between the required coagulant dosage and the TOC of the water to be treated. Other important factors include pH and the concentration of divalent cations. Ozone may benefit or retard coagulation, depending on coagulant type and the water quality characteristic that is dominant in setting the optimum coagulant dosage.

Algal-derived DOC was difficult to remove; high coagulant doses were required and removal was strongly influenced by solution pH and algal source. Widrig et al. (1996) investigated the removal of algal-derived organic material by preozonation and coagulation. Preozonation enhanced DOC removal to varying degrees depending on organic quality that was determined by algal source. These results suggest that the unpredictable nature of ozone's ability to enhance coagulation in actual treatment practice may be related to changes in DOC caused by seasonal shifts in algal speciation and dominance. Preozonation produced dramatic changes in the chemical character of the organic matrix produced by algae. These results suggest that, although use of ozone may not improve DOC removals in all cases, there may be advantages to ozone use that are related to desirable quality changes in the residual DOC.

Schneider and Tobiasson (2000) investigate that preozonation effects on coagulation. The effects of preozonation on interactions among coagulants, particles, and natural organic matter were examined at bench scale through a series of jar tests using different organic matter, pH values, and coagulants. When alum was used as a coagulant, preozonation hindered turbidity and dissolved organic matter removal at the conditions tested. When cationic polymers were used as the coagulant, however, preozonation led to small but statistically significant increases in the removal of both turbidity and DOM. When polyaluminum chloride was used as coagulant for several natural waters, preozonation aided turbidity and DOM removal in one instance and hindered removal of particles and organic materials in another instance. Preozonation reduces the surface charge of particulates, leading to better coagulation by charge neutralization.

Interactions between aluminum species and dissolved silica in aqueous solution have been shown to play a large part in the coagulation of suspensions by aluminum salts. These effects are quite distinct from those associated with polymeric or colloidal silica. At a fixed aluminum concentration, coagulation may be enhanced by low levels of dissolved silica, especially at pH values around 6. At higher pH values, a strong inhibition of coagulation by aluminum sulphate is found at silica levels around 10 mgL^{-1} , which is typical of those found in many natural waters. Electrophoretic mobility measurements of clay particles in the presence of aluminum and dissolved silica show that the latter can modify the charge neutralizing behavior of hydrolyzed aluminum species, providing at least a partial explanation of the observed effects (Duan and Gregory, 1996).

The transition between stable colloidal dispersions and coagulated or flocculated systems is a decisive process in practical applications of million of tons of bentonites (containing the clay mineral montmorillonite). Dispersion into the colloidal state requires the transformation of the original bentonite into the sodium form, for instance by soda activation. Therefore, the coagulation of sodium montmorillonite dispersions by inorganic and organic cations and the influence of compounds of practical interest such as phosphates, cationic and anionic surfactants, alcohols, bentaine-like molecules and polymers like polyphosphates, tannates, polyethylene oxides with cationic and anionic end groups, and carboxy methylcellulose. Montmorillonite particles with adsorbed bentaine-like molecules provide an example of lysosphere stabilization (Lagaly and Ziesmer, 2002).

As a new kind of water and wastewater treatment reagents, inorganic polymer flocculants (IPFs) are in a trend of rapid development. Among them, iron-based IPF without any toxic problems is greatly expected. Wang and Tang (2000) investigated that a new protocol for preparation of iron-based IPF. Three kinds of silica, named silicaA, silicaB and silicaC, are prepared and used as modifiers to tailor-make polyferric silicate (PFSi), denoted PFSiA, PFSiB and PFSiC, respectively, in accordance to the above silica. The experiment results show that the species distribution of PFSi is mainly decided by the kinds of silica introduced and Si/Fe ratio adopted. SilicaA and silicaB function as precipitation preventing reagents during the hydrolysis of Fe(III). At certain amount of basicity, Fe_a (monomers) increases with increase of Si/Fe ratio, while Fe_c (colloidal species) decreases markedly. Although the formation of Fe_c is inhibited, the stabilization

of Feb (oligomers or polymers) can still not be achieved. Silica C on the other hand exhibits little effect on the species distribution of modified Fe(III) solutions.

Recently, aluminum silicate polymer composite (PASiC) was produced by two approaches: (1) hydroxylation of the mixture of AlCl_3 and fresh polysilicate (PASiCc); (2) hydroxylated polyaluminum-chloride (PAC) combined with fresh polysilicate (PASiCm). The coagulation behavior of PASiC and PAC under conditions typical for coagulation and flocculation in water treatment was investigated by studying the rate of floc size development, the variety of streaming current value, the efficiency of turbidity removal, and the effect of pH on the turbidity removal efficiency, and the stability of PASiC. Compared with PAC, PASiC may enhance aggregating efficiency and give better coagulating effects, but weaken charge effectiveness in coagulation process or become unstable when stored for longer time, especially at higher B value and lower Al/Si ratio. With the increase of B value and the decrease of Al/Si ratio, the coagulation efficiency of PASiC increases and at the same B value and Al/Si ratio, PASiCc seems to give a little better coagulation effect than PASiCm but less stability (Gao et al., 2002).

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Humic Acid

Aldrich humic acid was used for the preparation of humic acid solutions. Humic acid stock solution (1000 mgL^{-1}) was prepared by dissolving humic acid sodium salt in distilled/deionized water and filtering through paper. Humic acid solutions for the experiments were prepared by diluting the stock solution with distilled/deionized water.

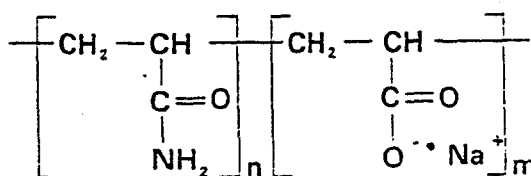
For monitoring color (Color_{436}), and organic matter content (UV_{254}) of humic acid solutions, absorbance values of the samples were recorded at 436 nm and 254 nm.

3.1.2. Titanium Dioxide Powder

Degussa P-25 TiO_2 was used as the photocatalyst. The primary particle size was 20-30 nm, and BET surface area was $50 \pm 15 \text{ m}^2\text{g}^{-1}$. The crystal structure of the TiO_2 was composed of 70 per cent anatase and 30 per cent rutile.

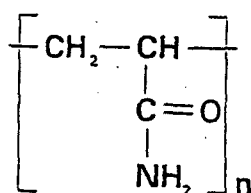
3.1.3. Coagulating Agents

Alum ($\text{Al}_2(\text{SO}_4)_3$) solution (10 per cent) was prepared using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ crystals, ferric chloride (FeCl_3) solution (10 per cent) was prepared using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ crystal, anionic, and nonionic polyelectrolyte solutions (5 per cent) were prepared using synthetic polymers. These coagulants were used in Ömerli Drinking Water Treatment plant



Anionic polymer

Figure 3.1 Molecular formula of anionic polymer



Non-ionic polymer

Figure 3.2 Molecular formula of nonionic polymer

Table 3.1 Characteristic of polymers

	Charge Density	Molecular Weight	Approximate Bulk Density	Approximate Brookfield Viscosity (cps)
Anionic Polymer	Very Low	Very High	0.8	5.0 g/L 450 2.5 g/L 200 1.0 g/L 80
Nonionic Polymer	Very Low	Very High	0.8	5.0 g/L 350 2.5 g/L 150 1.0 g/L 60

3.1.4. Laboratory Equipment

Following laboratory equipments and instruments were used during differing steps of the experiments.

Hettich EBA 8S Centrifuge: It was used for the removal of photocatalyst the suspensions were centrifuged for 10 min.

Ozone Generator PCI Model GL-1 Type: It was used for the ozonation experiments.

Shimadzu UV 160 Double Beam Spectrophotometer: UV-visible absorption spectra were recorded employing Hellma quartz cuvettes 1.0 cm optical path length.

Scaltec Balance: Balance was used for weighting certain amounts of TiO₂, and coagulants.

Ultra Sonic Waterbath LC30: In photocatalytic experiments the homogeneous suspensions was provided by sonification of the slurry.

Framo-Geratechnik M21/1 Magnetic Stirrer: It was used for the continuous mixing of the suspensions throughout the reaction time during photocatalytic treatment and coagulation experiments.

WTW pH Meter-pH 526: pH values were measured to observe pH changes during the experiments. The pH meter was calibrated with pH 4 and pH 7 buffer solutions.

Memmert Oven: It was used to dry the glassware.

Sterile Millex – HA Millipore Filter: The suspensions were filtered through 45- μ m Millipore syringe filter to remove the residual catalyst and flocs.

3.2. Methods

3.2.1. Ozonation

An oxygen feed ozone generator with a capacity of producing 1.1 kg ozone per day at the concentration of 2.5 per cent weight was employed. Tubular type ceramic porous diffuser with 10 cm length was used to transfer ozone gas into water in the cylindrical reactor. The diffuser was placed horizontally at the bottom of the reactor. Teflon tubing was used for the ozone gas lines. The applied ozone output of the generator was adjusted by changing the electrical current of the ozone generator. The flowrate and the ozone concentration of the feed gas to the reactor were 1.9 Lmin⁻¹ and 2.5 mgL⁻¹ respectively. 10 L humic acid samples were used in ozonation experiments.

In this study, 50 mgL⁻¹ humic acid samples were 50 per cent treated in terms of Color₄₃₆ by ozonation, and applied ozone dose was 3.41 mg O₃ per mg C, in addition, contact time was 6.5 minutes.

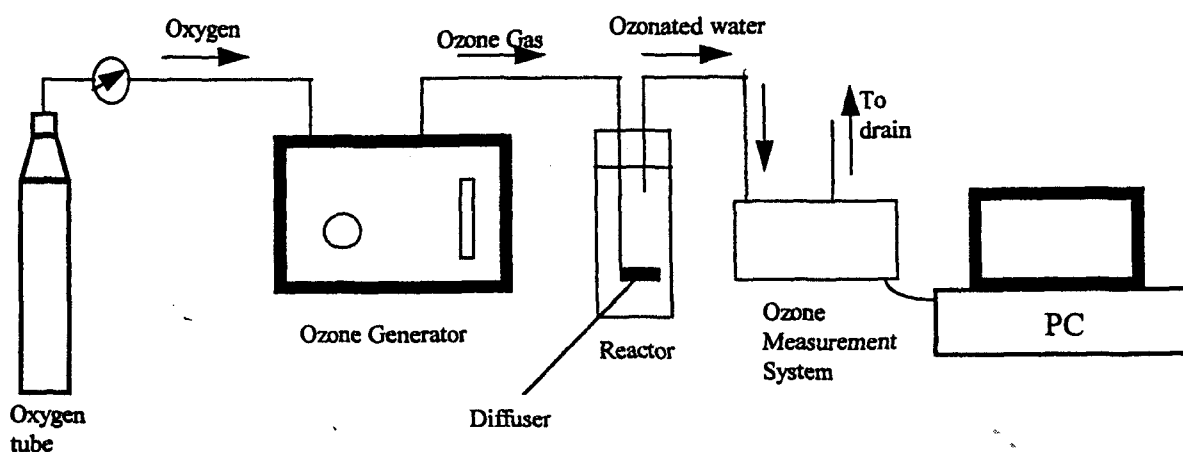


Figure 3.3 Experimental set-ups for ozonation experiments.

3.2.2. Photocatalysis Experiments

The light source was 125 W Black Light Fluorescent Lamp (BLF) having an output spectrum of 320 to 440 nm with a maximum emission at 365 nm. A cylindrical glass photo reactor with a diameter of 7.5 cm and height of 3.5 cm was used in the experiments. A magnetic stirrer provided continuous stirring. A mirror casing enclosed the photoreactor, and the whole system was placed in a box. The inner walls of the box were covered with Al-foil.

Raw humic acid samples were photocatalytically treated. 50 mL of samples was added into the photo reactor containing 0.025 mgmL^{-1} titanium dioxide. For the homogenization of the slurry, sonicator was used for 2 min. This homogeneous mixture was placed on the magnetic stirrer for continuous stirring through out the reaction period (30 min). At the end of each reaction period, volume loss was compensated by distilled/deionized water.

In order to separate TiO_2 from the humic acid solution, the reactor content was centrifuged at $10000 \text{ cycles min}^{-1}$ for 10 min. using HETTICH EBA 8S centrifuge at a rate of 5000 rpm. Then, the cleared liquid was filtered using $0.45 \mu\text{m}$ Millipore Millex-HA cellulose based membrane filters, which were attached to 10 mL syringes.

3.2.3. Sequential Oxidation

Sequential oxidation of humic acids was studied in a combined system including ozonation and photocatalysis. Ozonation was employed as a pretreatment step for partial

oxidation of humic acid solution prior to photocatalysis. The method described in Section 3.2.1. was used in ozonation. Partial oxidation was defined by 50 per cent reduction in Color_{436} obtained by applying ozone. The pretreated humic acid samples were then oxidized photocatalytically for 15 min as described previously in Section 3.2.2.

3.2.4. Coagulation Experiments

A graduated cylinder of 100 mL was employed in order to observe the coagulation and the subsequent sedimentation of treated and untreated humic acid. The diameter of the cylinder was 2 cm and height of the cylinder was 26 cm. Certain concentrations of coagulant were added to treated and untreated humic acid solutions. pH was adjusted to 5.5. Alum or ferric chloride-only tests were conducted two speeds. The two speeds used were a rapid mix at 120 rpm for two minutes and a flocculation step at 30 rpm for 20 minutes for the slow floc growth stage, followed by a 60-minute settling period. Then, clear supernatant was filtered through 0.45 μm membrane filter, before Color_{436} and UV_{254} were measured.

Polymer/alum or ferric chloride tests were conducted in a very similar fashion to that of the alum or ferric chloride-only tests, with the exception that the first step was to add the pre-determined dose of alum or ferric chloride to beaker and stir at high shear (120 rpm) for two minutes. The polymer was then added and stirring at high speed continued for a further 2 min. The normal procedure for alum or ferric chloride-only test was then followed. Clear supernatant was filtered through 0.45 μm membrane filter, before Color_{436} and UV_{254} were measured.

4. RESULTS AND DISCUSSION

In this study, ozonation, photocatalytic oxidation, sequential oxidation, and coagulation experiments were carried out in order to examine coagulation properties on four different coagulants/combinations. In the figures and tables, H stand for untreated humic acid solution; C stand coagulation; O stand for ozonation; P stands for photocatalytic treatment, and S stands for sequential oxidation. Characterization of untreated and treated humic acids, and the percent removal efficiencies based on Color_{436} and UV_{254} were given in Table 4.1. The initial humic acid concentration was 50 mgL^{-1} for all treatment methods.

Table 4.1 Color_{436} and UV_{254} parameters for the untreated and treated humic acid solutions

	Color_{436} (m^{-1})	Color_{436} Removal (per cent)	UV_{254} (m^{-1})	UV_{254} Removal (per cent)
H	23.8	-	118	-
H+O	12.7	47	81	31
H+P	11.9	50	91	23
H+S	6.2	72	52	57

Higher percentage removals in Color_{436} than UV_{254} indicate rapid decoloration obtained in comparison to organic matter degradation obtained by ozonation, photocatalytic treatment, and sequential oxidation.

4.1. Coagulation of Humic Acid with Alum

The experiments were conducted according to the procedure outlined in the Materials and Methods section. After 60 minutes of sedimentation and filtration period, Color_{436} and UV_{254} measurements were carried out in the supernatant to assess the effect of coagulation on the color and UV absorbance in the solution.

4.1.1. Untreated Humic Acid Coagulation with Alum

For comparison, experimental results of 20 mgL⁻¹, 30 mgL⁻¹, 40 mgL⁻¹, and 50 mgL⁻¹ humic acid solutions with alum coagulation were presented in terms of UV₂₅₄, Color₄₃₆, and TOC in Figure 4.1, Figure 4.2, and Figure 4.3, respectively.

Different alum doses (10 mgL⁻¹, 12 mgL⁻¹, 14 mgL⁻¹, 16 mgL⁻¹, 18 mgL⁻¹) were used for 20 mgL⁻¹ humic acid solution in the experiment. Increasing the coagulant dose led to an increase in UV₂₅₄, Color₄₃₆ and TOC removals. 57 per cent UV₂₅₄, 70 per cent Color₄₃₆, and 45 per cent TOC removals were achieved by 10 mgL⁻¹ alum addition. Then, 85 per cent Color₄₃₆, 72 per cent UV₂₅₄ and 60 per cent TOC removals were obtained by 12 mgL⁻¹ alum addition. Incremental addition up to 14 mgL⁻¹ revealed 86 per cent UV₂₅₄, 95 per cent Color₄₃₆, and 79 per cent TOC removals. Further increase did not result in improvement in removal efficiency. Therefore, the optimum alum dose was found to be 14 mgL⁻¹ for 20 mgL⁻¹ humic acid solution.

Various concentrations of alum doses (10 mgL⁻¹, 15 mgL⁻¹, 20 mgL⁻¹, 25 mgL⁻¹, 30 mgL⁻¹) were applied for 30 mg L⁻¹ humic acid solution. Alum additions (10 mgL⁻¹) led to 50 per cent UV₂₅₄, 60 per cent Color₄₃₆, and 40 per cent TOC removals. Removal percentages of UV₂₅₄, Color₄₃₆, and TOC values by 15 mgL⁻¹ alum additions increased up to 72, 80 and 63 per cent, respectively. The optimum alum dose is 20 mgL⁻¹ and the percentage removals of UV₂₅₄, Color₄₃₆, and TOC at the optimum dose were 90, 95, and 80 per cent, respectively, for 30 mgL⁻¹ humic acid solution. Then, increasing the coagulant dose did not lead to increases in UV₂₅₄, Color₄₃₆, and TOC removal.

Concentration of applied alum doses were 10 mgL⁻¹, 15 mgL⁻¹, 20 mgL⁻¹, 25 mgL⁻¹, and 40 mgL⁻¹ for 40 mgL⁻¹ humic acid coagulation with alum. According to Figure 4.1, Figure 4.2, and Figure 4.3, 52 per cent UV₂₅₄, 63 per cent Color₄₃₆, and 45 per cent TOC removals were achieved by 15 mgL⁻¹ alum additions. After 15 mgL⁻¹ alum addition, 20 mgL⁻¹ alum dose was applied and 72 per cent UV₂₅₄, 79 per cent Color₄₃₆ and 63 per cent TOC removals were obtained for 40 mgL⁻¹ humic acid. As a result, the optimum alum dose was found to be 25 mgL⁻¹ for 40 mgL⁻¹ humic acid solution. The removal percentage of UV₂₅₄, Color₄₃₆, and TOC were 89, 94, and 80 per cent for the optimum alum dose.

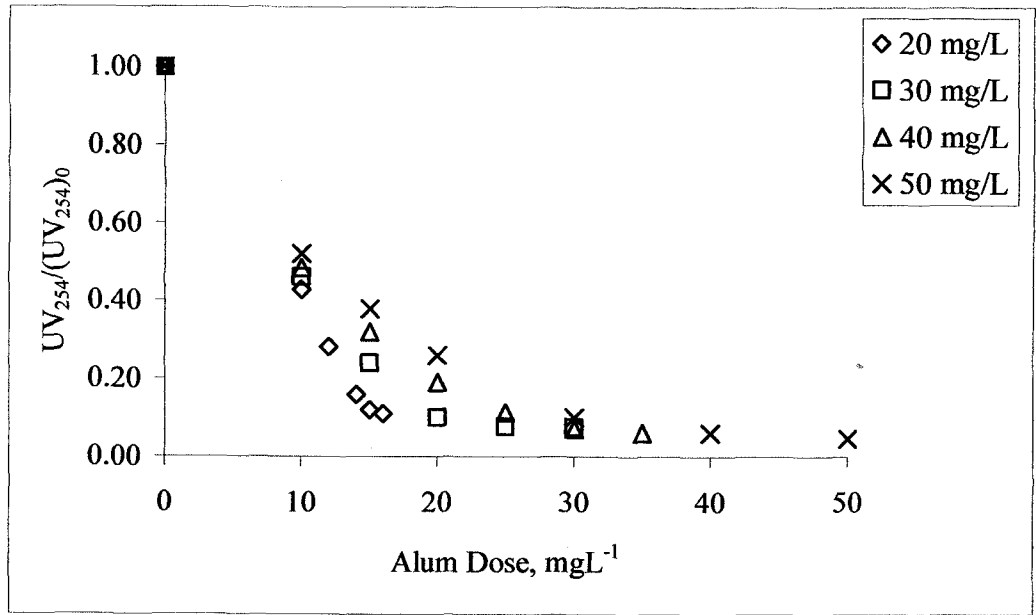


Figure 4.1 Comparison of the coagulation profiles based on UV₂₅₄ for untreated humic acid.

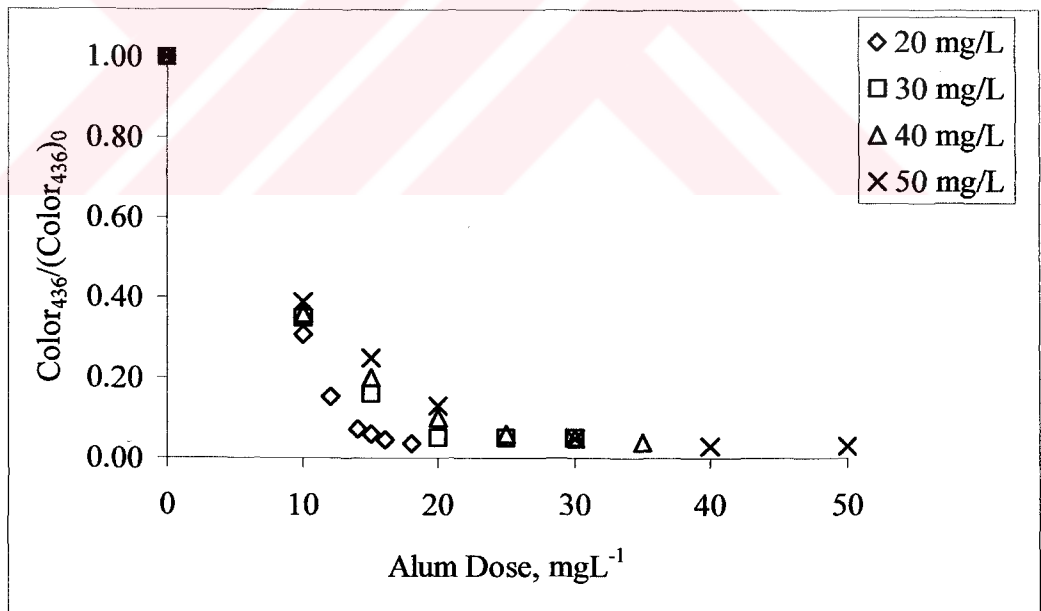


Figure 4.2 Comparison of the coagulation profiles based on Color₄₃₆ for untreated humic acid.

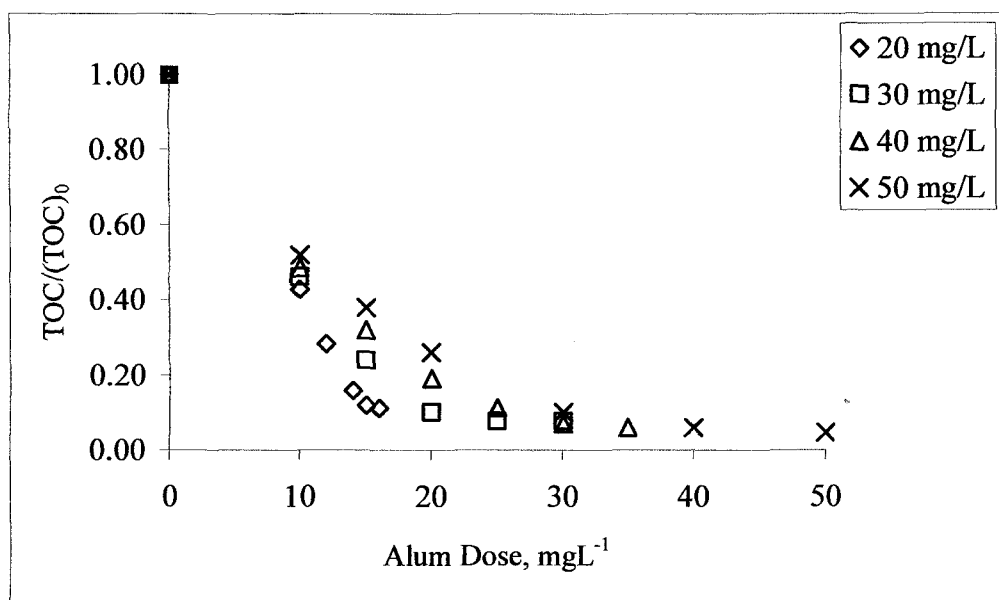


Figure 4.3 Comparison of the coagulation profiles based on TOC for untreated humic acid.

Different concentrations of alum (10 mgL^{-1} , 20 mgL^{-1} , 30 mgL^{-1} , 40 mgL^{-1} , and 50 mgL^{-1}) were applied for 50 mgL^{-1} humic acid solution coagulation with alum. According to Figure 4.1, Figure 4.2, and Figure 4.3, 10 mgL^{-1} alum additions led to 53 per cent UV_{254} , 67 per cent Color_{436} , and 52 per cent TOC removals. Then, 20 mgL^{-1} alum addition led to an increase in the removal percentages of UV_{254} , Color_{436} , and TOC values these are 84, 90, and 77 per cent, respectively. The optimum alum dose was found to be 30 mgL^{-1} for 50 mgL^{-1} humic acid solution. The removal percentages of UV_{254} , Color_{436} , and TOC were 94, 97 and, 87 per cent for the optimum alum dose. Further increase did not result in improvement in the removal efficiency.

4.1.2. Treated Humic Acid Coagulation with Alum

In most cases, ozonation has adverse effects on the coagulation mainly due to the interactions between ozone and humic acid in solution. In water that are not ozonated, there is a distribution of large and small molecules. When the proper dose of alum is added to such water, aluminum hydroxide precipitates form. Much of the organic matter is removed by sorption on to the floc surface. In waters that are ozonated, there is usually a shift in the distribution of humic acid toward smaller, more oxygenated compounds. These smaller compounds are typically more highly charged, and a more

compounds. These smaller compounds are typically more highly charged, and a more reactive surface area of aluminum hydroxide solids is needed to obtain the same removal of DOC. Hence, the optimum alum dose increases or the amount of DOC removed at a given alum dose decreases (O'Melia et al., 1999).

Removal percentages of 50 mgL⁻¹ untreated, ozonated, photocatalytically and sequentially oxidized humic acid were presented in same figure for comparison of oxidation methods. Experimental results of treated and untreated humic acid solutions with alum presented as UV₂₅₄ and Color₄₃₆ in Figure 4.4 and Figure 4.5, respectively.

4.1.2.1. Coagulation Profiles for Ozonated Humic Acid with Alum

In order to evaluate affect of ozonation on coagulation properties of humic acid, 50 mgL⁻¹ humic acid was 50 per cent ozonated in terms of Color₄₃₆. Then, coagulation experiments were done according to Materials and Methods section. After coagulation experiments, Color₄₃₆ and UV₂₅₄ values were reported.

Concentrations of applied alum doses were 10 mgL⁻¹, 20 mgL⁻¹, 30 mgL⁻¹, 40 mgL⁻¹ and, 50 mgL⁻¹ for ozonated humic acid solution. Increasing the coagulant dosage led to an increase in UV₂₅₄ and Color₄₃₆ removals. The removal percentages of UV₂₅₄ and Color₄₃₆ were achieved 33 and 44 per cent by 10 mgL⁻¹ alum additions. Then, 57 per cent UV₂₅₄ and 68 per cent Color₄₃₆ removals were obtained by 20 mgL⁻¹ alum additions. Incremental addition up to 30 mgL⁻¹ revealed 76 per cent UV₂₅₄ and 84 per cent Color₄₃₆ removals. Further increase did not result in improvement in removal efficiency. Therefore, the optimum alum dosage was found to be 30 mgL⁻¹ for ozonated humic acid solution.

4.1.2.2. Coagulation Profiles for Photocatalytically Treated Humic Acid with Alum

In order to investigate the effect of photocatalytic degradation on the coagulation properties of humic acid, 50 per cent degraded (in Color₄₃₆) humic acid was used. Firstly, photocatalysis experiments were done and then coagulation experiment were carried out

according to Materials and Methods section. After coagulation experiments, Color_{436} and UV_{254} values were reported.

Applied alum concentrations were 10 mgL^{-1} , 20 mgL^{-1} , 30 mgL^{-1} , 40 mgL^{-1} , and 50 mgL^{-1} for photocatalytically treated humic acid solution. Increasing the coagulant dose led to an increase in UV_{254} and Color_{436} removals. The removal percentages of UV_{254} and Color_{436} rapidly increased after 10 mgL^{-1} alum dose. In addition, the removal percentages of UV_{254} and Color_{436} were obtained as 47 and 52 per cent by using 10 mgL^{-1} alum. Following 20 mgL^{-1} alum application, 67 per cent UV_{254} and 77 per cent Color_{436} removals were achieved. Nevertheless, after 30 mgL^{-1} alum dosage, the same percentage removals of UV_{254} and Color_{436} were obtained by increasing alum dose. Therefore, the optimum alum dose was found to be 30 mgL^{-1} for photocatalytically humic acid. The percentage removal of UV_{254} and Color_{436} were 91 per cent for optimum alum dose of 30 mgL^{-1} .

4.1.2.3. Coagulation Profiles for Sequentially Treated Humic Acid with Alum

In order to evaluate the effect of sequential oxidation on the coagulation properties of humic acid, 50 mgL^{-1} humic acid solutions were 50 per cent treated in terms of Color_{436} by ozonation. Then humic acid solutions were 50 per cent treated in terms of Color_{436} photocatalytically. After sequential oxidation, coagulation experiment were carried out according to Materials and Methods section. After coagulation experiments, Color_{436} and UV_{254} values were reported.

Concentrations of applied alum dose were 10 mgL^{-1} , 20 mgL^{-1} , 30 mgL^{-1} , 40 mgL^{-1} , and 50 mgL^{-1} for sequentially treated humic acid solution. Increasing the coagulant dosage led to a little increase in UV_{254} and Color_{436} removals. The removal percentages of UV_{254} and Color_{436} were achieved 27 and 37 per cent by 10 mgL^{-1} alum additions. Then, 53 per cent UV_{254} and 61 per cent Color_{436} removals were obtained by 20 mgL^{-1} alum additions. Incremental addition up to 30 mgL^{-1} revealed 64 per cent UV_{254} and 73 per cent Color_{436} removals. Further increase did not result in improvement in removal efficiency even though; the removal percentages of UV_{254} and Color_{436} showed a little decrease with increasing alum dose. Therefore, the optimum alum dosage was found to be 30 mgL^{-1} for sequentially treated humic acid solution. The removal percentage of UV_{254} and Color_{436} were 64 and 73 per cent for optimum alum dose.

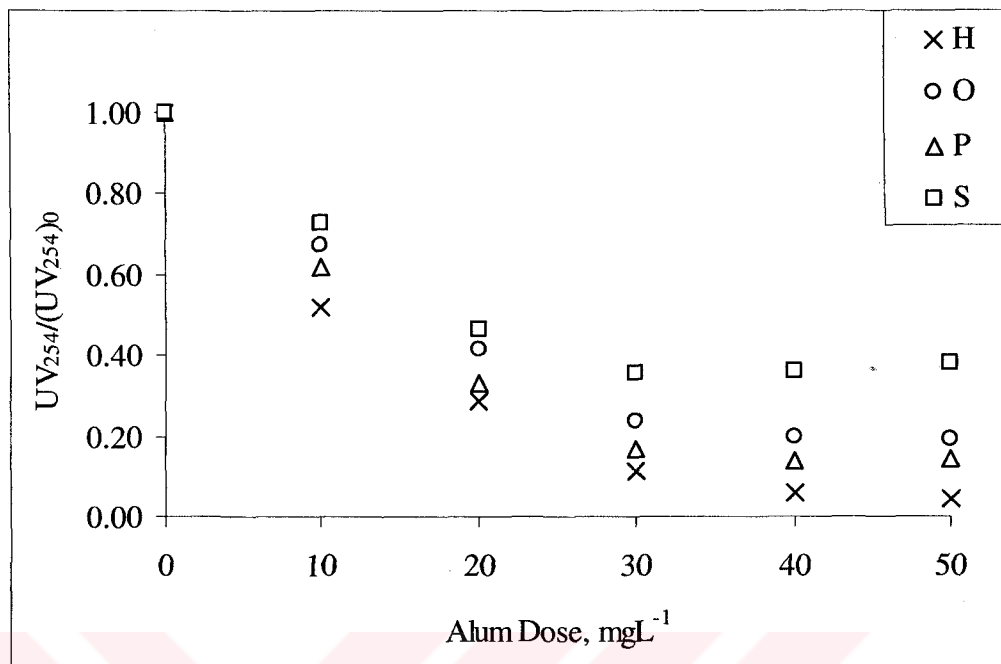


Figure 4.4 Comparison of the coagulation profiles based on UV₂₅₄ for untreated and treated humic acid.

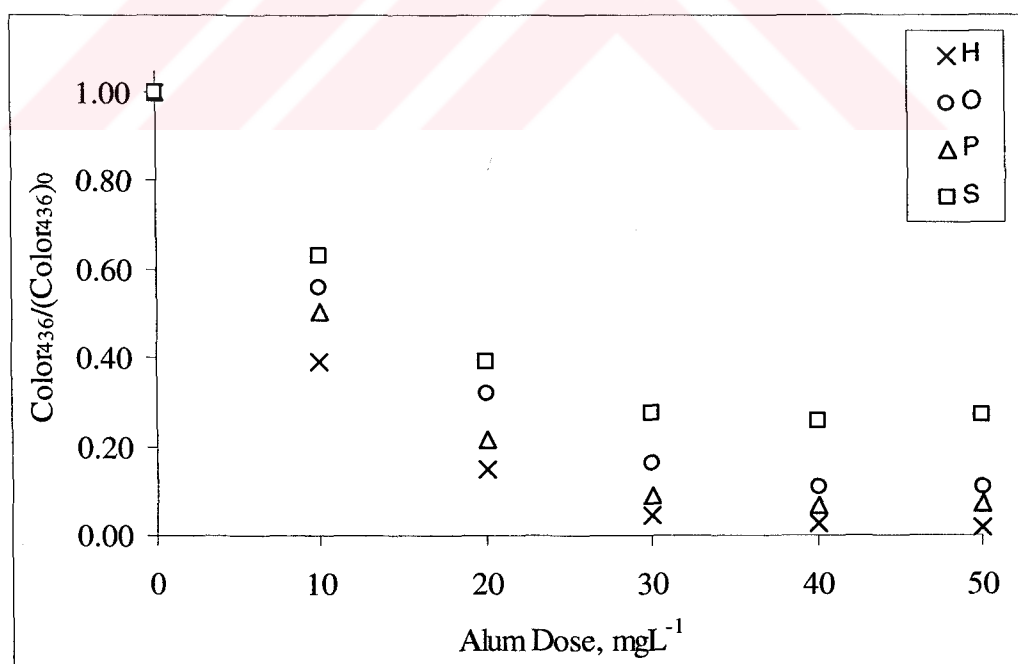


Figure 4.5 Comparison of the coagulation profiles based on Color₄₃₆ for untreated and treated humic acid.

4.2. Coagulation of Humic Acid with Ferric Chloride

The experiments were conducted according to the procedure outlined in the Materials and Methods section. Untreated, ozonated, photocatalytically and sequentially oxidized humic acid were used. After 60 minutes sedimentation and filtration period, Color_{436} and UV_{254} measurements were conducted in the supernatant to assess the effect of coagulation on the color and UV absorbance in the solution.

4.2.1. Untreated Humic Acid Coagulation with Ferric Chloride

Experimental results for comparison of 20 mgL^{-1} , 30 mgL^{-1} , 40 mgL^{-1} , and 50 mgL^{-1} humic acid solutions with ferric chloride coagulation were presented in terms of UV_{254} , Color_{436} , and TOC in Figure 4.6, Figure 4.7, and Figure 4.8, respectively.

Different ferric chloride dosages (20 mgL^{-1} , 25 mgL^{-1} , 30 mgL^{-1} , 35 mgL^{-1} , 40 mgL^{-1}) were used for 20 mgL^{-1} humic acid solution. Increasing the coagulant dosage led to an increase in UV_{254} , Color_{436} and TOC removals. 39 per cent UV_{254} , 46 per cent Color_{436} , and 37 per cent TOC removals achieved by 20 mgL^{-1} ferric chloride addition. Then, 63 per cent Color_{436} , 65 per cent UV_{254} , and 53 per cent TOC removals were obtained by 25 mgL^{-1} ferric chloride addition. Incremental addition up to 30 mgL^{-1} revealed 81 per cent UV_{254} and 87 per cent Color_{436} removal. Further increase did not result in improvement in removal efficiency. Therefore, the optimum ferric chloride dosage was found to be 30 mgL^{-1} for 20 mgL^{-1} humic acid solution.

Various concentration of ferric chloride doses (35 mgL^{-1} , 40 mgL^{-1} , 45 mgL^{-1} , 50 mgL^{-1} , 55 mgL^{-1}) were applied for 30 mgL^{-1} humic acid solution. According to Figure 4.6, Figure 4.7, and Figure 4.8, 35 mgL^{-1} ferric chloride led to 61 per cent UV_{254} , 66 per cent Color_{436} , and 57 per cent TOC removals. 40 mgL^{-1} ferric chloride addition increased the removal percentages of UV_{254} , Color_{436} , and TOC values as 77, 79, 73 per cent, respectively. The optimum ferric chloride dose is 45 mgL^{-1} and the percentage removal of UV_{254} , Color_{436} and TOC at optimum dose were 89, 91, and 81 per cent. Then, increasing coagulant dose did not lead to an increase in UV_{254} , Color_{436} , and TOC removal.

Concentration of applied ferric chloride doses were 30 mgL^{-1} , 40 mgL^{-1} , 50 mgL^{-1} , 60 mgL^{-1} , 70 mgL^{-1} for 40 mgL^{-1} humic acid solution. Increasing the ferric chloride dose led to an increase in the removal percentages of UV_{254} , Color_{436} and TOC values. According to results of experiment, 47 per cent UV_{254} , 52 per cent Color_{436} and 44 per cent TOC removals were achieved by 30 mgL^{-1} ferric chloride addition. After this dose, 40 mgL^{-1} ferric chloride dose was applied and 67 per cent UV_{254} , 71 per cent Color_{436} and 61 per cent TOC removal was obtained for 40 mgL^{-1} humic acid solution. The optimum ferric chloride dose was found to be 50 mgL^{-1} . The removal percentage of UV_{254} , Color_{436} and TOC was 84, 86, and 79 per cent for the optimum ferric chloride dose as 50 mgL^{-1} . Further increase did not lead to an increase in the removal efficiency.

Applied ferric chloride concentrations were 40 mgL^{-1} , 50 mgL^{-1} , 60 mgL^{-1} , 70 mgL^{-1} , 80 mgL^{-1} for 50 mgL^{-1} humic acid solution. Using 40 mgL^{-1} ferric chloride led to 52 per cent UV_{254} , 55 per cent Color_{436} , and 53 per cent TOC removal. Then, 50 mgL^{-1} ferric chloride addition increased the removal percentages of UV_{254} , Color_{436} , and TOC values as 79 per cent, 82 per cent and 75 per cent, respectively. The optimum ferric chloride dose was found to be 60 mgL^{-1} for 50 mgL^{-1} humic acid solution. The percentage of UV_{254} , Color_{436} and TOC removal were 88, 92, and 85 per cent for the optimum ferric chloride dose as. Further increase did not result in improvement in removal efficiency.

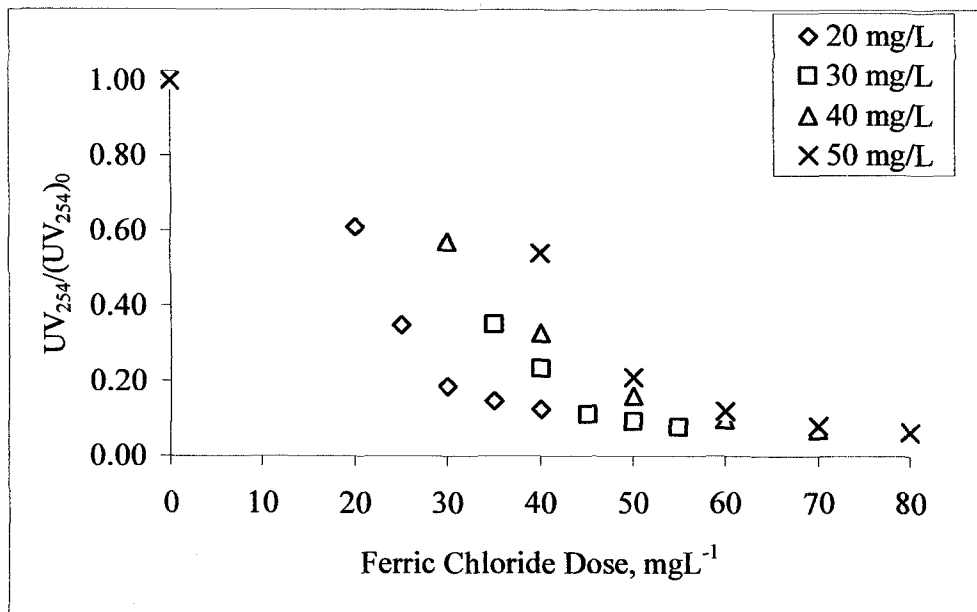


Figure 4.6 Comparison of the coagulation profiles based on UV_{254} for untreated humic acid.

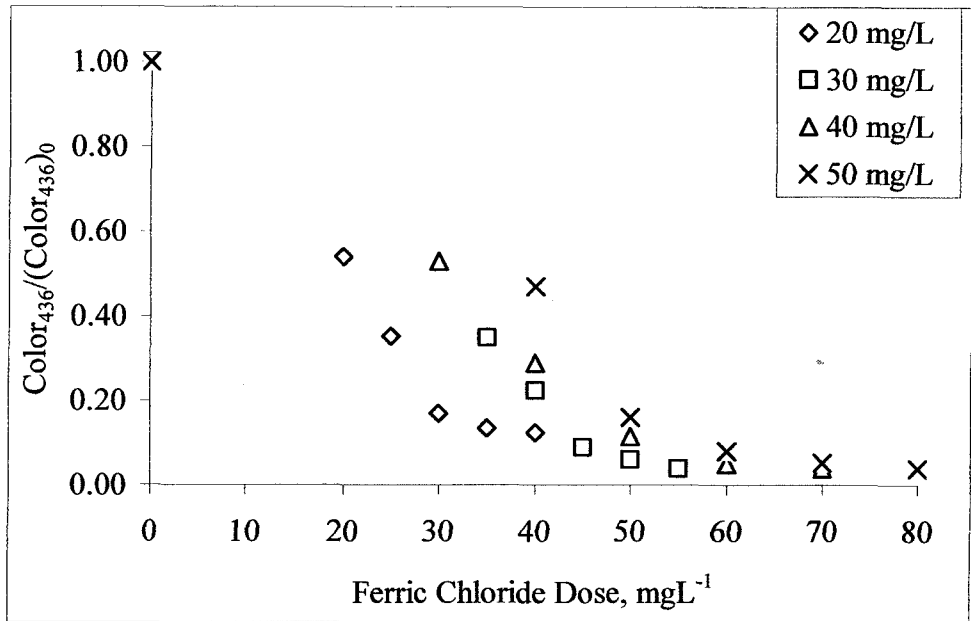


Figure 4.7 Comparison of the coagulation profiles based on Color₄₃₆ for untreated humic acid.

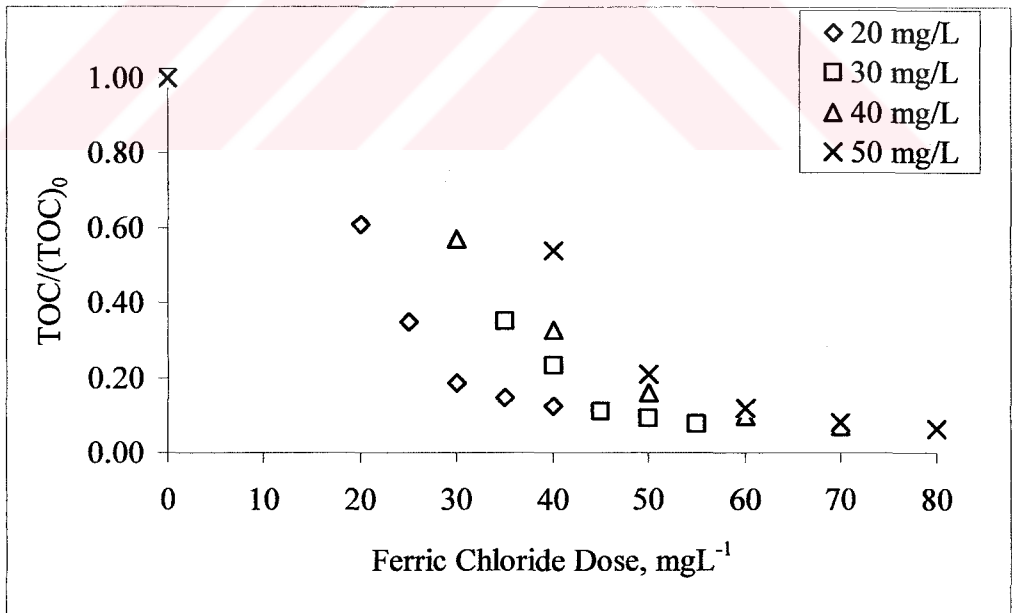


Figure 4.8 Comparison of the coagulation profiles based on TOC for untreated humic acid.

4.2.2. Coagulation Profiles for Treated Humic Acid with Ferric Chloride

In this study, ozonation, photocatalytic, and coagulation experiments were carried out in order to examine the coagulation properties of humic acid with ferric chloride. Experimental results for comparison of treated humic acid solutions with ferric chloride coagulation presented as UV_{254} and $Color_{436}$ in Figure 4.9 and Figure 4.10, respectively.

4.2.2.1. Coagulation Profiles for Ozonated Humic Acid with Ferric Chloride

In order to evaluate affect of preozonation on coagulation properties of humic acid, 50 mgL^{-1} humic acid was ozonated. Then, coagulation experiments were carried out according to Materials and Methods section. $Color_{436}$ and UV_{254} values were recorded.

Concentrations of applied ferric chloride dosages were 40 mgL^{-1} , 50 mgL^{-1} , 60 mgL^{-1} , 70 mgL^{-1} , 80 mgL^{-1} . Increasing the coagulant dose led to an increasing trend in UV_{254} and $Color_{436}$ removals up to the application of 60 mgL^{-1} ferric chloride dose. The optimum ferric chloride dosage was 60 mgL^{-1} . The percentages of UV_{254} and $Color_{436}$ removals were 77 and 85 per cent for the optimum ferric chloride dosage, respectively. After the addition of 60 mgL^{-1} ferric chloride, removal percentages of the parameters did not increase.

4.2.2.2. Coagulation Profiles for Photocatalytically Treated Humic Acid with Ferric Chloride

In order to investigate the effect of photocatalytic degradation on the coagulation properties of humic acid, 50 per cent degraded in terms of $Color_{436}$ humic acid was used. After photocatalytic experiments coagulation experiment were performed according to Materials and Methods section.

Applied ferric chloride dosages were 40 mgL^{-1} , 50 mgL^{-1} , 60 mgL^{-1} , 70 mgL^{-1} , 80 mgL^{-1} . Increasing the coagulant dose led to an increase in UV_{254} and $Color_{436}$ removals. The removal percentages of UV_{254} and $Color_{436}$ rapidly increased after 40 mgL^{-1} ferric chloride dose and reached an optimum dose of 60 mgL^{-1} . Nevertheless, after optimum dose, there were the same removal percentages of UV_{254} and $Color_{436}$. The

percentage removal of UV_{254} and $Color_{436}$ were 85 and 91 per cent for optimum ferric chloride dosage.

4.2.2.3. Coagulation Profiles for Sequentially Treated Humic Acid with Ferric Chloride

In order to evaluate the effect of sequential oxidation on the coagulation properties of humic acid, 50 mgL^{-1} humic acid solutions were 50 per cent treated by ozonation in terms of $Color_{436}$. Then humic acid solutions were 50 per cent treated photocatalytically in terms of $Color_{436}$. Then, coagulation experiments were carried out according to the Materials and Methods section.

Concentrations of applied ferric chloride dosages were 40 mgL^{-1} , 50 mgL^{-1} , 60 mgL^{-1} , 70 mgL^{-1} , 80 mgL^{-1} . Increasing the coagulant dosage led to an increase in UV_{254} and $Color_{436}$ removals. Optimum ferric chloride dosage was 70 mgL^{-1} and the removal percentages of UV_{254} and $Color_{436}$ was 74 and 79 per cent for optimum ferric chloride dosage. Further additions of ferric chloride did not result in improved removal efficiencies of the parameters.

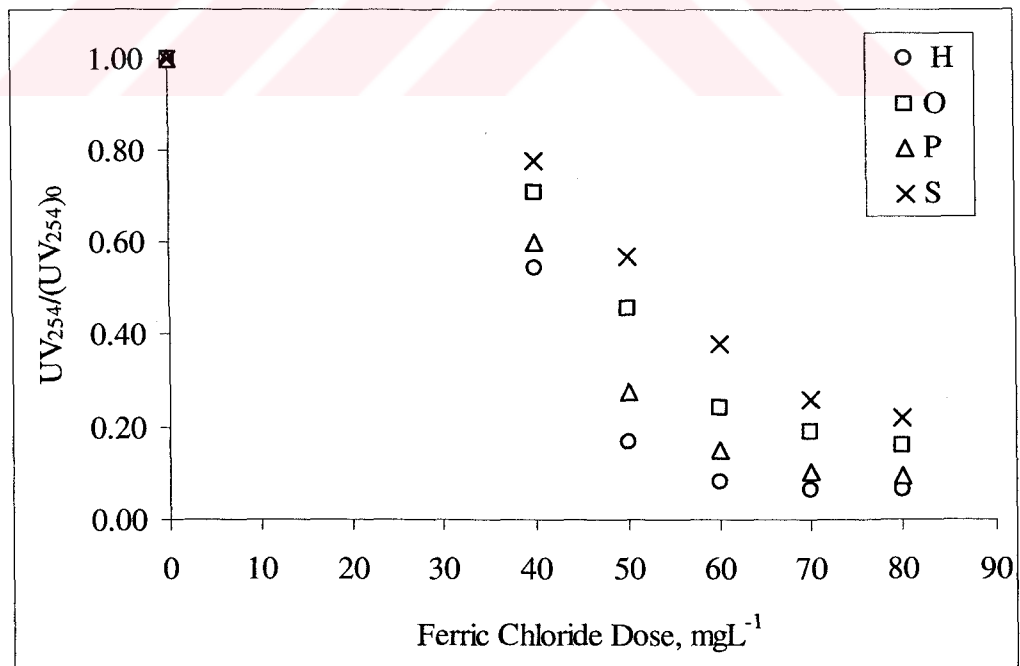


Figure 4.9 Comparison of the coagulation profiles based on UV_{254} for untreated and treated humic acid.

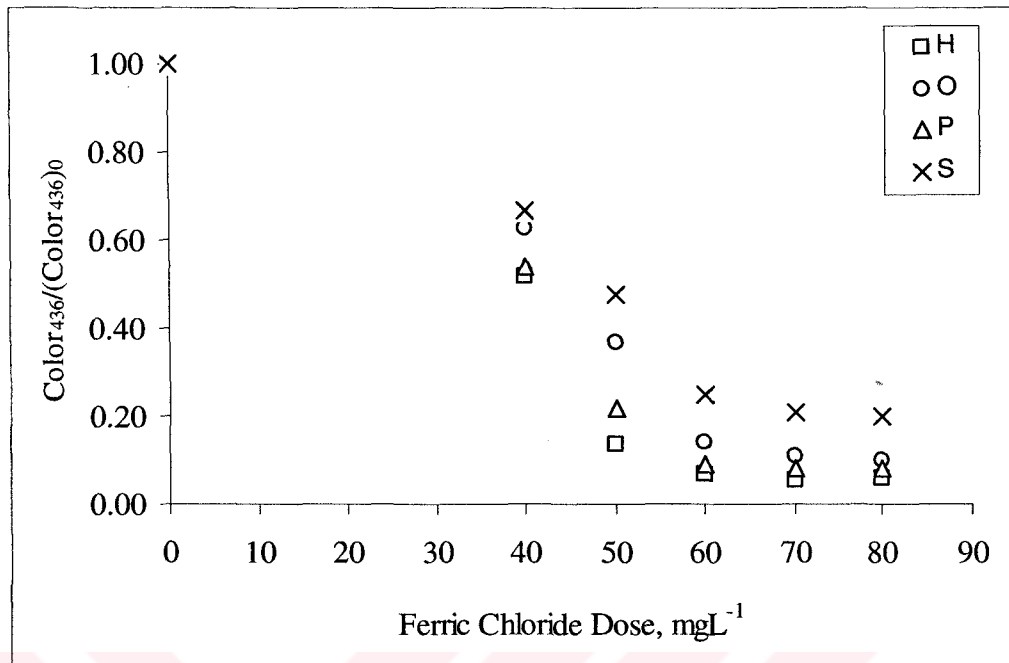


Figure 4.10 Comparison of the coagulation profiles based on Color_{436} for untreated and treated humic acid.

4.3. Coagulation of Humic Acid with Combination of Alum and Polymer

4.3.1. Coagulation of Untreated Humic Acid with Combinations of Alum and Anionic Polymer

In order to investigate the coagulation properties of humic acid (50 mgL^{-1}), coagulation experiments were carried out in the presence of 30 mgL^{-1} , 20 mgL^{-1} , 10 mgL^{-1} alum and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color_{436} and UV_{254} measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL^{-1} for 50 mgL^{-1} humic acid. Therefore, in the combined coagulation experiments, alum dosages were taken in the range of $30 \text{ mgL}^{-1} - 10 \text{ mgL}^{-1}$ to determine the effect of anionic polymer on the coagulation properties of untreated humic acid. The related coagulation profiles are presented in the following Figures 4.11, Figure 4.12 and, Figure 4.13.

In the presence 30 mgL⁻¹ alum, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were reported as 88, 96, and 86 per cent, respectively. When 30 mgL⁻¹ alum used with 0.5 mgL⁻¹ anionic polymer, a slight enhancement in the removal efficiencies were observed as 94, 98, and 91 per cent in UV₂₅₄, Color₄₃₆ and TOC, respectively. Therefore, alum dose was reduced to 20 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, removal percentages of UV₂₅₄, Color₄₃₆, and TOC were found to be 83, 89, and 81 per cent, respectively. When using only 20 mgL⁻¹ alum, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were obtained 71, 85, and 69 per cent, respectively. When using 10 mgL⁻¹ alum with 1.5 mgL⁻¹ anionic polymer, removal percentages of UV₂₅₄, Color₄₃₆, and TOC were increased to 57, 61 and 59 per cent, respectively. When 10 mgL⁻¹ alum were applied alone, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were found to be 48, 58, and 46 per cent, respectively. As a result, using anionic polymer with alum led to an increase the removal percentages of UV₂₅₄, Color₄₃₆, and TOC. Applied anionic polymer doses combining with alum were 0.5 mgL⁻¹ for 30 mgL⁻¹ alum dose, 1.0 mgL⁻¹ for 20 mgL⁻¹ alum dose, and 1.5 mgL⁻¹ for 10 mgL⁻¹ alum dose.

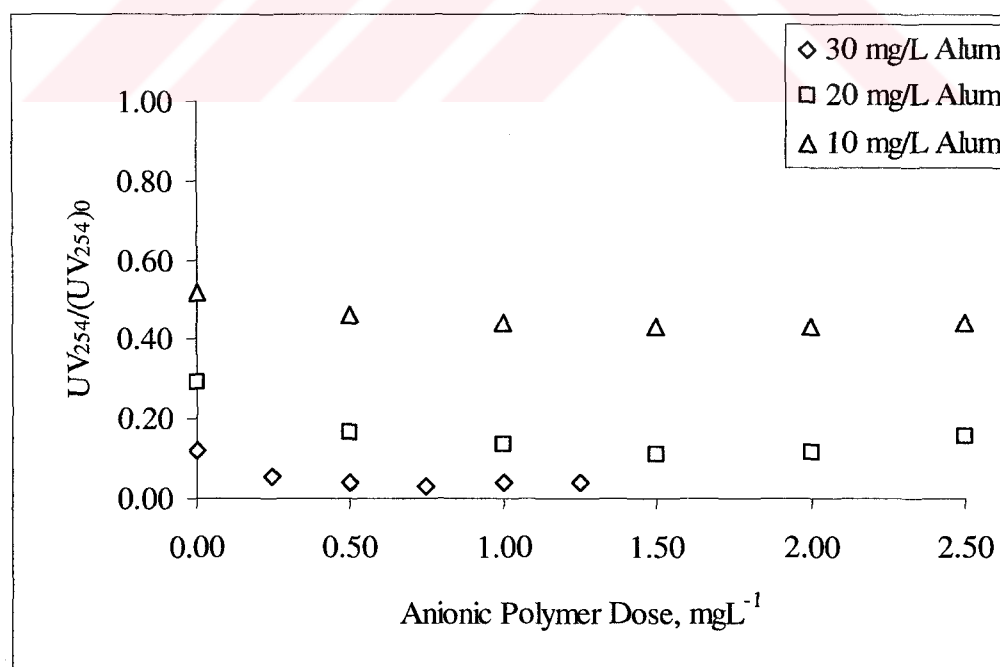


Figure 4.11 UV₂₅₄ functions of anionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

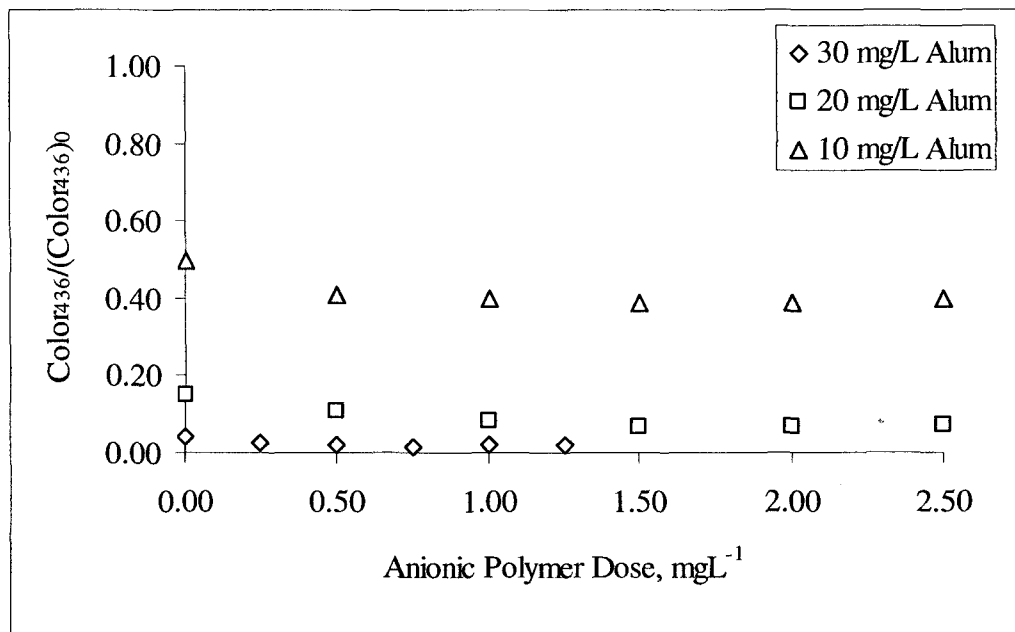


Figure 4.12 Color_{436} functions of anionic polymer dosage for 50 mgL^{-1} untreated humic acid.

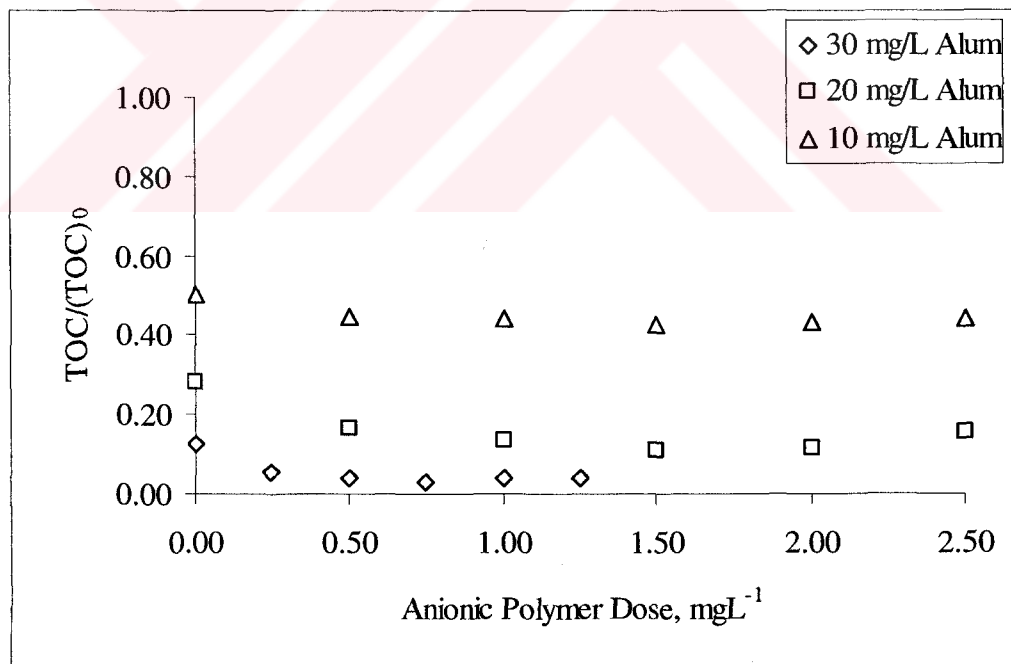


Figure 4.13 TOC functions of anionic polymer dosage for 50 mgL^{-1} untreated humic acid.

4.3.2. Coagulation of Treated Humic Acid with Combinations of Alum and Anionic Polymer

4.3.2.1. Coagulation of Ozonated Humic Acid with Combinations of Alum and Anionic Polymer

In order to evaluate the coagulation properties of ozonated humic acid solution, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozonation. Then coagulation experiments were carried out in the presence of 30 mgL⁻¹, 20 mgL⁻¹, 10 mgL⁻¹ alum and varying doses of anionic polymer. Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL⁻¹ for ozonated humic acid as given in Figure 4.4 and Figure 4.5 at Section 4.1. Therefore, alum dosages were taken in the range of 30 mgL⁻¹ – 10 mgL⁻¹ to determine the effect of anionic polymer on the coagulation properties of ozonated humic acid in the combined coagulation experiments. The related coagulation profiles are presented in the following Figure 4.14 and Figure 4.15.

The removal percentages of UV₂₅₄ and Color₄₃₆ were reported as 73 per cent and 84 per cent, respectively in the presence 30 mgL⁻¹ alum. When 30 mgL⁻¹ alum used with 0.5 mgL⁻¹ anionic polymer, enhancement in the removal efficiencies were observed as 84 per cent and 94 per cent in UV₂₅₄ and Color₄₃₆ respectively. Therefore, when alum dose was reduced to 20 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 74 per cent and 83 per cent, respectively. When using only 20 mgL⁻¹ alum, the removal percentages of UV₂₅₄ and Color₄₃₆ were obtained as 68 and 77 per cent respectively. When using 10 mgL⁻¹ alum with 1.5 mgL⁻¹ anionic polymer, the removal percentages of UV₂₅₄ and Color₄₃₆ were increased to 45 and 50 per cent, respectively. However, when 10 mgL⁻¹ alum were applied, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 33 and 43 per cent, respectively. As a result, using anionic polymer with alum led to an increase in the removal percentages of UV₂₅₄ and Color₄₃₆ for all alum dosages. Used anionic polymer dosages combining with alum were 0.5 mgL⁻¹ for 30 mgL⁻¹ alum dose, 1.0 mgL⁻¹ for 20 mgL⁻¹ alum dose, and 1.5 mgL⁻¹ for 10 mgL⁻¹ alum dose.

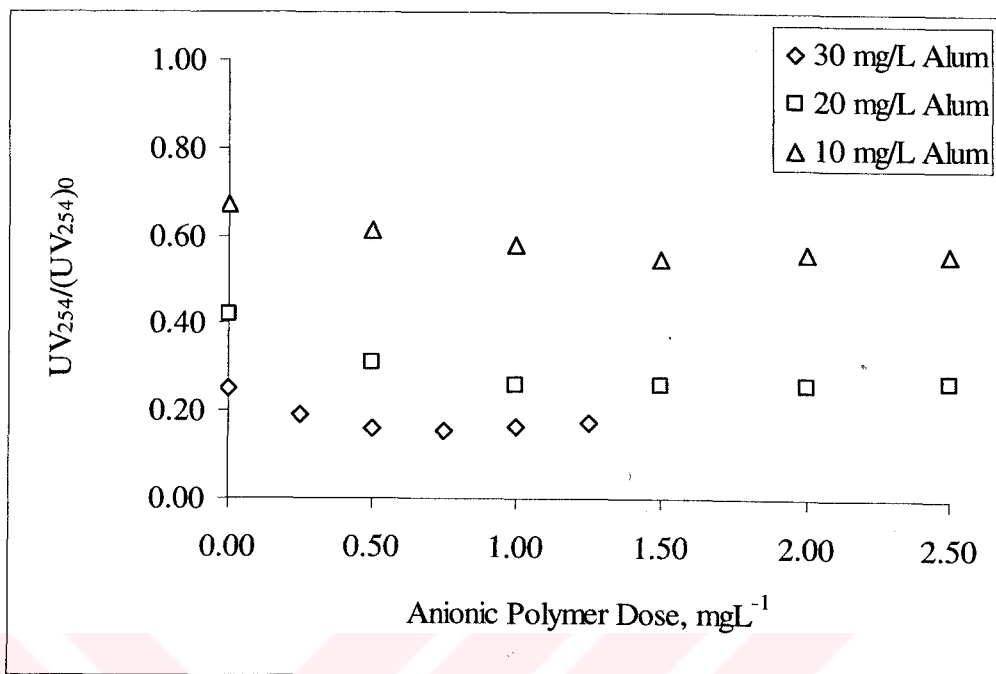


Figure 4.14 UV₂₅₄ functions of anionic polymer dose for ozonated humic acid.

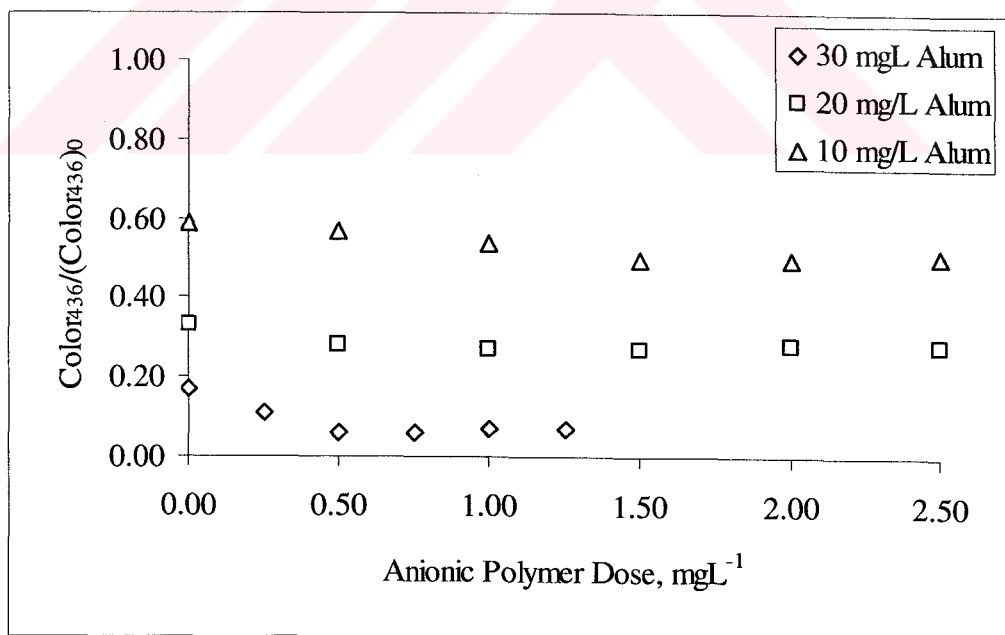


Figure 4.15 Color₄₃₆ functions of anionic polymer dose for ozonated humic acid.

4.3.2.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Alum and Anionic Polymer

In order to evaluate the coagulation properties of photocatalytically oxidized humic acid solution, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by photocatalytically. Then coagulation experiments were carried out in the presence of 30 mgL⁻¹, 20 mgL⁻¹, 10 mgL⁻¹ alum and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods Section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL⁻¹ for photocatalytically oxidized humic acid as given in Figure 4.4 and Figure 4.5 at Section 4.1. Therefore, in the combined coagulation experiments, alum dosages were taken in the range of 30 mgL⁻¹ – 10 mgL⁻¹ to determine the effect of anionic polymer on the coagulation experiment of photocatalytically oxidized humic acid. The related coagulation profiles are presented in the following Figure 4.16 and Figure 4.17.

The removal percentages of UV₂₅₄ and Color₄₃₆ were obtained as 86 and 92 per cent by 30 mgL⁻¹ alum, respectively. When 30 mgL⁻¹ alum were used with 0.5 mgL⁻¹ anionic polymer, the removal efficiencies of UV₂₅₄ and Color₄₃₆ were increased to 91 and 97 per cent, respectively. Therefore, when alum dose was reduced to 20 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 81 per cent and 87 per cent, respectively. When 20 mgL⁻¹ alum were applied alone, the removal percentages of UV₂₅₄ and Color₄₃₆ were obtained 67 and 79 per cent, respectively. When using 10 mgL⁻¹ alum with 1.5 mgL⁻¹ anionic polymer, removal percentages of UV₂₅₄ and Color₄₃₆ were increased to 47 per cent and 53 per cent, respectively. However, when 10 mgL⁻¹ alum were applied alone, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 38 and 48 per cent, respectively. As a result, using anionic polymer with alum led to an increase in the removal percentages of UV₂₅₄ and Color₄₃₆ for photocatalytically oxidized humic acid solution. In addition, applying anionic polymer combining with alum led to decrease of used alum doses. Applied anionic polymer dosages combining with alum were 0.5 mgL⁻¹ for 30 mgL⁻¹ alum dose, 1.0 mgL⁻¹ for 20 mgL⁻¹ alum dose, and 1.5 mgL⁻¹ for 10 mgL⁻¹ alum dose.

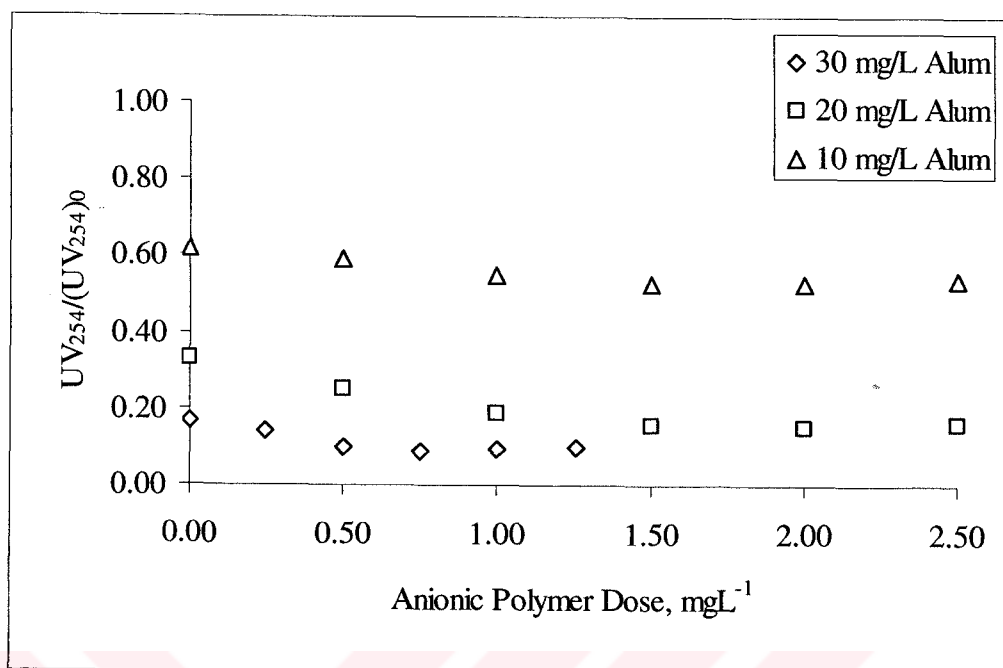


Figure 4.16 UV_{254} functions of anionic polymer dosage for photocatalytically treated humic acid.

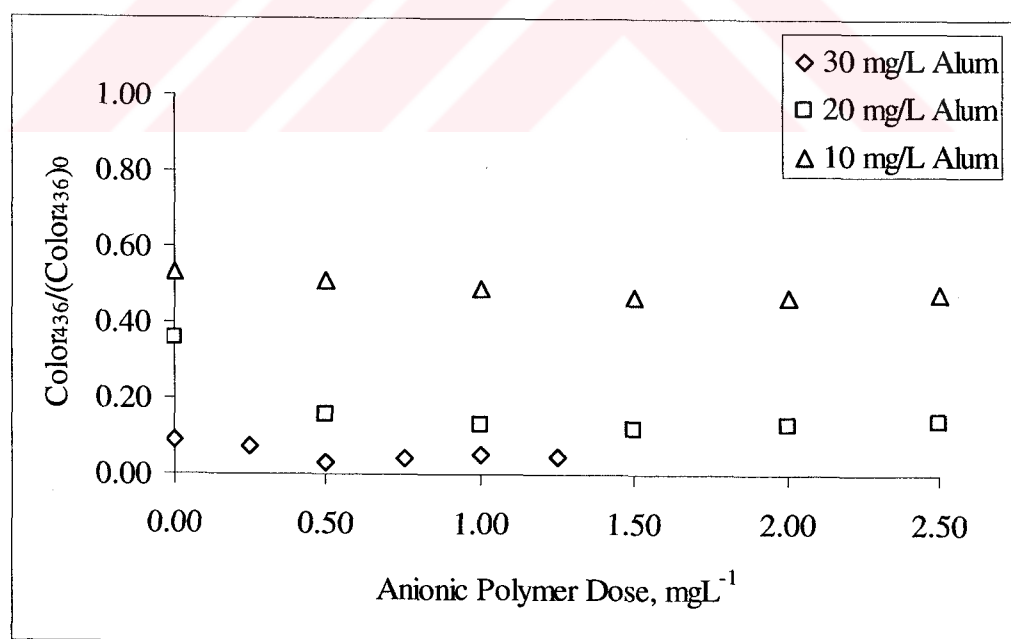


Figure 4.17 $Color_{436}$ functions of anionic polymer dosage for photocatalytically treated humic acid.

4.3.2.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Alum and Anionic Polymer

In order to investigate the coagulation properties of sequentially oxidized humic acid, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozone. Following humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by photocatalytically. Then coagulation experiments were carried out in the presence of 30 mgL⁻¹, 20 mgL⁻¹, 10 mgL⁻¹ alum, and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL⁻¹ for sequentially treated humic acid as given in Figure 4.4 and Figure 4.5 at Section 4.1. Therefore, in the combined coagulation experiments, alum dosages were taken in the range of 30 mgL⁻¹ – 10 mgL⁻¹ to determine the effect of anionic polymer on the coagulation experiment of sequentially oxidized humic acid. The related coagulation profiles are presented in the following Figure 4.18 and Figure 4.19.

In the presence of 30 mgL⁻¹ alum, the removal percentages of UV₂₅₄ and Color₄₃₆ were reported as 64 and 74 per cent, respectively. When 30 mgL⁻¹ alum used with 0.5 mgL⁻¹ anionic polymer, a slight enhancement in the removal efficiencies were observed as 78 per cent in UV₂₅₄ and 86 per cent in Color₄₃₆. Therefore, alum dose was reduced to 20 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, the removal percentage of UV₂₅₄ was found to be 61 per cent and Color₄₃₆ was found to be 70 per cent. When using only 20 mgL⁻¹ alum, the removal percentages of UV₂₅₄ and Color₄₃₆ were obtained as 53 per cent and 61 per cent, respectively. When using 10 mgL⁻¹ alum with 1.5 mgL⁻¹ anionic polymer the removal percentage of UV₂₅₄ and Color₄₃₆ were increased to 36 and 44 per cent, respectively. However, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 29 and 37 per cent, respectively for the application of 10 mgL⁻¹ alum. A result of these experiments, using anionic polymer with alum led to an increase in the removal percentages of UV₂₅₄ and Color₄₃₆ for sequentially oxidized humic acid. Used anionic polymer combined with alum 0.5 mgL⁻¹ for 30 mgL⁻¹ alum dose, 1.0 mgL⁻¹ for 20 mgL⁻¹ alum dose, and 1.5 mgL⁻¹ for 10 mgL⁻¹ alum dose were obtained by coagulation.

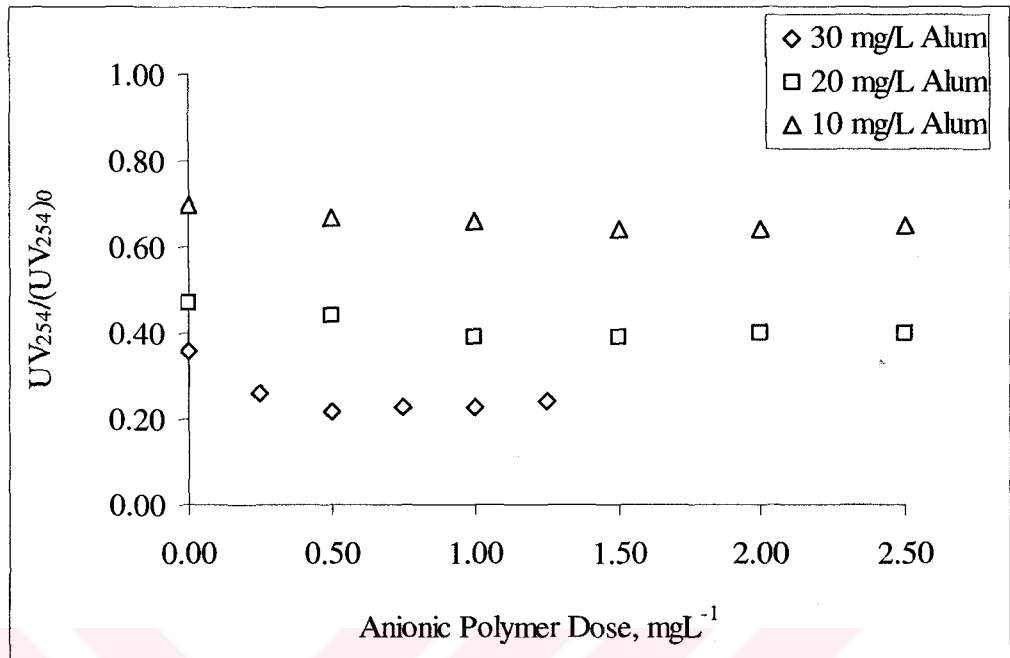


Figure 4.18 UV₂₅₄ functions of anionic polymer dosage for sequentially oxidized humic acid.

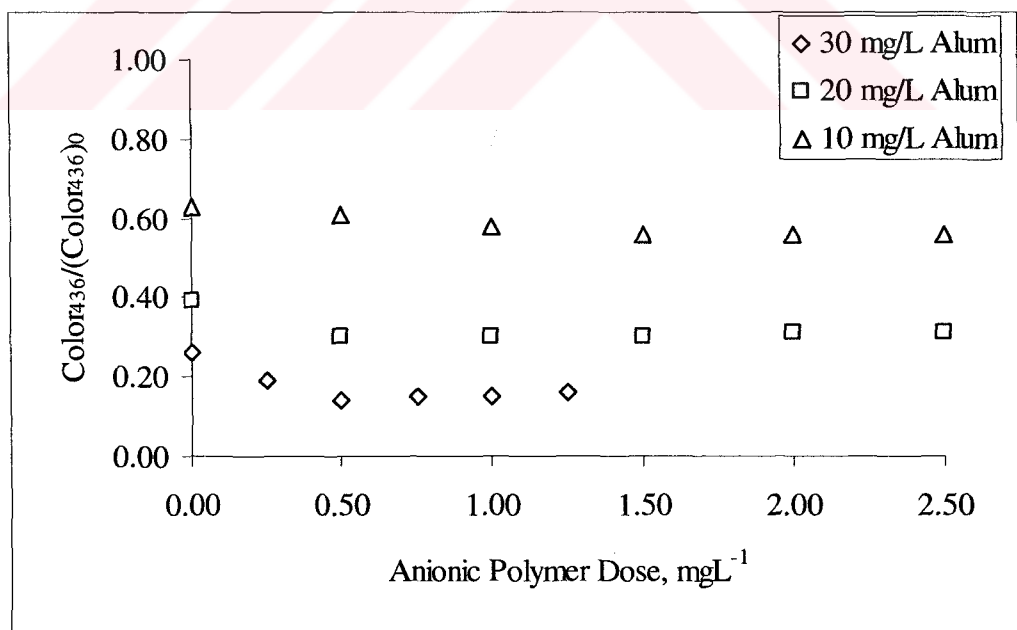


Figure 4.19 Color₄₃₆ functions of anionic polymer dosage for sequentially oxidized humic acid.

4.3.3. Coagulation of Untreated Humic Acid with Combinations of Alum and Nonionic Polymer

In order to investigate the coagulation properties of untreated humic acid (50 mgL^{-1}) solution, coagulation experiments were carried out in the presence of 30 mgL^{-1} , 20 mgL^{-1} , 10 mgL^{-1} alum and varying doses of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color_{436} and UV_{254} measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL^{-1} for 50 mgL^{-1} humic acid as given in Figure 4.4 and 4.5 at Section 4.1. Therefore, alum dosages were taken in the range of $30 \text{ mgL}^{-1} - 10 \text{ mgL}^{-1}$ to determine the effect of anionic polymer on the coagulation experiment of untreated humic acid, in the combined coagulation experiments. The related coagulation profiles for whole nonionic polymer doses are presented in the following Figure 4.20, Figure 4.21 and, Figure 4.22 as UV_{254} , Color_{436} and TOC, respectively.

In the presence of 30 mgL^{-1} alum, the removal percentages of UV_{254} , Color_{436} , and TOC were reported as 88, 96, and 86 per cent, respectively. When 30 mgL^{-1} alum used with 0.4 mgL^{-1} nonionic polymer, a slight enhancement in the removal efficiencies were observed as 98, 99, and 98 per cent in UV_{254} , Color_{436} and TOC, respectively. Therefore, alum dose was reduced to 20 mgL^{-1} and nonionic polymer dose was increased to 0.8 mgL^{-1} , the removal percentages of UV_{254} , Color_{436} , and TOC were found to be 87, 95, and 86 per cent, respectively. When applied only 20 mgL^{-1} alum, the removal percentages of UV_{254} , Color , and TOC were obtained 71 per cent, 85 per cent, and 69 per cent, respectively. When using 10 mgL^{-1} alum with 1.2 mgL^{-1} nonionic polymer, the removal percentages of UV_{254} , Color_{436} , and TOC were increased to 57, 62, and 55 per cent, respectively. However, application of 10 mgL^{-1} alum alone led to an increase of the removal percentages of UV_{254} , Color_{436} , and TOC these were found to be 48, 58, and 46 per cent, respectively. As a result, using nonionic polymer with alum led to an increase in the removal percentages of UV_{254} , Color_{436} , and TOC for untreated humic acid solution. Used nonionic polymer dosages combining with alum were 0.2 mgL^{-1} for 30 mgL^{-1} alum dose, 0.8 mgL^{-1} for 20 mgL^{-1} alum dose, and 1.2 mgL^{-1} for 10 mgL^{-1} alum dose.

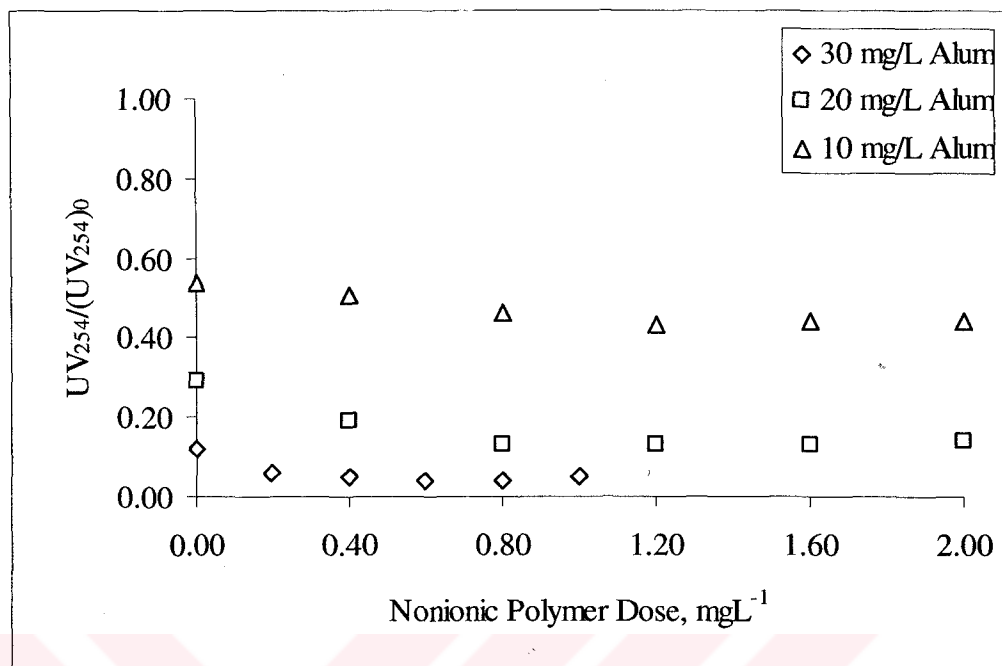


Figure 4.20 UV₂₅₄ functions of nonionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

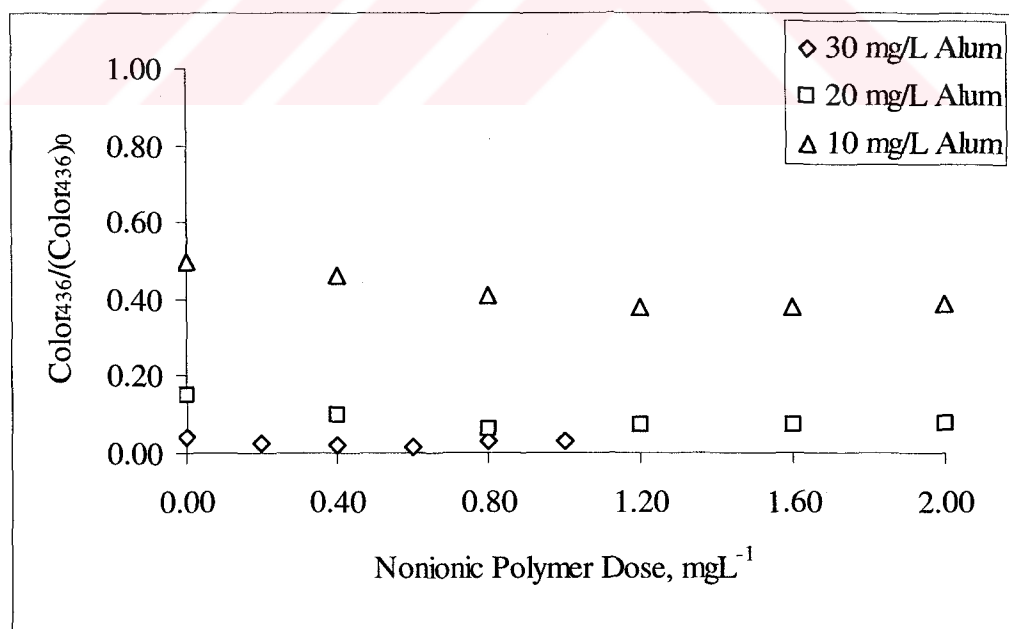


Figure 4.21 Color₄₃₆ functions of nonionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

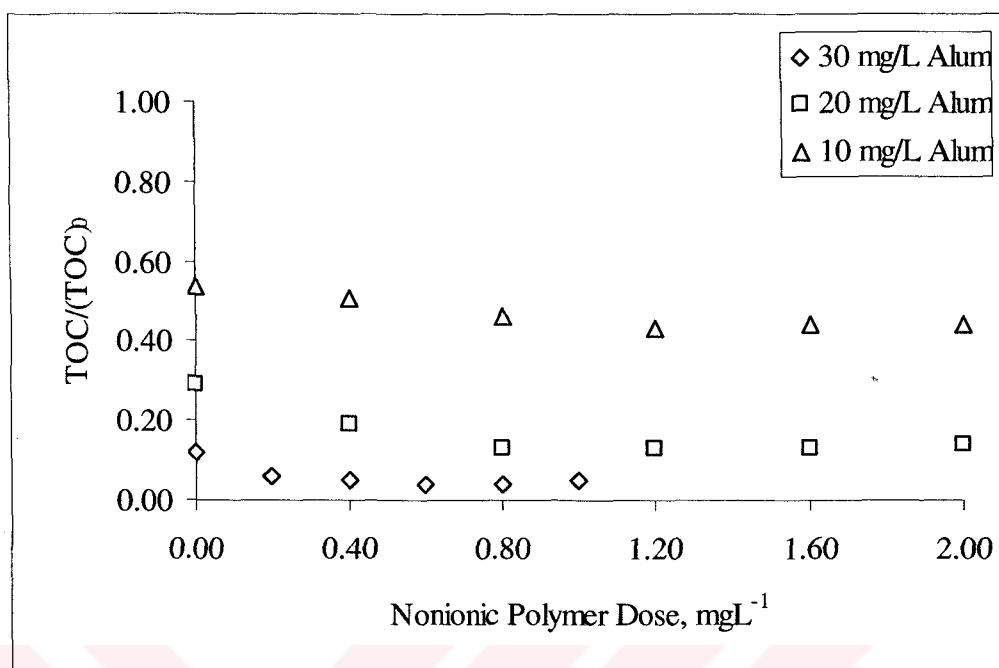


Figure 4.22 TOC functions of nonionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

4.3.4. Coagulation of Treated Humic Acid with Combinations of Alum and Nonionic Polymer

4.3.4.1. Coagulation of Ozonated Humic Acid with Combinations of Alum and Nonionic Polymer

In order to investigate the coagulation properties of ozonated humic acid, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozonation. Then coagulation experiments were carried out in the presence of 30 mgL⁻¹, 20 mgL⁻¹, 10 mgL⁻¹ alum and varying dosages of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL⁻¹ for 50 ozonated humic acid as given in Figures 4.4 and 4.5. Therefore, in the combined coagulation experiments, alum dosages were taken in the range of 30 mgL⁻¹ – 10 mgL⁻¹ to determine the effect of nonionic polymer on the coagulation experiment of sequentially

oxidized humic acid. The related coagulation profiles are presented in the following Figure 4.23 and Figure 4.24.

The removal percentages of UV_{254} and $Color_{436}$ were reported as 73 and 83 per cent respectively in the presence 30 mgL^{-1} alum. When 30 mgL^{-1} alum used with 0.6 mgL^{-1} nonionic polymer, enhancement in the removal efficiencies were observed as 88 and 93 per cent in UV_{254} and $Color_{436}$, respectively. Therefore, when alum dose was reduced to 20 mgL^{-1} and the nonionic polymer dose was increased to 0.8 mgL^{-1} , the removal percentages of UV_{254} and $Color_{436}$ were found to be 78 and 86 per cent, respectively. When 20 mgL^{-1} alum were applied alone, the removal percentages of UV_{254} and $Color_{436}$ were obtained as 68 and 77 per cent, respectively. When using 10 mgL^{-1} alum with 1.2 mgL^{-1} nonionic polymer, the removal percentages of UV_{254} and $Color_{436}$ were increased to 40 and 49 per cent, respectively. However, when 10 mgL^{-1} alum were applied alone, the removal percentages of UV_{254} and $Color_{436}$ were found to be 33 and 41 per cent, respectively. As a result, using nonionic polymer with alum led to an increase in the removal percentages of UV_{254} and $Color_{436}$ for ozonated humic acid solutions. Used nonionic polymer dosages combining with alum were 0.4 mgL^{-1} for 30 mgL^{-1} alum dose, 0.8 mgL^{-1} for 20 mgL^{-1} alum dose, and 1.2 mgL^{-1} for 10 mgL^{-1} alum dose.

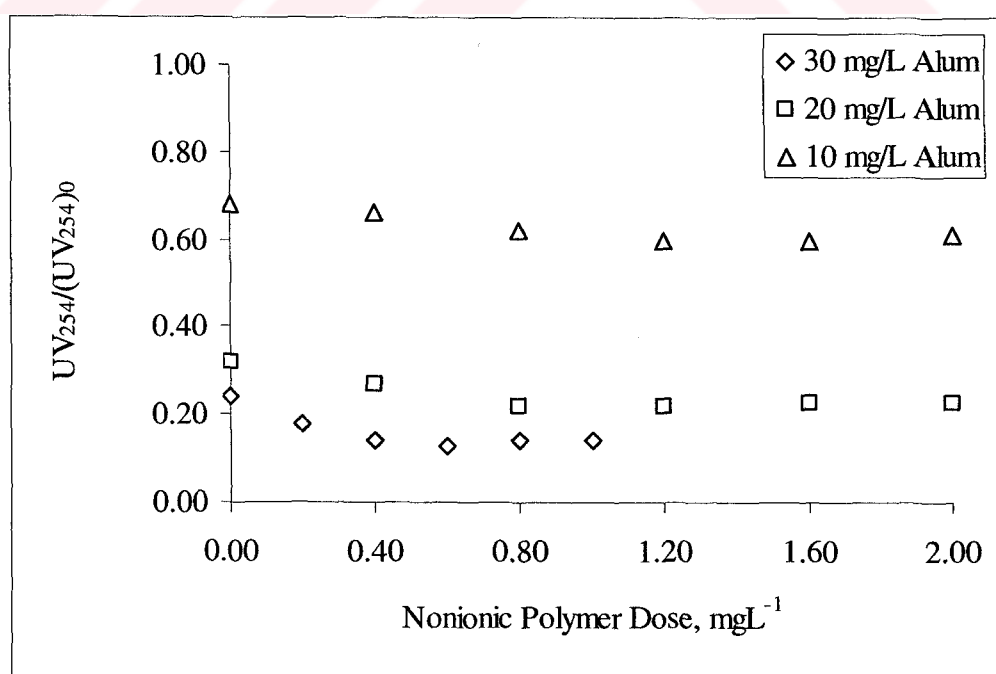


Figure 4.23 UV_{254} functions of nonionic polymer dosage for ozonated humic acid.

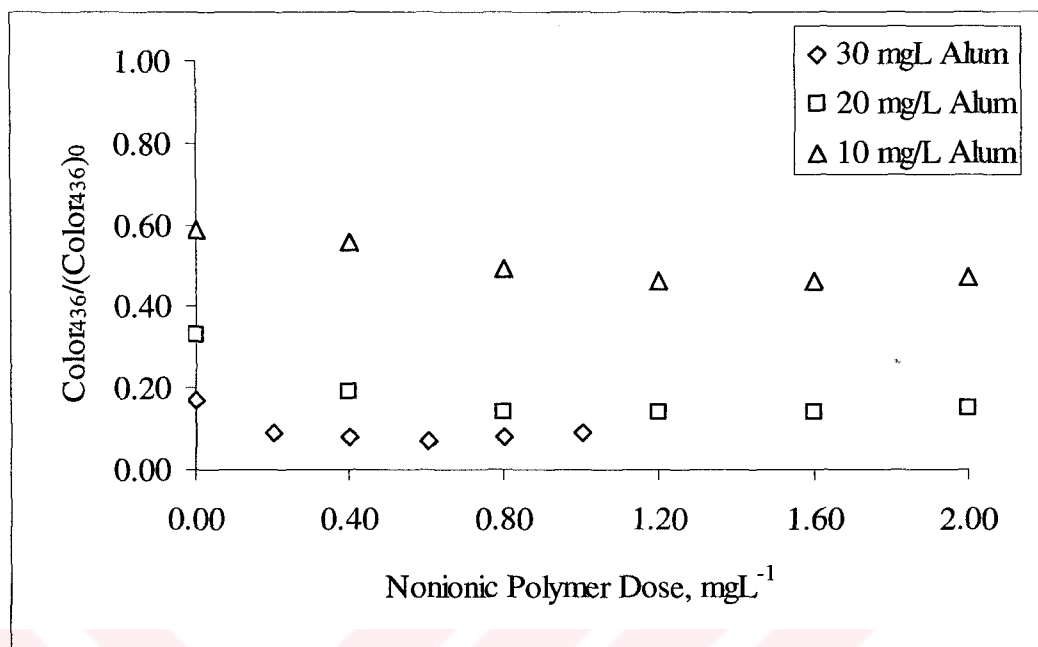


Figure 4.24 Color₄₃₆ functions of nonionic polymer dosage for ozonated humic acid.

4.3.4.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Alum and Nonionic Polymer

In order to evaluate the coagulation properties of photocatalytically treated humic acid solution, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by photocatalytically. Then coagulation experiments were carried out in the presence of 30 mgL⁻¹, 20 mgL⁻¹, 10 mgL⁻¹ alum and combining with varying doses of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods Section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the alum addition. The optimum alum doses was found to be 30 mgL⁻¹ for photocatalytically treated humic acid in Figure 4.4 and Figure 4.5. Therefore, alum doses were taken in the range of 30 mgL⁻¹ – 10 mgL⁻¹ to determine the effects of anionic polymer on the coagulation experiment of photocatalytically oxidized humic acid in the combined coagulation experiments. The related coagulation profiles are presented in the following Figure 4.25 and Figure 4.26 as UV₂₅₄ and Color₄₃₆.

In the presence of 30 mgL^{-1} alum, the removal percentages of UV_{254} and Color_{436} were obtained as 86 and 92 per cent, respectively. When 30 mgL^{-1} alum was used with 0.6 mgL^{-1} nonionic polymer, the removal efficiencies of UV_{254} and Color_{436} were increased to 93 and 96 per cent, respectively. When alum dose was reduced to 20 mgL^{-1} and the nonionic polymer dose was increased to 0.8 mgL^{-1} , the removal percentages of UV_{254} and Color_{436} were found to be 90 and 92 per cent, respectively. When using only 20 mgL^{-1} alum, the removal percentages of UV_{254} and Color_{436} were obtained as 67 and 79 per cent, respectively. When using 10 mgL^{-1} alum with 1.2 mgL^{-1} nonionic polymer, the removal percentages of UV_{254} and Color_{436} were increased to 46 and 54 per cent, respectively. However, when 10 mgL^{-1} alum were applied alone, the removal percentages of UV_{254} and Color_{436} were found to be 38 and 47 per cent, respectively. As a result, using nonionic polymer with alum led to an increase of the removal percentages of UV_{254} and Color_{436} for photocatalytically oxidized humic acid solutions. Applied nonionic polymer dosages in the coagulation experiments of photocatalytically treated humic acid combining with alum were 0.4 mgL^{-1} for 30 mgL^{-1} alum dose, 0.8 mgL^{-1} for 20 mgL^{-1} alum dose, and 1.2 mgL^{-1} for 10 mgL^{-1} alum dose.

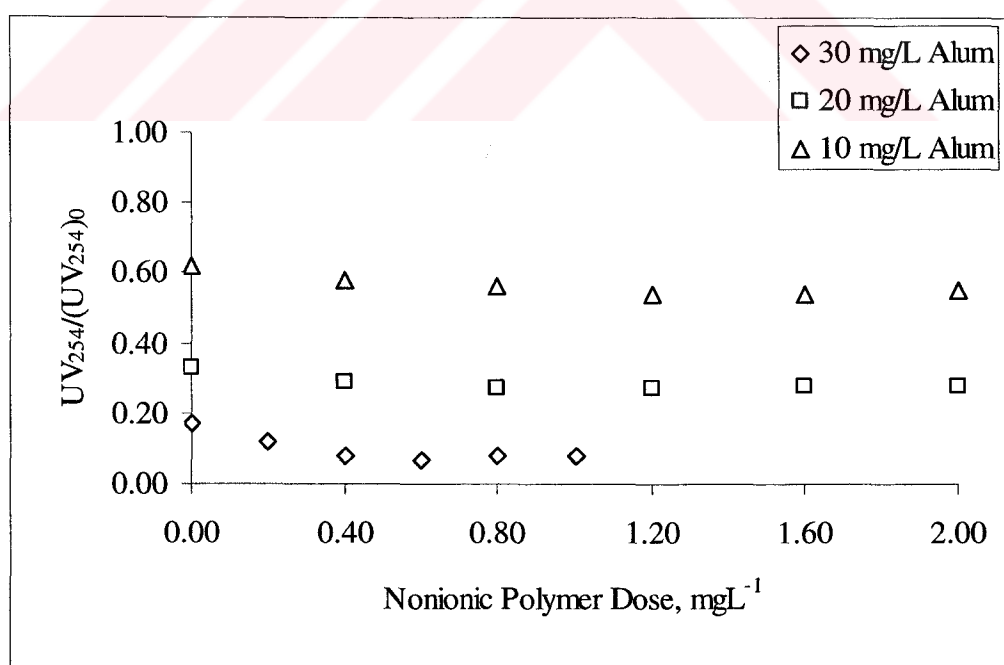


Figure 4.25 UV_{254} functions of nonionic polymer dosage for photocatalytically treated humic acid.

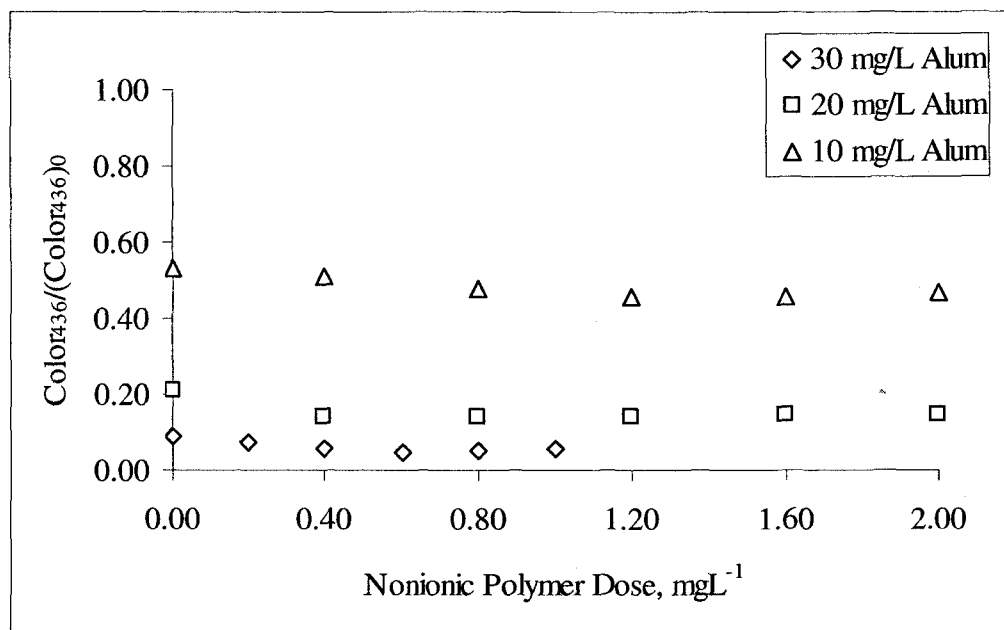


Figure 4.26 Color₄₃₆ functions of nonionic polymer dosage for photocatalytically treated humic acid.

4.3.4.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Alum and Nonionic Polymer

In order to investigate the coagulation properties of sequentially oxidized humic acid solution, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozonation. Following humic acid solutions were treated photocatalytically. Then coagulation experiments were carried out in the presence of 30 mgL⁻¹, 20 mgL⁻¹, 10 mgL⁻¹ alum and varying dosages of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the alum addition. The optimum alum dosage was found to be 30 mgL⁻¹ for sequentially treated humic acid as given in Figure 4.4 and Figure 4.5. Therefore, alum dosages were taken in the range of 30 mgL⁻¹ – 10 mgL⁻¹ to determine the effect of anionic polymer on the coagulation experiment of sequentially oxidized humic acid in the combined coagulation experiments. The related coagulation profiles are presented in the following Figure 4.27 and Figure 4.28.

In the presence of 30 mgL^{-1} alum, the removal percentages of UV_{254} and of Color_{436} were reported as 64 and 73 per cent, respectively. When 30 mgL^{-1} alum used with 0.4 mgL^{-1} nonionic polymer, a slight enhancement in the removal efficiencies were observed as 79 and 82 per cent in UV_{254} and Color_{436} , respectively. Therefore, alum dose was reduced to 20 mgL^{-1} and the nonionic polymer dose was increased to 0.8 mgL^{-1} , removal percentages of UV_{254} and Color_{436} were found to be 61 and 68 per cent, respectively. When 20 mgL^{-1} alum were used alone, the removal percentages of UV_{254} , Color_{436} , and TOC were obtained as 53 and 61 per cent, respectively. When using 10 mgL^{-1} alum with 1.2 mgL^{-1} nonionic polymer, removal percentages of UV_{254} and Color_{436} were increased to 37 and 42 per cent, respectively. However, the application of 10 mgL^{-1} alum alone led to an increase of the removal percentages of UV_{254} and Color_{436} these were found to be 29 and 37 per cent, respectively. As a result, using nonionic polymer with alum led to an increase in the removal percentages of UV_{254} , Color_{436} and TOC for sequentially oxidized humic acid solutions. Applied nonionic polymer doses in the coagulation experiments of sequentially oxidized humic acid combining with alum were 0.4 mgL^{-1} for 30 mgL^{-1} alum dose, 0.8 mgL^{-1} for 20 mgL^{-1} alum dose, and 1.2 mgL^{-1} for 10 mgL^{-1} alum dose.

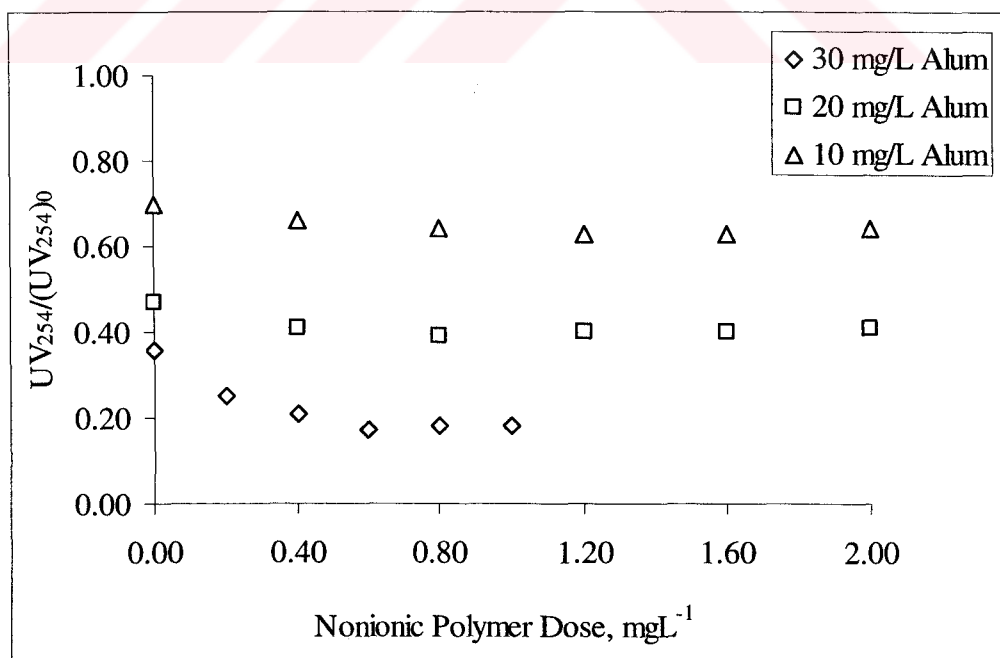


Figure 4.27 UV_{254} functions of nonionic polymer dosage for sequentially oxidized humic acid.

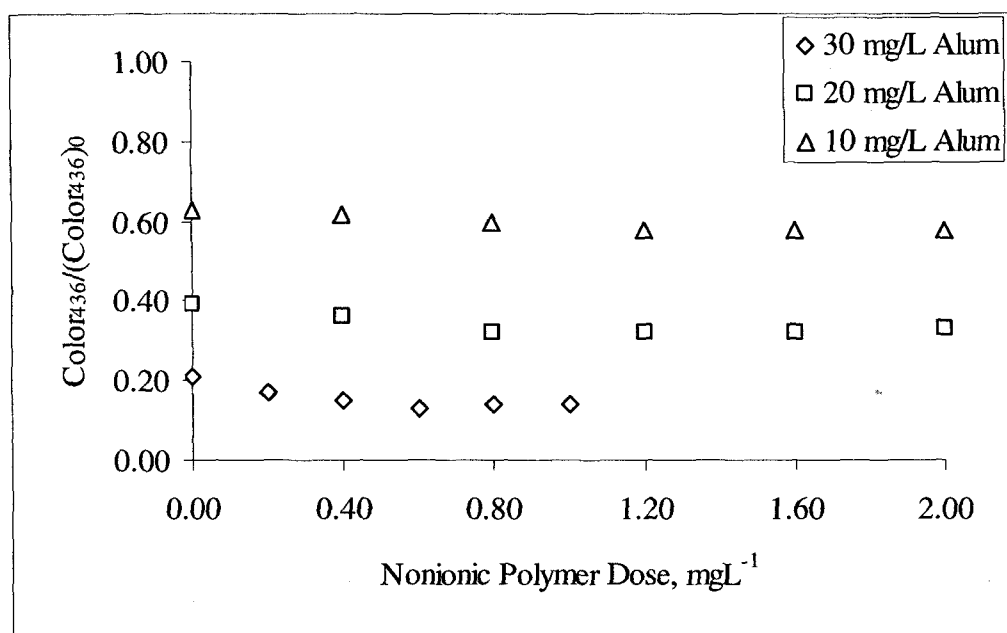


Figure 4.28 Color₄₃₆ functions of nonionic polymer dosage for sequentially oxidized humic acid.

4.4. Coagulation of Humic Acid with Combinations of Ferric Chloride and Polymer

4.4.1. Coagulation of Untreated Humic Acid with Combinations of Ferric chloride and Anionic Polymer

In order to investigate the coagulation properties of humic acid (50 mgL⁻¹), coagulation experiments were carried out in the presence of 60 mgL⁻¹, 50 mgL⁻¹, 40 mgL⁻¹ ferric chloride and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 60 mgL⁻¹ for 50 mgL⁻¹ humic acid as given in Figure 4.9, Figure 4.10, and Figure 4.11. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of 60 mgL⁻¹ – 40 mgL⁻¹. The related coagulation profiles are presented in the following Figure 4.29, Figure 4.30, and Figure 4.31.

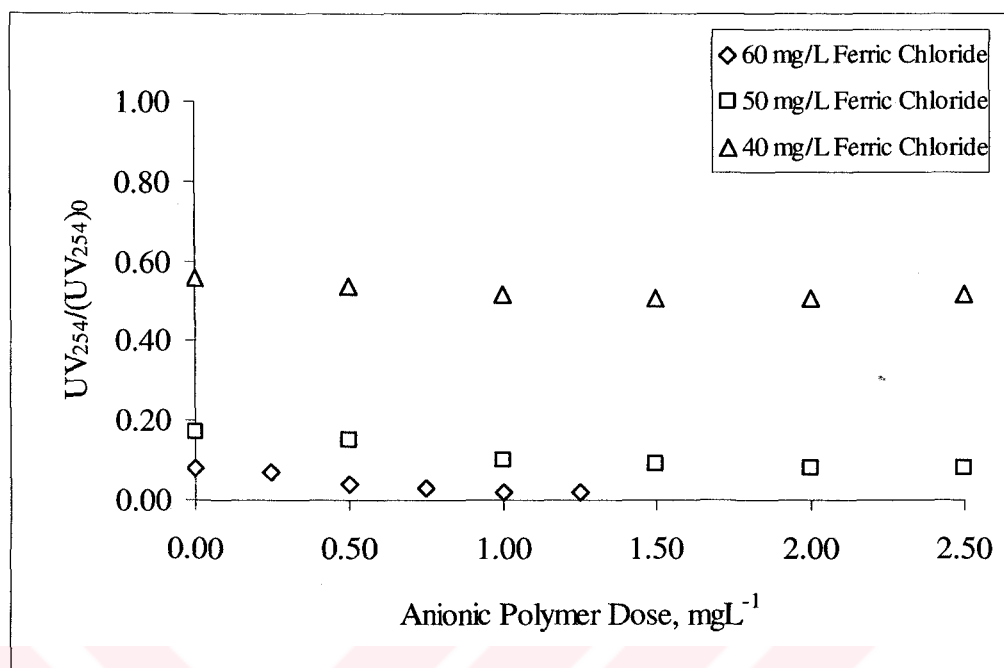


Figure 4.29 UV₂₅₄ functions of anionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

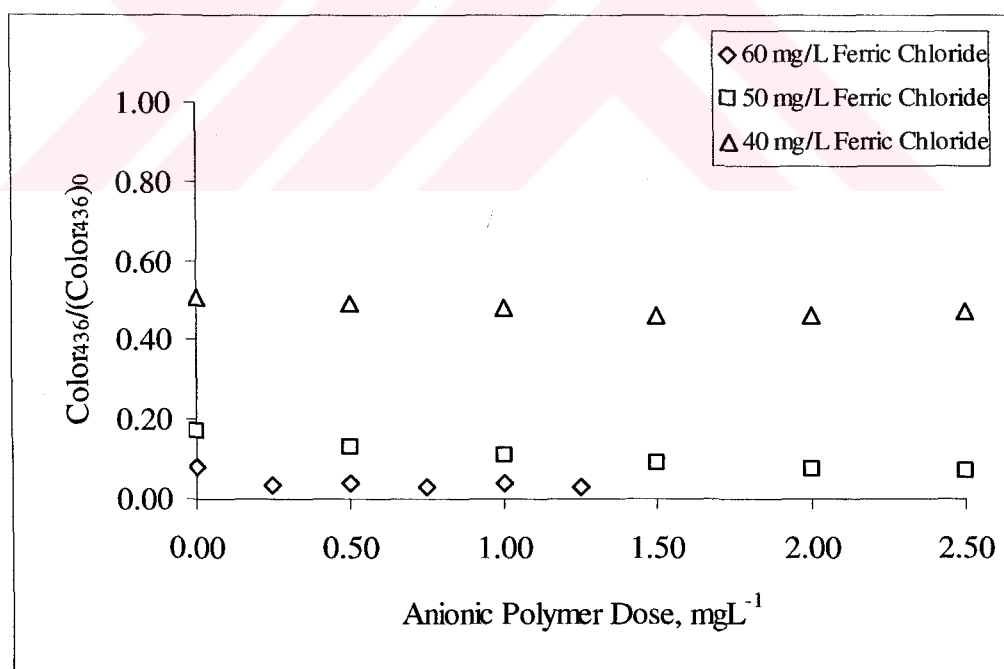


Figure 4.30 Color₄₃₆ functions of anionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

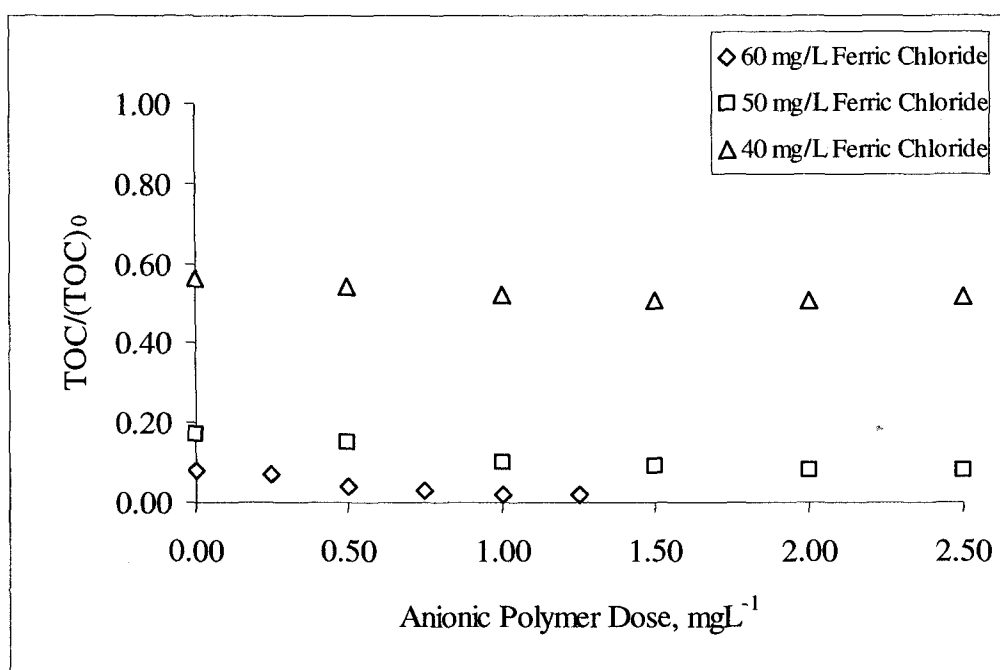


Figure 4.31 TOC functions of anionic polymer dosage for 50 mgL⁻¹ untreated humic acid.

In the presence of 60 mgL⁻¹ ferric chloride, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were reported as 92, 93, and, 88 per cent, respectively. When 60 mgL⁻¹ ferric chloride used with 0.25 mgL⁻¹ anionic polymer, a slight enhancement in the removal efficiencies were observed as 93, 96, and 91 per cent in UV₂₅₄, Color₄₃₆ and TOC, respectively. Therefore, ferric chloride dose was reduced to 50 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were found to be 90, 89, and 89 per cent, respectively. When 50 mgL⁻¹ ferric chloride were used alone, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were obtained 83, 86, and 77 per cent, respectively. When using 40 mgL⁻¹ ferric chloride with 1.5 mgL⁻¹ anionic polymer, the removal percentages of UV₂₅₄, Color₄₃₆, and TOC were increased to 49, 53 and 47 per cent, respectively. However, the application of 40 mgL⁻¹ ferric chloride alone led to an increase in the removal percentages of UV₂₅₄, Color₄₃₆, and TOC these were found to be 45, 49, and 37 per cent, respectively. As a result, using anionic polymer with ferric chloride led to an increase in the removal percentages of UV₂₅₄, Color₄₃₆, and TOC. Used anionic polymer dosages combining with ferric chloride were 0.25 mgL⁻¹ for 60 mgL⁻¹ ferric chloride dose, 1.0 mgL⁻¹ for 50 mgL⁻¹ ferric chloride dose, and 1.5 mgL⁻¹ for 40 mgL⁻¹ ferric chloride dose.

4.4.2. Coagulation of Treated Humic Acid with Combinations of Ferric Chloride and Anionic Polymer

4.4.2.1. Coagulation of Ozonated Humic Acid with Combinations of Ferric Chloride and Anionic Polymer

In order to investigate the coagulation properties of ozonated humic acid, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozone. Then coagulation experiments were carried out in the presence of 60 mgL⁻¹, 50 mgL⁻¹, 40 mgL⁻¹ ferric chloride and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 60 mgL⁻¹ for ozonated humic acid. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of 60 mgL⁻¹ – 40 mgL⁻¹. The related coagulation profiles are presented in the following Figure 4.32 and Figure 4.33.

The removal percentages of UV₂₅₄ and Color₄₃₆ were reported as 76 and 85 per cent, respectively in the presence 60 mgL⁻¹ ferric chloride. When 60 mgL⁻¹ ferric chloride used with 0.5 mgL⁻¹ anionic polymer, enhancement in the removal efficiencies were observed as 81 and 88 per cent in UV₂₅₄ and Color₄₃₆, respectively. Therefore, when ferric chloride dose was reduced to 50 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 70 and 76 per cent, respectively. When using only 50 mgL⁻¹ ferric chloride, the removal percentages of UV₂₅₄ and Color₄₃₆ were obtained as 54 and 63 per cent, respectively. However, using 40 mgL⁻¹ ferric chloride with 1.5 mgL⁻¹ anionic polymer, the removal percentages of UV₂₅₄ and Color₄₃₆ were increased to 41 and 46 per cent, respectively. However, when 40 mgL⁻¹ ferric chloride were applied alone, the removal percentages of UV₂₅₄ and Color were found to be 29 and 37 per cent, respectively. As a result, using anionic polymer with ferric chloride led to an increase the removal percentages of UV₂₅₄ and Color₄₃₆. Used anionic polymer dosages with ferric chloride were 0.5 mgL⁻¹ for 60 mgL⁻¹ ferric chloride dose, 1.0 mgL⁻¹ for 50 mgL⁻¹ ferric chloride dose, and 1.5 mgL⁻¹ for 40 mgL⁻¹ ferric chloride dose.

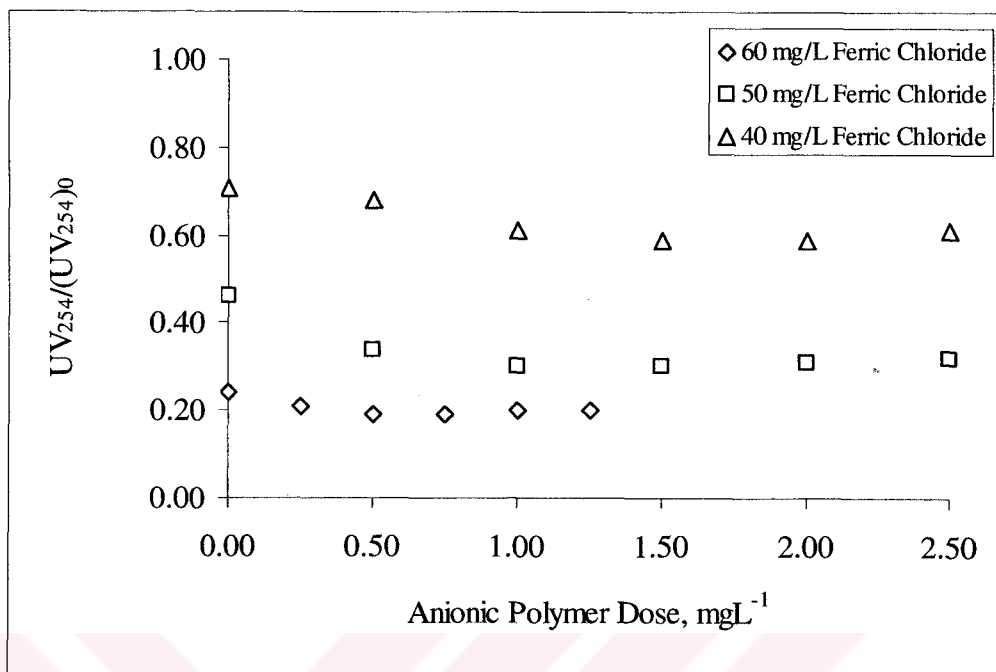


Figure 4.32 UV₂₅₄ functions of anionic polymer dosage for ozonated humic acid.

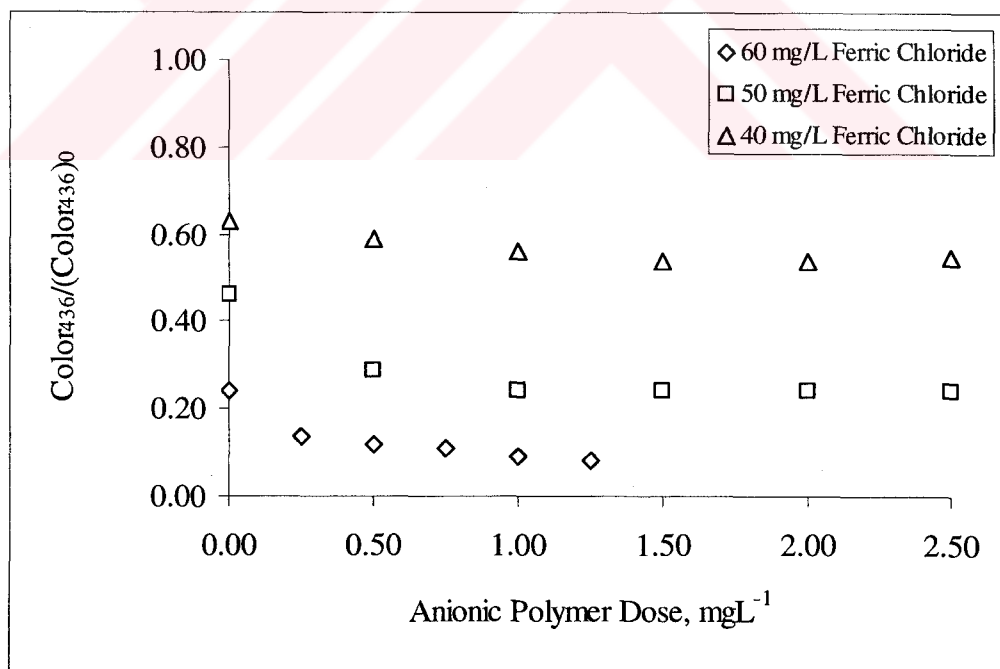


Figure 4.33 Color₄₃₆ functions of anionic polymer dosage for ozonated humic acid.

4.4.2.2. Coagulation of Photocatalytically Treated Humic Acid with Combinations of Ferric Chloride and Anionic Polymer

In order to evaluate the coagulation properties of photocatalytically treated humic acid, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by photocatalytically. Then coagulation experiments were carried out in the presence of 60 mgL⁻¹, 50 mgL⁻¹, 40 mgL⁻¹ ferric chloride and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 60 mgL⁻¹ for photocatalytically treated humic acid as given in Figure 4.9 and Figure 4.10. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of 60 mgL⁻¹ – 40 mgL⁻¹ to determine the effect of anionic polymer on the coagulation experiment of photocatalytically oxidized humic acid in the combined coagulation experiments. The related coagulation profiles are presented in the following Figure 4.34 and Figure 4.35.

Using 60 mgL⁻¹ ferric chloride led to an increase of the removal percentages of UV₂₅₄ and Color₄₃₆ these are 86 and 92 per cent, respectively. When 60 mgL⁻¹ ferric chloride were used with 0.6 mgL⁻¹ anionic polymer, the removal efficiencies of UV₂₅₄ and Color₄₃₆ were increased to 90 and 94 per cent, respectively. Therefore, when ferric chloride dose was reduced to 50 mgL⁻¹ and the anionic polymer dose was increased to 1.0 mgL⁻¹, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 82 and 85 per cent, respectively. When 50 mgL⁻¹ ferric chloride were used alone, the removal percentages of UV₂₅₄ and Color₄₃₆ were obtained as 67 and 79 per cent, respectively. When using 40 mgL⁻¹ ferric chloride with 1.5 mgL⁻¹ anionic polymer, the removal percentages of UV₂₅₄ and Color₄₃₆ were increased to 48 and 53 per cent, respectively. However, when 40 mgL⁻¹ ferric chloride were applied alone, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 40 and 46 per cent, respectively. As a result, using anionic polymer with ferric chloride led to an increase in the removal percentages of UV₂₅₄ and Color₄₃₆. Used anionic polymer doses combining with ferric chloride were 0.5 for 60 mgL⁻¹ ferric chloride dose, 1.0 for 50 mgL⁻¹ ferric chloride dose, and 1.5 for 40 mgL⁻¹ ferric chloride dose.

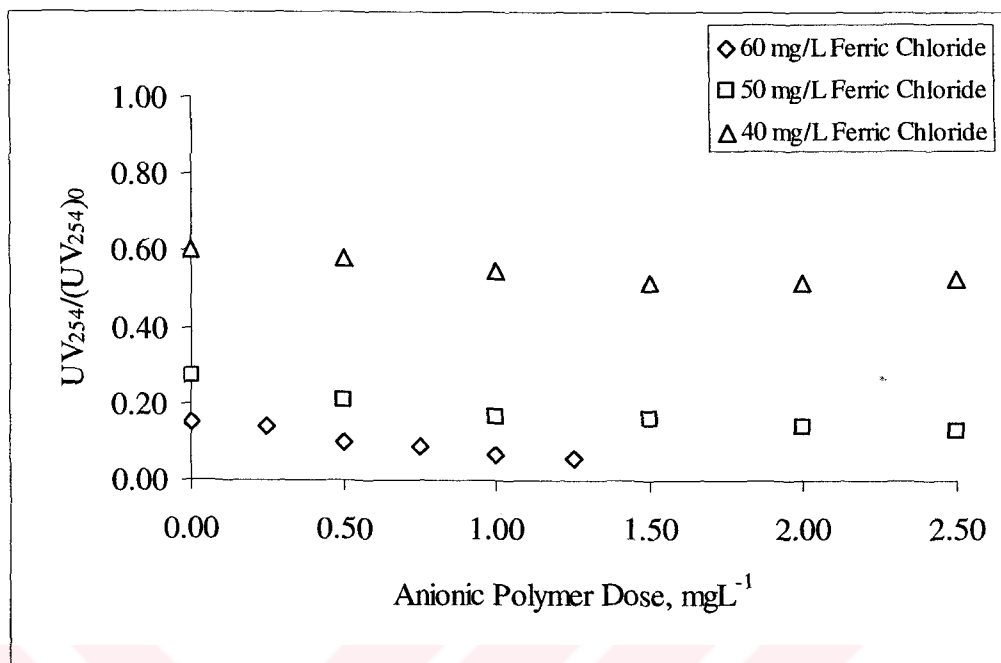


Figure 4.34 UV_{254} functions of anionic polymer dosage for photocatalytically treated humic acid.

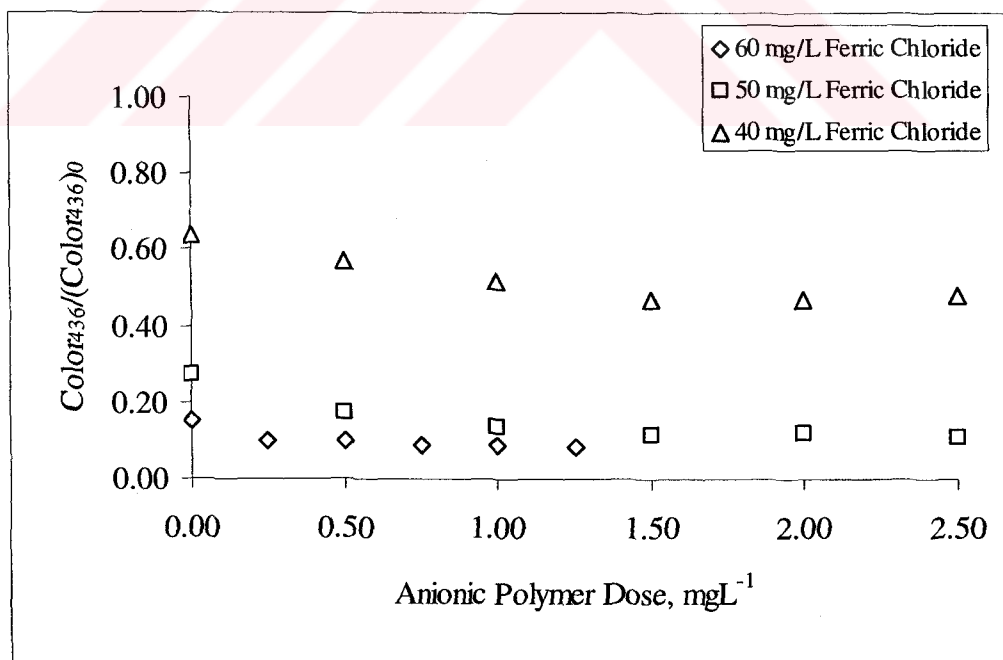


Figure 4.35 $Color_{436}$ functions of anionic polymer dosage for photocatalytically treated humic acid.

4.4.2.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Ferric Chloride and Anionic Polymer

In order to investigate the coagulation properties of sequentially oxidized humic acid, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozonation. Following humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by photocatalytically. Then coagulation experiments were carried out in the presence of 70 mgL⁻¹, 60 mgL⁻¹, 50 mgL⁻¹ ferric chloride and varying dosages of anionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of anionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 70 mgL⁻¹ for sequentially treated humic acid as given in Figure 4.9 and Figure 4.10. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of 70 mgL⁻¹ – 50 mgL⁻¹. The related coagulation profiles are presented in the following Figure 4.36 and Figure 4.37.

In the presence of 70 mgL⁻¹ ferric chloride, the removal percentages of UV₂₅₄ and Color₄₃₆ were reported as 64 and 74 per cent, respectively. When 70 mgL⁻¹ ferric chloride used with 0.75 mgL⁻¹ anionic polymer, a slight enhancement in the removal efficiencies were observed as 75 and 82 per cent in UV₂₅₄ and Color₄₃₆, respectively. Therefore, ferric chloride dose was reduced to 60 mgL⁻¹ and the anionic polymer dose was increased to 1.5 mgL⁻¹, the removal percentages of UV₂₅₄ and Color₄₃₆ were found to be 52 and 63 per cent, respectively. When using only 50 mgL⁻¹ ferric chloride, the removal percentages of UV₂₅₄ and Color₄₃₆ were obtained 43 and 52 per cent, respectively. When using 60 mgL⁻¹ ferric chloride with 2 mgL⁻¹ anionic polymer removal percentages of UV₂₅₄ and Color₄₃₆ were increased to 31 and 42 per cent, respectively. However, application of 50 mgL⁻¹ ferric chloride led to an increase in the removal percentages of UV₂₅₄ and Color₄₃₆ these were found to be 22 and 33 per cent, respectively. As a result, using anionic polymer with ferric chloride led to an increase in the removal percentages of UV₂₅₄ and Color₄₃₆. Applied anionic polymer doses in the coagulation experiments of sequentially oxidized humic acid combining with ferric chloride were 0.75 mgL⁻¹ for 70 mgL⁻¹ ferric chloride, 1.5 mgL⁻¹ for 60 mgL⁻¹ ferric chloride, and 2 mgL⁻¹ for 50 mgL⁻¹ ferric chloride.

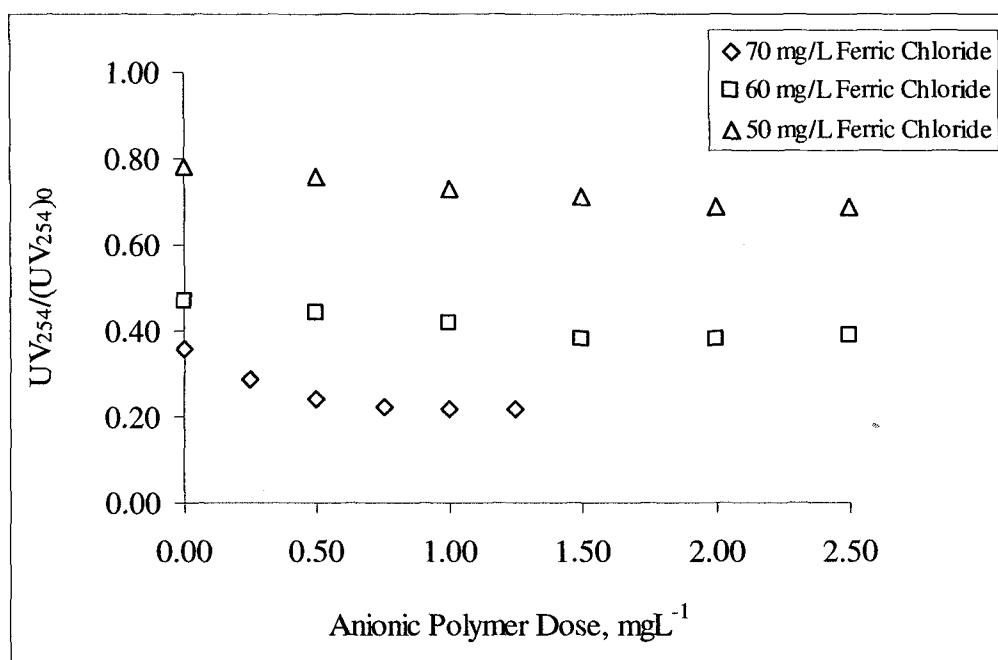


Figure 4.36 UV₂₅₄ functions of anionic polymer dosage for sequentially oxidized humic acid.

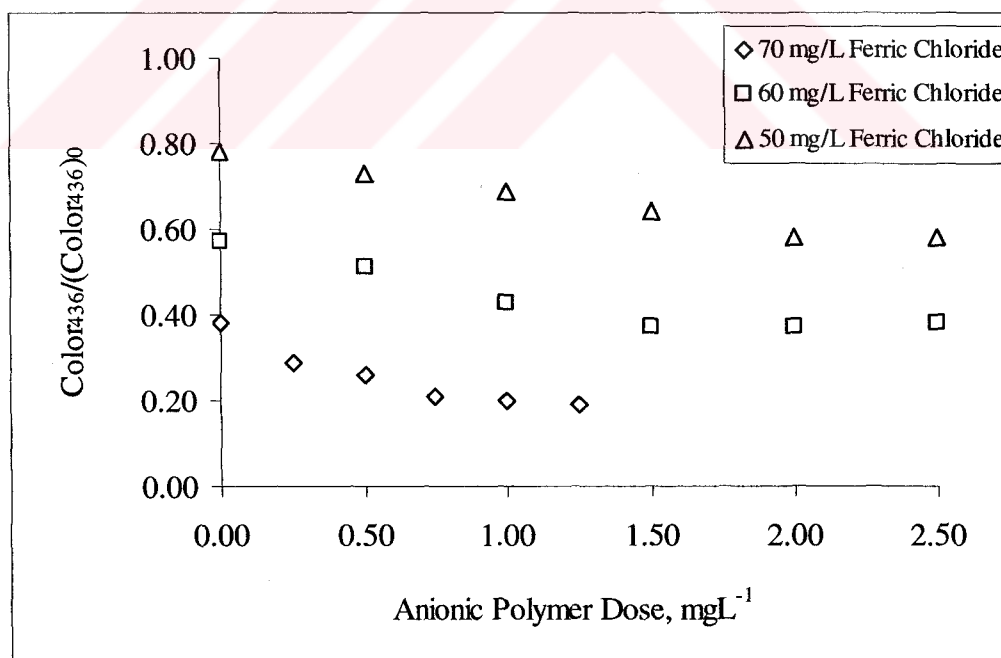


Figure 4.37 Color₄₃₆ functions of anionic polymer dosage for sequentially oxidized humic acid.

4.4.3. Coagulation of Untreated Humic Acid with Combinations of Ferric Chloride and Nonionic Polymer

In order to investigate the coagulation properties of untreated humic acid solutions (50 mgL^{-1}), coagulation experiments were carried out in the presence of 60 mgL^{-1} , 50 mgL^{-1} , 40 mgL^{-1} ferric chloride and varying doses of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color_{436} and UV_{254} measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 60 mgL^{-1} for 50 mgL^{-1} humic acid in Figure 4.9, Figure 4.10 and, Figure 4.11. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of $60 \text{ mgL}^{-1} - 40 \text{ mgL}^{-1}$ to determine the effect of nonionic polymer on the coagulation experiment of untreated humic acid in the combined coagulation experiments.. The related coagulation profiles are presented in the following Figure 4.38, Figure 4.39 and Figure 4.40.

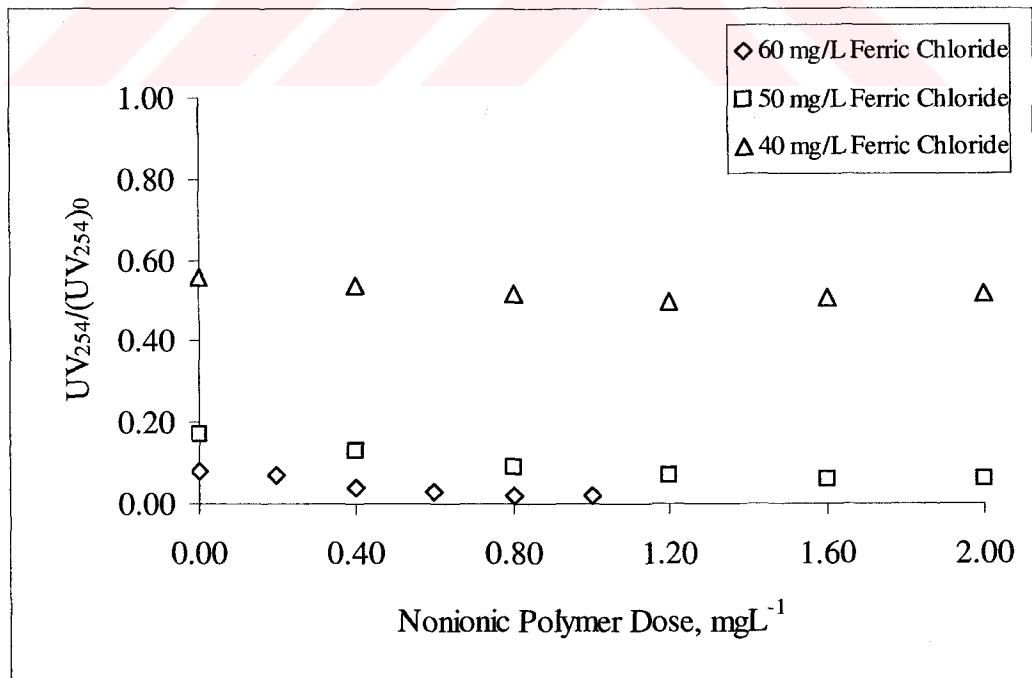


Figure 4.38 UV_{254} functions of nonionic polymer dose for 50 mgL^{-1} untreated humic acid.

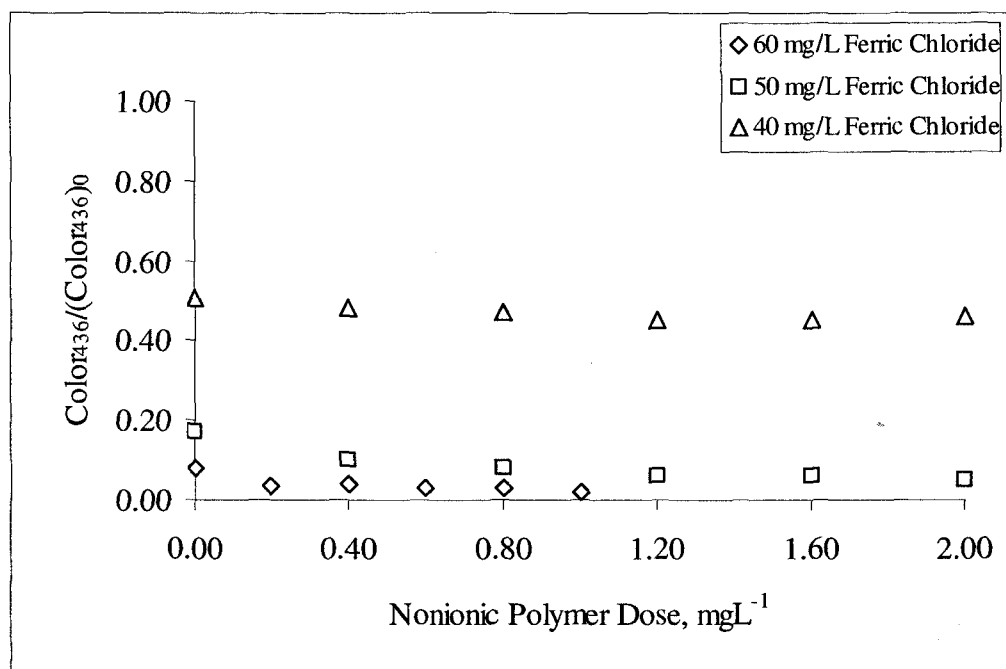


Figure 4.39 Color_{436} functions of nonionic polymer dosage for 50 mgL^{-1} untreated humic acid.

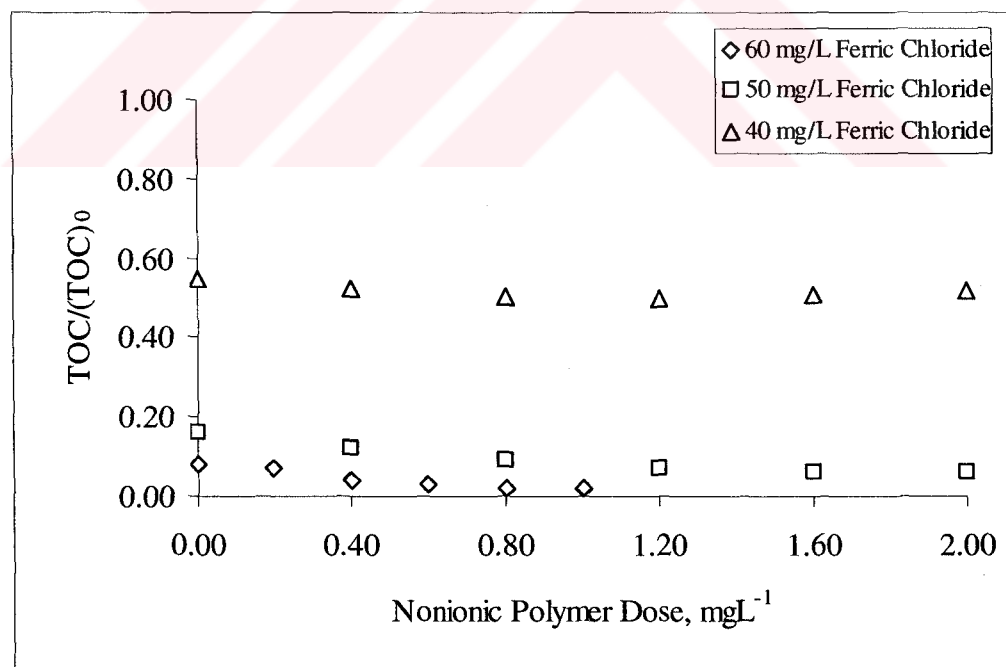


Figure 4.40 TOC functions of nonionic polymer dosage for 50 mgL^{-1} untreated humic acid.

In the presence of 60 mgL^{-1} ferric chloride, the removal percentages of UV_{254} , Color_{436} , and TOC were reported as 92, 93, and 87 per cent, respectively. When 60 mgL^{-1} ferric chloride used with 0.4 mgL^{-1} nonionic polymer, a slight enhancement in the removal efficiencies were observed as 96, 98, and 91 per cent in UV_{254} , Color_{436} and TOC, respectively. Therefore, ferric chloride dose was reduced to 50 mgL^{-1} and the nonionic polymer dose was increased to 0.8 mgL^{-1} , removal percentages of UV_{254} , Color_{436} , and TOC were found to be 91, 92, and 86 per cent, respectively. When 50 mgL^{-1} ferric chloride were used alone, the removal percentages of UV_{254} , Color_{436} , and TOC were obtained 83, 86, and 79 per cent, respectively. When using 40 mgL^{-1} ferric chloride with 1.2 mgL^{-1} nonionic polymer, the removal percentages of UV_{254} , Color_{436} , and TOC were increased to 50, 58, and 47 per cent, respectively. However, an application of 40 mgL^{-1} ferric chloride alone led to an increase in the removal percentages of UV_{254} , Color_{436} , and TOC those were found to be 45, 49, and, 41 per cent, respectively. As a result, using nonionic polymer with ferric chloride led to an increase the removal percentages of UV_{254} , Color_{436} , and TOC. Used nonionic polymer dosages combining with ferric chloride were 0.4 mgL^{-1} for 60 mgL^{-1} ferric chloride dose, 0.8 mgL^{-1} for 50 mgL^{-1} ferric chloride dose, and 1.2 mgL^{-1} for 40 mgL^{-1} ferric chloride dose.

4.4.4. Coagulation of Treated Humic Acid with Combinations of Ferric chloride and Nonionic Polymer

4.4.4.1. Coagulation of Ozonated Humic Acid with Combinations of Ferric Chloride and Nonionic Polymer

In order to investigate the coagulation properties of ozonated humic acid, 50 mgL^{-1} humic acid solutions were 50 per cent treated in terms of Color_{436} by ozonation. Then coagulation experiments were carried out in the presence of 60 mgL^{-1} , 50 mgL^{-1} , 40 mgL^{-1} ferric chloride and varying dosages of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color_{436} and UV_{254} measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 60 mgL^{-1} for ozonated humic acid. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of $60 \text{ mgL}^{-1} - 40 \text{ mgL}^{-1}$.

The removal percentages of UV_{254} and $Color_{436}$ were reported as 76 per cent and 86 per cent, respectively in the presence of 60 mgL^{-1} ferric chloride. When 60 mgL^{-1} ferric chloride used with 0.6 mgL^{-1} nonionic polymer, enhancement in the removal efficiencies were observed as 89 and 91 per cent in UV_{254} and $Color_{436}$, respectively. Therefore, when ferric chloride dose was reduced to 50 mgL^{-1} and the nonionic polymer dose was increased to 1.2 mgL^{-1} , removal percentages of UV_{254} and $Color_{436}$ were found to be 62 and 71 per cent, respectively. When using only 50 mgL^{-1} ferric chloride, the removal percentages of UV_{254} and $Color_{436}$ were obtained as 54 and 63 per cent, respectively. When using 40 mgL^{-1} ferric chloride with 1.6 mgL^{-1} nonionic polymer, removal percentages of UV_{254} and $Color_{436}$ were increased to 35 and 44 per cent, respectively. However, when 40 mgL^{-1} ferric chloride were applied alone, the removal percentages of UV_{254} and $Color_{436}$ were found to be 29 and 37 per cent, respectively. As a result, using nonionic polymer with ferric chloride led to an increase the removal percentages of UV_{254} and Color. Used nonionic polymer dosages combining with ferric chloride were 0.6 mgL^{-1} for 60 mgL^{-1} ferric chloride dose, 1.2 mgL^{-1} for 50 mgL^{-1} ferric chloride dose, and 1.6 mgL^{-1} for 40 mgL^{-1} ferric chloride dose.

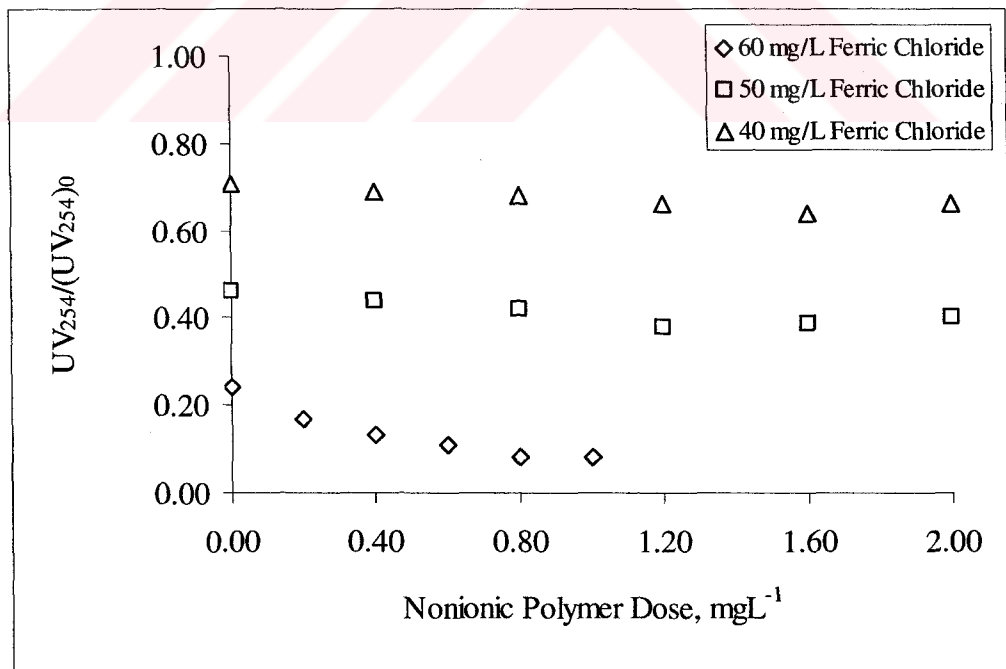


Figure 4.41 UV_{254} functions of nonionic polymer dosage for ozonated humic acid.

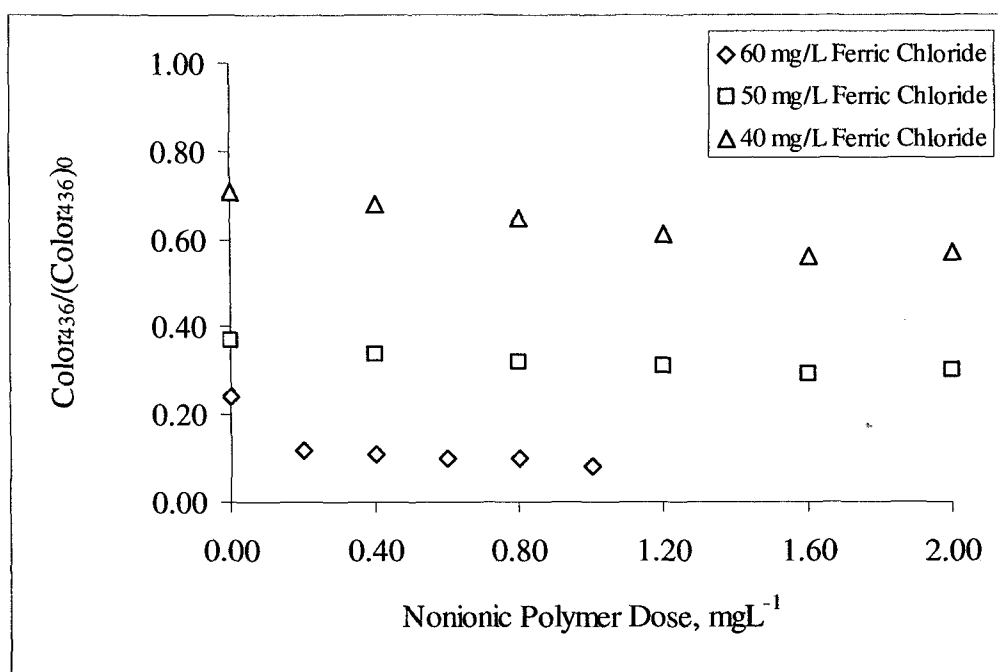


Figure 4.42 Color₄₃₆ functions of nonionic polymer dosage for ozonated humic acid.

4.4.4.2. Coagulation of Photocatalytically Treated Humic Acid with Combination of Ferric Chloride and Nonionic Polymer

In order to evaluate the coagulation properties of photocatalytically treated humic acid solutions, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by photocatalytically. Then coagulation experiments were carried out in the presence of 60 mgL⁻¹, 50 mgL⁻¹, 40 mgL⁻¹ ferric chloride and varying doses of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dose was found to be 60 mgL⁻¹ for photocatalytically treated humic acid solution (in Figure 4.9 and Figure 4.10). Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of 60 mgL⁻¹ – 40 mgL⁻¹ to determine the effect of nonionic polymer on the coagulation experiment of photocatalytically treated humic acid in the combined coagulation experiments. The related coagulation profiles are presented in the following Figure 4.43 and Figure 4.44 as UV₂₅₄ and Color₄₃₆, respectively.

Applied 60 mgL^{-1} ferric chloride led to an increase of the removal percentages of UV_{254} and Color_{436} these are 85 and 91 per cent, respectively. When 60 mgL^{-1} ferric chloride were used with 0.2 mgL^{-1} nonionic polymer, the removal efficiencies of UV_{254} and Color_{436} were increased to 89 and 93 per cent, respectively. Therefore, when ferric chloride dose was reduced to 50 mgL^{-1} and the nonionic polymer dose was increased to 1.2 mgL^{-1} , removal percentages of UV_{254} and Color_{436} were found to be 79 and 85 per cent, respectively. When using only 50 mgL^{-1} ferric chloride, the removal percentages of UV_{254} and the removal percentages of Color_{436} were obtained 73 and 78 per cent, respectively. When using 40 mgL^{-1} ferric chloride with 1.6 mgL^{-1} nonionic polymer, removal percentages of UV_{254} and Color_{436} were increased to 47 and 54 per cent, respectively. However, an application of 40 mgL^{-1} ferric chloride alone, the removal percentages of UV_{254} and Color_{436} were found to be 40 and 46 per cent, respectively. As a result, using nonionic polymer with ferric chloride led to an increase the removal percentages of UV_{254} and Color_{436} . Used nonionic polymer dosages combining with ferric chloride were 0.2 for 60 mgL^{-1} ferric chloride dose, 1.2 for 50 mgL^{-1} ferric chloride dose, and 1.6 for 40 mgL^{-1} ferric chloride dose.

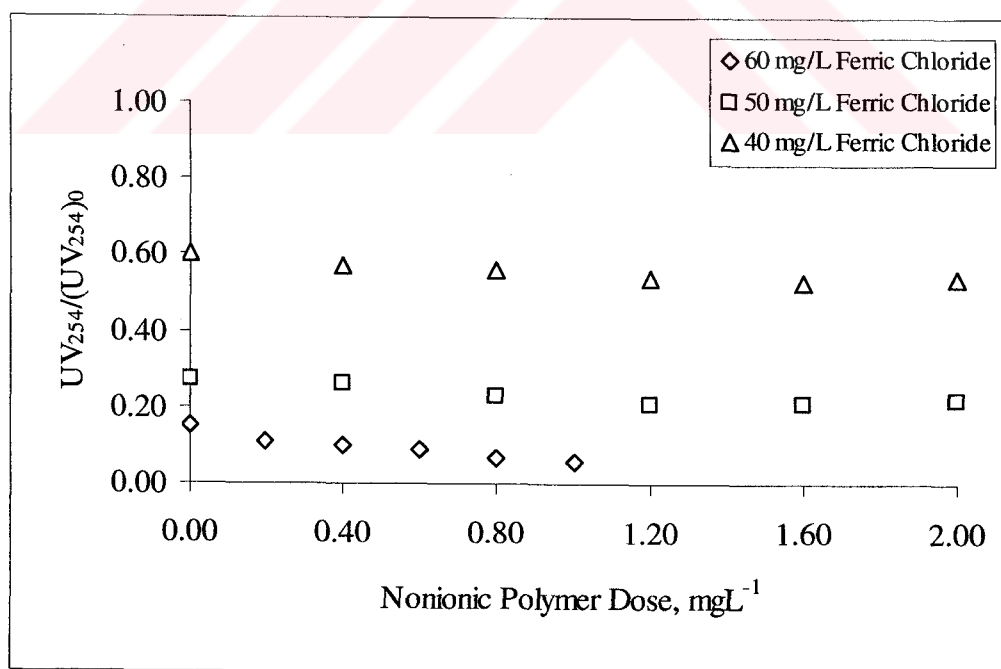


Figure 4.43 UV_{254} functions of nonionic polymer dosage for photocatalytically treated humic acid.

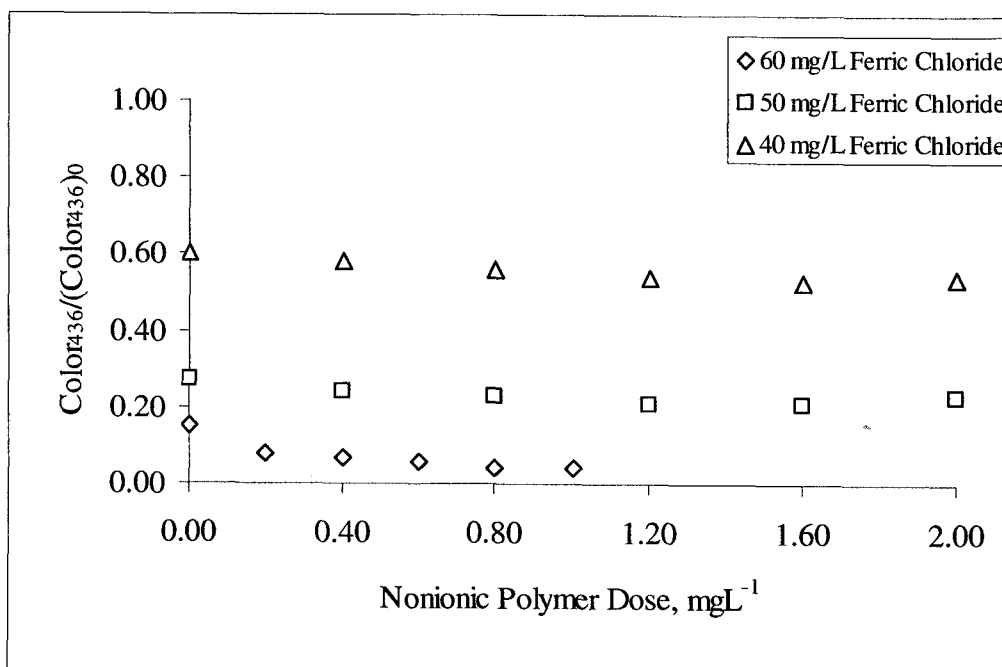


Figure 4.44 Color₄₃₆ Functions of Nonionic Polymer Dosage for Photocatalytically Treated Humic Acid.

4.4.4.3. Coagulation of Sequentially Oxidized Humic Acid with Combinations of Ferric Chloride and Nonionic Polymer

In order to investigate the coagulation properties of sequentially oxidized humic acid solutions, 50 mgL⁻¹ humic acid solutions were 50 per cent treated in terms of Color₄₃₆ by ozonation. Following humic acid solutions were 50 per cent treated in terms of Color₄₃₆ photocatalytically. Then coagulation experiments were carried out in the presence of 70 mgL⁻¹, 60 mgL⁻¹, 50 mgL⁻¹ ferric chloride, and varying dosages of nonionic polymer. The experiments were conducted according to the procedure outlined in the Materials and Methods section. Following the sedimentation and filtration period, Color₄₃₆ and UV₂₅₄ measurements were conducted in the supernatant to assess the effect of the presence of nonionic polymer with respect to the ferric chloride addition. The optimum ferric chloride dosage was found to be 70 mgL⁻¹ for sequentially treated humic acid as given in Figure 4.9 and Figure 4.10. Therefore, in the combined coagulation experiments, ferric chloride dosages were taken in the range of 70 mgL⁻¹ – 50 mgL⁻¹ to determine the effect of nonionic polymer in the combined coagulation experiments. The related coagulation profiles are presented in the following Figure 4.45 and Figure 4.46.

In the presence of 70 mgL^{-1} ferric chloride, the removal percentages of UV_{254} and Color_{436} were reported as 62 and 73 per cent, respectively. When 70 mgL^{-1} ferric chloride used with 0.8 mgL^{-1} nonionic polymer, the removal efficiencies were observed as 81 and 87 per cent in UV_{254} and Color_{436} , respectively. Therefore, ferric chloride dose was reduced to 60 mgL^{-1} and nonionic polymer dose was increased to 1.2 mgL^{-1} , the removal percentages of UV_{254} and Color_{436} were found to be 53 and 60 per cent, respectively. When 60 mgL^{-1} ferric chloride were used alone, the removal percentages of UV_{254} and Color_{436} were obtained as 43 and 52 per cent, respectively. When using 50 mgL^{-1} ferric chloride with 1.6 mgL^{-1} nonionic polymer removal percentages of UV_{254} and Color_{436} were increased to 53 and 60 per cent, respectively. However, an application of 50 mgL^{-1} ferric chloride alone led to an increase in the removal percentages of UV_{254} and Color_{436} those were found to be 22 and 33 per cent, respectively. As a result, using nonionic polymer with ferric chloride led to an increase in the removal percentages of UV_{254} and Color_{436} . Used nonionic polymer dosages combining with ferric chloride were 0.8 mgL^{-1} for 60 mgL^{-1} ferric chloride dose, 1.2 mgL^{-1} for 50 mgL^{-1} ferric chloride dose, and 1.6 mgL^{-1} for 40 mgL^{-1} ferric chloride dose.

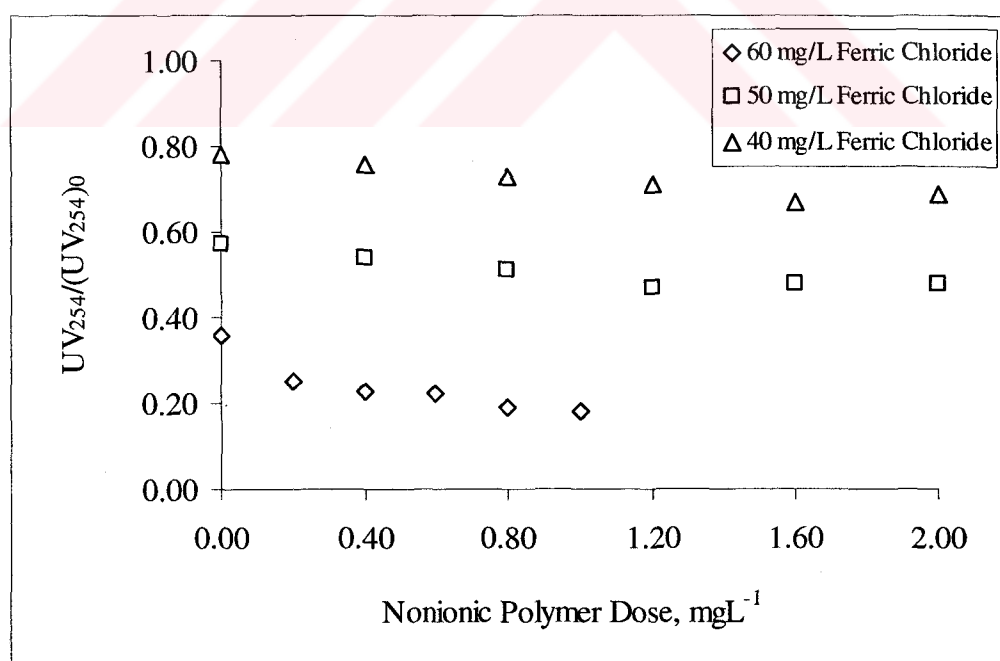


Figure 4.45 UV_{254} functions of nonionic polymer dosage for sequentially oxidized humic acid.

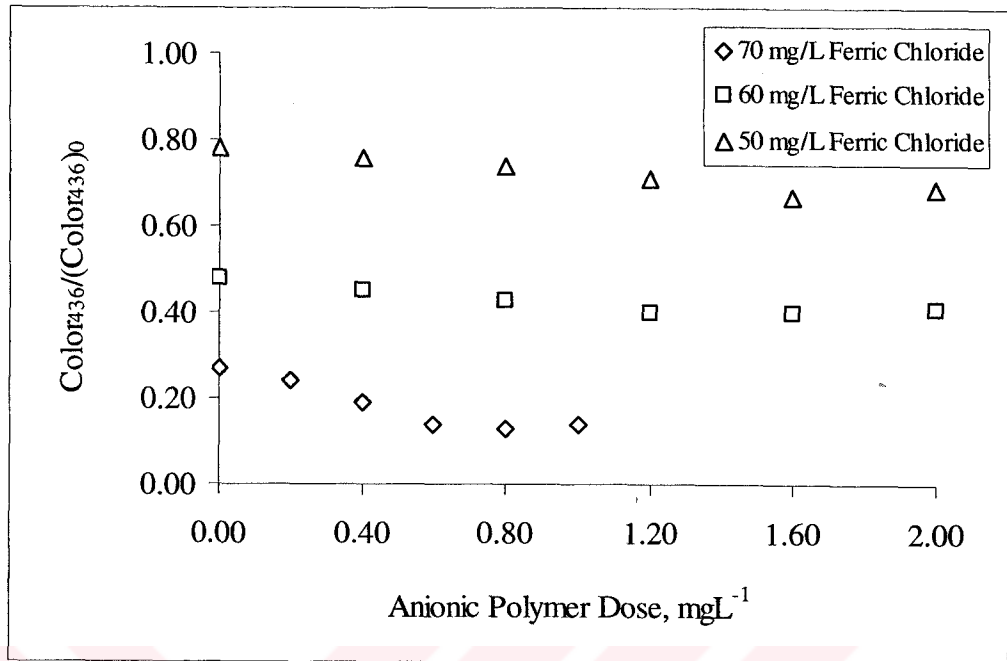


Figure 4.46 Color₄₃₆ functions of nonionic polymer dosage for sequentially oxidized humic acid.

4.5. Evaluation of Humic Acid Coagulation Properties

4.5.1. Coagulation Properties of Humic Acid with Alum

In order to evaluate the coagulation characteristics of the untreated humic acid and treated humic acid solutions in a general perspective, the removal percentages of Color₄₃₆ and UV₂₅₄ values for optimum alum dose are given in Table 4.2 and Table 4.3. All the coagulation profiles obtained for the untreated and treated humic acid solutions were plotted on the same graph in Figure 4.1 for UV₂₅₄ and Figure 4.2 for Color₄₃₆ in the Section 4.1.

4.5.1.1. Coagulation Properties of Untreated Humic Acid with Alum

According to Table 4.2, optimum alum dosages were increased with increasing humic acid concentration. In practice, optimum coagulant dosages were determined by TOC concentration for most surface water supplies. A stoichiometric relationship exists

between coagulants and TOC concentration in the water to be treated. This relationship depends on the types of organic matter substances to be treated, the coagulant type, and solution conditions (Black et al., 1963).

Table 4.2 The removal percentages of different concentration of humic acid for optimum alum dose

Concentration of Humic Acid mgL⁻¹	TOC mgL⁻¹	Optimum Alum Dose mgL⁻¹	Color₄₃₆ Removal (per cent)	UV₂₅₄ Removal (per cent)
20	7.2	14	95	86
30	10.8	20	95	90
40	14.4	25	94	89
50	18	30	97	94

4.5.1.2. Coagulation Properties of Treated Humic Acid with Alum

According to the result of the coagulation experiments, pretreatments significantly altered the coagulation properties of humic acid with alum for both UV₂₅₄ and Color₄₃₆ values. Coagulation properties, optimum alum dosages, and removal percentages of treated and untreated humic acid for various alum dosages were explained in Section 4.2. Ozonation did not lead to a decrease in the optimum alum dosage. To the contrary, ozonation has an adverse effect on coagulation. As shown on Table 4.3, ozone results in the decrease in removal of humic substances. Similar results were seen for both photocatalytically and sequentially treated humic acid. However, a removal percentage of photocatalytically treated humic acid with alum was shown lower decrease than ozonated humic acid solutions. Sequentially oxidized humic acid solutions was shown the lowest removal percentages of UV₂₅₄ and Color₄₃₆ values for optimum alum dosages. The removal percentages of untreated and treated humic acid with alum are shown in Table 4.3.

In most cases, ozonation has adverse effects on the coagulation mainly due to the interactions between ozone and humic acid in solution. Effect of preozonation on

coagulation is that the ozonation led to an increase in the organic anionic charge of the molecules that sorbs to metal hydroxide surfaces. This increase in negative surface charge was reported to increase the coagulant demand. In addition, the amount of TOC removed by coagulation decreased with increasing ozone dosage because of the transformation of the NOM into more hydrophilic, less adsorbable molecules (Edwards et al., 1992).

A common ozonation by product is oxalate had an adverse effect on the coagulation and filtration of turbidity and TOC when alum was used as the only coagulant. This was measured as an increase in the optimal alum dosage required for adequate treatment or by increased settled turbidity for a given alum dosages (Becker et al., 1995).

Table 4.3. Removal percentages of untreated and treated humic acid with alum

Concentration of Humic Acid mgL⁻¹	Optimum Alum Dose mgL⁻¹	Color₄₃₆ Removal (per cent)	UV₂₅₄ Removal (per cent)
H	30	97	94
H+O	30	84	76
H+P	30	91	81
H+S	30	73	64

Schneider et al., (2000), O'Melia et al., (1999), and Tobiasson et al., (1995) obtained similar results. Recent literature covers publications about the effects of ozonation on molecular size distribution of humic substances (Chiang et al., 2002; Myllykangas et al., 2002). In addition, Kerc (2002) investigated the oxidation of humic substances by sequential oxidation including ozonation and photocatalysis. It was stated that, the oxidative degradation of humic acids was found to be efficient in both UV₂₅₄ and Color₄₃₆. It was reported that molecular size distributions were greatly affected by oxidations.

Similarly Bekbölet et al., (1996) investigated affect of the photocatalytic oxidation on humic substances. They found that the attack of the produced oxidants as $\cdot\text{OH}/\cdot\text{HO}_2$

radicals might result in structural changes of via hydroxylation, decarboxylation, and depolymerization in humic acid molecule producing less hydrophobic, less adsorbing, and less aromatic characters. For these results, photocatalytic treatment of humic substances slightly hindered the removal of humic substances by coagulation. Because of the these adverse effects of ozonation and photocatalytic oxidation of humic acid, sequential oxidation led to decrease of removal of humic acid by coagulation.

4.5.2. Coagulation Properties of Humic Acid with Ferric Chloride

In order to evaluate the coagulation characteristics of untreated and treated humic acid solutions in a general perspective, the removal percentage of Color_{436} and the removal percentage of UV_{254} values at optimum ferric chloride dose are given in Table 4.4 and Table 4.5, respectively. All the coagulation profiles obtained for the untreated and treated humic acid solutions were plotted on the same graph in Figure 4.6 for UV_{254} and Figure 4.7 for Color_{436} in the Section 4.2.

4.5.2.1. Coagulation Properties of Untreated Humic Acid with Ferric Chloride

Optimum ferric chloride dosages are determined by UV_{254} values. According to Table 4.4, optimum ferric chloride dosages are increase with increased humic acid concentration. The same result were seen for coagulation of humid acid with alum

Table 4.4 The removal percentage of different concentration of humic acid at optimum ferric chloride dose

Concentration of Humic Acid mgL^{-1}	Optimum Ferric Chloride Dose mgL^{-1}	Color_{436} Removal (per cent)	UV_{254} Removal (per cent)
20	30	91	87
30	45	92	89
40	50	90	88
50	60	92	88

There are relationship between the concentration of humic acid and optimum ferric chloride dosages. Due to the negative charge of the natural organic matter, there is a relationship between the required dosage of coagulant and the TOC concentration in the water to be treated. This relationship determined primarily by the type of natural organic matter, coagulant type and solution conditions such as pH, hardness and temperature (O'Melia et al., 1999).

4.5.2.2. Coagulation Properties of Treated Humic Acid with Ferric Chloride

The removal percentages of untreated and treated humic acid with ferric chloride are shown in Table 4.5. Tobiasson et al., (1995) obtained similar results. According to results of experiments, pretreatments significantly altered the coagulation properties of humic acid with ferric chloride for both UV_{254} and $Color_{436}$. The optimum ferric chloride doses are determined according to UV_{254} values. Ozonation do not lead to a decrease in the optimum ferric chloride dosage. To the contrary, ozonation has an adverse effect on coagulation. Ozone leads to slight decrease in the removal of both UV_{254} and $Color_{436}$ values of humic acid. Same results are seen for both photocatalytically and sequentially treated humic acid. Removal percentage of photocatalytically treated humic acid with ferric chloride has shown same result with ozonated humic acid solutions. Sequentially oxidization led to the increase in optimum ferric chloride dose. Sequentially oxidized humic acid has shown the lowest removal percentages of UV_{254} and $Color_{436}$ values for optimum ferric chloride dosage of humic acid solutions.

Table 4.5 Removal percentages of untreated and treated humic acid with ferric chloride

	Optimum Ferric Chloride Dose mgL^{-1}	Color₄₃₆ Removal (per cent)	UV₂₅₄ Removal (per cent)
H	60	92	88
H+O	60	85	77
H+P	60	91	85
H+S	70	79	73

4.5.3. Coagulation Properties of Combinations with Alum and Polymer

In order to compare the coagulation efficiencies of the treated and untreated humic acid solutions with alum and polymer, the removal percentage of Color₄₃₆ and UV₂₅₄ values for optimum polymer doses are presented in below Table 4.6, Table 4.7, Table 4.8. All the coagulation profiles obtained for the untreated and treated humic acid solutions were plotted on the same graph in the Section 4.3.

4.5.3.1. Coagulation of Humic Substances Combining with Alum and Anionic Polymer

Anionic and nonionic polymers are referred to as either coagulant aid or flocculants (Letterman et al., 1990, and Mallevalle et al., 1984). Adding coagulant aids is an attempt to enhance the coagulation efficiency and economize the dosage of the primary coagulant (Lee et al., 1998).

According to Table 4.6, removal percentages of untreated humic acid are increased by coagulation of combining with alum and anionic polymer. Applied anionic polymer as coagulant aid led to decrease of used alum doses. Using anionic polymer with alum is led to improvement in the removal percentages of untreated humic substances for optimum alum dose. Moreover similar removal percentages were obtained by using anionic polymer combined with alum when less alum dose was applied. Removal percentage of humic acid by coagulation was enhanced by anionic polymer (Bolto et al., 2001).

It is possible to improve organic matter removal following ozonation when polymer is used for coagulation (Orren et al., 2000). Using anionic polymer with alum is lead to an increase in removal percentages of UV₂₅₄ and Color₄₃₆ values for treated humic acid. For preozonated humic substances, polymer gives better removal percentage than using only alum (O'Melia et al., 1999). However, the removal percentages of treated humic acid are less than the removal percentage of untreated humic acid. The best results were obtained with aluminum sulfate and ferric chloride combining with anionic and nonionic polymer (Amokrane et al., 1997). In general, applied high dosage of alum combined with low dosages of anionic polymer give better performance than the using low dosage of alum and high dosage of anionic polymer.

Table 4.6 Removal Percentages of Color₄₃₆ and UV₂₅₄ values of untreated humic acid by combination with alum and anionic polymer

Alum Dose mgL ⁻¹	Anionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
30	0	96	88		
30	0.5	98	96	2	8
20	0	84	72		
20	1.0	92	85	8	13
10	0	50	48		
10	1.5	61	57	11	9

Table 4.7 Removal Percentages of Color₄₃₆ and UV₂₅₄ values of ozonated humic acid by combination with alum and anionic polymer

Alum Dose mgL ⁻¹	Anionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
30	0	83	75		
30	0.5	94	84	11	9
20	0	77	68		
20	1.0	85	74	8	6
10	0	41	33		
10	1.5	50	45	9	12

Ozonation, photocatalytic oxidation and sequential oxidation led to decrease of removal percentages of humic acid by hydrolyzed metal salts coagulation. The reasons of these adverse effects on the coagulation are mainly due to the interactions between oxidizing agents and humic acid in solution. The effects of ozonation, photocatalytic oxidation and sequential oxidation on humic acid structure was explained in Section 4.5.1.

Ozonation, photocatalytic oxidation and sequential oxidation also affected the removal percentages of humic acid coagulation by combining with metal salts and anionic polymers. The removal percentages of humic acid by combination with anionic polymer were decreased by ozonation, photocatalytic oxidation, and sequential oxidation. However, anionic polymer led to improvement of the removal percentages of treated humic substances from water.

The reasons of the decreases of the removal percentages of humic substances are explained by the mechanisms of between the anionic polymer as coagulant aid and the primary coagulants. A certain amount of primary coagulant is necessary for destabilization of organic matter. The primary coagulant led to destabilization of the anionic part of the humic substances. Then, anionic or nonionic polymer used as coagulant aid. The anionic or nonionic polymer provides the number of bridges between the particles increases and therefore the percentage of flocculation increases (Petzold et al., 2003). The results of these mechanism, there are more highly charged flocs in the treated humic acid solution than the untreated humic acid solution (Schneider et al., 2000). According to this, increasing of the number of charged floc led to decrease of the performance of anionic polymer. As a result, using anionic polymer combining with alum led to increase of removal percentages of untreated and treated humic acid.

Table 4.8 Removal Percentages of Color₄₃₆ and UV₂₅₄ values of photocatalytically treated humic acid by combination with alum and anionic polymer

Alum Dose mgL⁻¹	Anionic Polymer Dose mgL⁻¹	Color₄₃₆ Removal (per cent)	UV₂₅₄ Removal (per cent)	Increase of Color₄₃₆ Removal (per cent)	Increase of UV₂₅₄ Removal (per cent)
30	0	91	83		
30	0.5	97	91	6	8
20	0	79	76		
20	1.0	87	81	8	5
10	0	47	38		
10	1.5	53	47	6	9

Table 4.9 Removal percentages of Color₄₃₆ and UV₂₅₄ values of sequentially oxidized humic acid by combination with alum and anionic polymer

Alum Dose mgL⁻¹	Anionic Polymer Dose mgL⁻¹	Color₄₃₆ Removal (per cent)	UV₂₅₄ Removal (per cent)	Increase of Color₄₃₆ Removal (per cent)	Increase of UV₂₅₄ Removal (per cent)
30	0	74	64		
30	0.5	86	78	12	14
20	0	61	53		
20	1.0	70	61	9	8
10	0	47	30		
10	1.5	54	36	7	6

4.5.3.2. Coagulation of Humic Substances Combining with Alum and Nonionic Polymer

According to Table 4.10, Table 4.11, Table 4.12 and Table 4.13, using nonionic polymer combined with alum are effective for treated and untreated humic acid. Removal percentages of untreated humic acid and treated humic acid was increased with nonionic polymer. Applied nonionic polymer as coagulant aid led to decrease of used alum doses. Using nonionic polymer combined with alum was led to an improvement in the removal percentages of untreated humic substances for optimum alum dose. However, removal efficiency of all humic acid solutions were lowered by low alum dosages combining with high nonionic polymer dosages.

Using nonionic polymer with alum is lead to an increase in removal percentages of UV₂₅₄ and Color₄₃₆ values for treated humic acid. However, removal percentages of treated humic acid are less than removal percentage of untreated humic acid. Treatments of humic substances lead to decrease in removal percentages of humic acid. Ozonation, photocatalytic oxidation and sequential oxidation led to a decrease in the removal percentages of humic acid by hydrolyzed metal salts coagulation. The reasons of these

results on the coagulation are mainly due to the interactions between oxidizing agents and humic acid in solution. The effects of ozonation, photocatalytic oxidation and sequential oxidation was explained in Section 4.5.1. Ozonation, photocatalytic oxidation and sequential oxidation also affected the removal percentages of humic acid coagulation by combining with metal salts and nonionic polymers. The removal percentages of humic acid by combination with nonionic polymer were decreased by ozonation, photocatalytic oxidation, and sequential oxidation. However, nonionic polymer led to increase of removal percentages of treated humic substances from water. Using nonionic polymer as coagulant aid also led to decrease in used primary coagulant.

The causes of the decreases of removal percentages of humic substances are explained by the mechanisms of between nonionic polymer as coagulant aids and the primary coagulants. These mechanism is explained in Section 4.5.3.1. The results of these mechanism, there are more highly charged flocs in the treated humic acid solution than the untreated humic acid solution (Schneider et al., 2000). Applied nonionic polymer combining with alum led to an increase in the removal percentages of untreated and treated humic acid.

Table 4.10 Removal percentages of Color₄₃₆ and UV₂₅₄ values of untreated humic acid by combination with alum and nonionic polymer

Alum Dose mgL⁻¹	Nonionic Polymer Dose mgL⁻¹	Color₄₃₆ Removal (per cent)	UV₂₅₄ Removal (per cent)	Increase of Color₄₃₆ Removal (per cent)	Increase of UV₂₅₄ Removal (per cent)
30	0	96	88		
30	0.2	97	96	1	8
20	0	84	72		
20	0.8	95	87	11	15
10	0	50	46		
10	1.2	62	57	12	11

Table 4.11 Removal percentages of Color₄₃₆ and UV₂₅₄ values of ozonated humic acid by combination with alum and nonionic polymer

Alum Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
30	0	83	75		
30	0.4	91	86	7	11
20	0	77	68		
20	0.8	86	78	7	8
10	0	41	33		
10	1.2	49	40	9	11

Table 4.12 Removal percentages of Color₄₃₆ and UV₂₅₄ values of photocatalytically treated humic acid by combination with alum and nonionic polymer

Alum Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
30	0	91	83		
30	0.4	95	92	4	9
20	0	79	76		
20	0.8	87	83	8	7
10	0	47	38		
10	1.2	54	46	7	8

Table 4.13 Removal percentages of Color₄₃₆ and UV₂₅₄ values of sequentially oxidized humic acid by combination with alum and nonionic polymer

Alum Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
30	0	74	64		
30	0.4	82	79	8	15
20	0	61	53		
20	0.8	68	61	7	8
10	0	37	30		
10	1.2	42	37	5	7

4.5.4. Coagulation Properties of Combinations with Ferric Chloride and Polymer

In order to evaluate the coagulation characteristics of the untreated and treated humic acid solutions with combination with ferric chloride and polymer, the removal percentage of Color₄₃₆ and UV₂₅₄ values at optimum polymer dose are given in Table 4.14, Table 4.15, Table 4.16 and, Table 4.17. All the coagulation profiles obtained for the untreated, ozonated, photocatalytically and sequentially treated humic acid solutions were plotted on the same graph in the Section 4.3.

4.5.4.1. Coagulation of Humic Substances Combining with Ferric Chloride and Anionic Polymer

Using anionic polymer with ferric chloride are very effective for untreated and treated humic acid. Removal percentage of untreated humic acid and treated humic acid has increased with anionic polymer. Removal percentages of untreated humic acid are increased by coagulation of combining with ferric chloride and anionic polymer. Applied anionic polymer as coagulant aid led to decrease of used ferric chloride doses. Using anionic polymer with ferric chloride is lead to improvement in the removal percentages of

untreated humic substances for optimum ferric chloride dose. Moreover similar removal percentages were obtained by using anionic polymer combining with ferric chloride when less ferric chloride dose was applied. Therefore, ferric chloride doses could be lowered for obtaining same performance.

Using anionic polymer with ferric chloride is led to an increase in removal percentages of UV_{254} and $Color_{436}$ values for treated humic acid. However, removal percentages of treated humic acid are less than removal percentage of untreated humic acid. Especially, ozonation and sequential oxidation decrease the removal percentage of UV_{254} and $Color_{436}$ values. The reasons of these adverse effects on the coagulation are mainly due to the interactions between oxidizing agents and humic acid in solution. The effects of ozonation, photocatalytic oxidation and sequential oxidation was explained in Section 4.5.1. The removal percentages of humic acid by combination with anionic polymer were decreased by ozonation, photocatalytic oxidation, and sequential oxidation. However, anionic polymer led to increase of removal percentages of treated humic substances from water. Therefore, removal percentages of treated humic acid were less than removal percentage of untreated humic acid. Ozonation and sequential oxidation have less removal percentage than photocatalytically treated humic acid. In addition, pretreatment lead to increase used anionic polymer dosage.

The reasons for the decrease in the removal percentages of humic substances are explained by the mechanisms of between the anionic polymer as a coagulant aid and the hydrolyzed metal salt coagulants. These mechanism were explained in Section 4.5.3.1. According to this coagulation mechanism, increasing of the applied primary coagulant dose led to a decrease in the coagulation performance of anionic polymer. As a result, using anionic polymer combining with ferric chloride led to increase of removal percentages of untreated and treated humic acid, but ozonation, photocatalytic oxidation, and sequential oxidation caused a decrease in removal percentages of humic acid. However, applied high dosages of ferric chloride combining with low doses of anionic polymer give better removal efficiency of humic acid than applied low doses of ferric chloride with high doses of anionic polymer.

Table 4.14 Removal percentage of Color₄₃₆ and UV₂₅₄ values of untreated humic acid by combination with ferric chloride and anionic polymer

Ferric chloride Dose mgL ⁻¹	Anionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
60	0	95	91		
60	0.25	97	93	2	2
50	0	86	82		
50	1.0	92	89	6	7
40	0	49	44		
40	1.5	53	49	4	5

Table 4.15 Removal percentages of Color₄₃₆ and UV₂₅₄ values of ozonated humic acid by combination with ferric chloride and anionic polymer

Ferric chloride Dose mgL ⁻¹	Anionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
60	0	85	76		
60	0.5	88	81	3	5
50	0	63	54		
50	1.0	76	70	13	6
40	0	37	29		
40	1.5	46	41	9	12

Table 4.16 Removal percentages of Color₄₃₆ and UV₂₅₄ values of photocatalytically treated humic acid by combination with ferric chloride and anionic polymer

Ferric chloride Dose mgL ⁻¹	Anionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
60	0	91	85		
60	0.5	93	90	2	5
50	0	78	73		
50	1.0	87	83	9	10
40	0	46	40		
40	1.5	53	48	7	8

Table 4.17 Removal percentages of Color₄₃₆ and UV₂₅₄ values of sequentially oxidized humic acid by combination with ferric chloride and anionic polymer

Ferric chloride Dose mgL ⁻¹	Anionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
70	0	73	62		
70	0.75	82	75	9	13
60	0	52	43		
60	1.5	63	60	11	7
50	0	33	22		
50	2.0	42	31	9	9

4.5.4.2. Coagulation of Humic Substances Combining with Ferric Chloride and Nonionic Polymer

According to result of coagulation experiments, using nonionic polymer with ferric chloride are very effective for untreated and treated humic acid. Removal percentage of untreated humic acid and treated humic acid has increased with nonionic polymer. According to Table 4.18, removal percentages of untreated humic acid are increased by coagulation of combining with ferric chloride and nonionic polymer. Applied nonionic polymer as coagulant aid led to decrease in the dose of ferric chloride. Using nonionic polymer with ferric chloride is lead to improvement in the removal percentages of untreated humic substances for optimum ferric chloride dose. Moreover similar removal percentages were obtained by using nonionic polymer combining with ferric chloride when less ferric chloride dose was applied. Therefore, ferric chloride doses could be lowered for obtaining the same result. Removal percentage of humic acid by coagulation was enhanced by nonionic polymer (Bolto et al., 2001).

Using nonionic polymer with ferric chloride is lead to an increase in removal percentages of UV_{254} and $Color_{436}$ values for treated humic acid. However, removal percentages of treated humic acid are less than removal percentage of untreated humic acid. Ozonation, photocatalytic oxidation and sequential oxidation led to decrease of removal percentages of humic acid by ferric chloride coagulation. The effects of ozonation, photocatalytic oxidation and sequential oxidation was explained in Section 4.5.1. The removal percentages of humic acid by combination with nonionic polymer were decreased by ozonation, photocatalytic oxidation, and sequential oxidation. However, removal percentages of treated humic acid were less than removal percentage of untreated humic acid. In addition, pretreatment lead to increase used nonionic polymer dosage.

The reasons of the decreases of removal percentages of humic substances are explained by the mechanisms of between the nonionic polymer and ferric chloride. The mechanism between the polymers and metal salts explained in Section 4.5.3.1. According to this coagulation mechanism, increasing of the applied ferric chloride dose led to increase of the performance of nonionic polymer. Therefore, high dosages of ferric chloride combining with low dosages of nonionic polymer led to the best removal percentages of

humic acid. As a result, using nonionic polymer combining with ferric chloride led to increase of removal percentages of untreated and treated humic acid, but ozonation, photocatalytic oxidation, and sequential oxidation caused the decrease of removal percentages of humic acid.

Table 4.18 Removal percentages of Color₄₃₆ and UV₂₅₄ values of untreated humic acid by combination with ferric chloride and nonionic polymer

Ferric chloride Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
60	0	95	91		
60	0.4	96	94	1	3
50	0	86	82		
50	0.8	93	90	7	8
40	0	49	44		
40	1.2	58	53	9	9

Table 4.19 Removal percentages of Color₄₃₆ and UV₂₅₄ values of ozonated humic acid by combination with ferric chloride and nonionic polymer

Ferric chloride Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
60	0	85	76		
60	0.6	91	86	6	10
50	0	63	54		
50	1.2	73	65	10	11
40	0	37	29		
40	1.6	46	38	9	9

Table 4.20 Removal percentages of Color₄₃₆ and UV₂₅₄ values of photocatalytically treated humic acid by combination with ferric chloride and nonionic polymer

Ferric chloride Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
60	0	91	85		
60	0.4	96	89	5	4
50	0	78	73		
50	1.2	85	81	7	8
40	0	46	40		
40	1.6	53	48	7	8

Table 4.21 Removal percentages of Color₄₃₆ and UV₂₅₄ values of sequentially oxidized humic acid by combination with ferric chloride and nonionic polymer

Ferric Chloride Dose mgL ⁻¹	Nonionic Polymer Dose mgL ⁻¹	Color ₄₃₆ Removal (per cent)	UV ₂₅₄ Removal (per cent)	Increase of Color ₄₃₆ Removal (per cent)	Increase of UV ₂₅₄ Removal (per cent)
70	0	73	62		
70	0.8	80	73	7	11
60	0	53	43		
60	1.2	60	51	7	8
50	0	33	22		
50	1.6	42	33	9	11

4.5.5. Comparison of Coagulation Properties of Alum and Ferric Chloride

Aluminum and iron salts are widely used as coagulants in water and wastewater treatment and in some other applications. They are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances. Their mode of action is generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate (Duan et al., 2003).

Ferric chloride is more favorable pH than alum (Volk et al., 2000). Compared with alum and ferric chloride coagulates forms a stronger, heavier floc, is less sensitive than alum to problems with filtrate quality upon instances of overdosing, and of course, does not contribute to aluminum residuals in the finished effluent. However, liquid ferric chloride is an acidic, corrosive, dark brown solution, which causes staining and necessitates special materials of construction. Aluminum salts work effectively, but their continued use is questioned due to chemical cost, the impact of residual aluminum upon receiving waters (Stephenson et al., 1996).

In this study, ferric chloride and alum were used as primary coagulant. The removal percentages of UV_{254} and $Color_{436}$ of untreated and treated humic acid were nearly the same for alum and ferric chloride. The coagulation mechanisms both ferric chloride and alum are similar, therefore there did not distinct between coagulation performance of alum and ferric chloride. However, determined optimum coagulant doses were different between these two hydrolyzing metal salts. The optimum ferric chloride doses were higher than the optimum alum doses for all humic acid solutions.

The relationship between polymers and metal salts are also similar. Alum and ferric chloride give same performance with anionic and nonionic polymers. Primary coagulant was necessary for stabilization of negatively charged particle. Therefore, certain amount of metal coagulant was necessary. As a result, applied high metal salt as primary coagulant combining with low doses of polymer led to better removal efficiency of humic acid than used low dosages of metal salts.

CONCLUSIONS

In this study, coagulation properties of untreated and treated humic acids with two different types of coagulant and two types of coagulant aid were investigated. Pretreatments were done by ozonation, photocatalytic oxidation and sequential oxidation in which ozonation was applied as a pretreatment stage for partial oxidation of humic acids prior to photocatalytic oxidation using TiO_2 .

Coagulation properties were evaluated depending on the pretreatments. Coagulation experiment result showed different characteristics for all of the samples. The effects of pretreatments were observed. Coagulation efficiency was decreased by pretreatments. The effect of different types of coagulants on coagulation characteristics of humic acids was studied.

The oxidative degradation of humic acids in a sequential system including ozonation and photocatalysis were found to be efficient in both Color_{436} and UV_{254} removals. The pretreatments affect the coagulation characteristics of humic acid. The reasons for these changes were attributed to the alterations in the molecular structure of humic acid due to ozonation and photocatalysis. In addition, coagulant characteristics affected coagulation.

Alum and ferric chloride were found to be efficient for removal of humic acids by coagulation. However, using alum and ferric chloride combining with anionic and nonionic polyelectrolyte more effective than the using only metal salts. Anionic and nonionic polyelectrolyte were effective coagulant aids for humic acids coagulation. Especially these coagulant aids more effective for untreated humic acid than the treated humic acid. Removal percentages of UV_{254} and Color_{436} values increased with using metal salts combining with anionic and nonionic polyelectrolyte. Furthermore, using metal salts combining with anionic and nonionic polyelectrolyte lead to decrease in used primary coagulant. Same removal percentages of UV_{254} and Color_{436} values obtained by using less alum and ferric chloride. Applied high dosage of metal salts combining with

polyelectrolyte more effective than the applied low dosage metal salt combining with polyelectrolyte.

There are very little differences between results of coagulation experiments using alum or ferric chloride. They were shown nearly same removal percentages of UV_{254} and $Color_{436}$ values for optimum coagulant dose. However, applied optimum coagulant doses were different. The optimum ferric chloride doses were higher than the optimum alum doses.



REFERENCES

- Abuzaid, N.S., Al-Malack, M.H., and El-Mubarak, A.H., "Separation of Colloidal Polymeric Waste Using a Local Soil", *Separation and Purification Technology*, Vol.13, pp.161-169, 1998.
- Amirtharajah, A. and O'Melia, C.R., "Coagulation Processes. Destabilization, Mixing and Coagulation" in AWWA, *A Handbook of Community Water Supplies*, pp. 269-361, 4th Edition, McGraw-Hill, Inc., USA, 1990.
- Backlund, P., "Degradation of Humic Material by Ultraviolet Light", *Chemosphere*, Vol. 25, No. 12, pp. 1869-1878, 1992.
- Bahnemann, D., Cunningham, J., and Fox, M. A., Pelizetti, E., Pichat, P. and Serpone, N., "Photocatalytic Treatment of Waters" in Helz, G.R. Zepp R. G., and Crosby D. G. (Eds.), *Aquatic and Surface Photochemistry*, pp 261-316, Lewis Publishers, USA, 1994.
- Becker, W.C., "Impact of Ozonation on Coagulation: Model and Natural Water Studies", Ph.D. Dissertation, The Johns Hopkins University, 1995.
- Benjamin, B.B., *Water Chemistry*, McGraw-Hill, New York, 2002.
- Bekbölet, M., "Destructive Removal of Humic Acids in Aqueous Media by Photocatalytic Oxidation with Illuminated Titanium Dioxide", *Journal of Environmental Science and Health*, Vol. 31 No. 6, pp. 845-858, 1996.
- Bekbölet, M. and Balcıoğlu, I., "Photocatalytic Degradation Kinetics of Humic Acid in Aqueous TiO₂ dispersions: The influence of Hydrogen Peroxide and Bicarbonate Ion", *Water Science and Technology*, Vol. 34, pp. 73-80, 1996.

Bekbölet, M., Boyacıoğlu, Z., and Özkaraova, B., "The Influence of Solution Matrix on the Photocatalytic Removal of Color from Natural Waters", *Water Science and Technology*, Vol. 38, No. 6, pp. 155-162, 1998.

Bekbölet, M. Çeçen, F., and Özköşemen, G., "Photocatalytic Oxidation and Subsequent Adsorption Characteristics of Humic Acids", *Water Science and Technology*, Vol. 34, No. 9, pp. 65-72, 1996.

Bekbölet, M. and Özköşemen, G., "A Preliminary Investigation on the Photocatalytic Degradation of Model Humic Acid", *Water Science and Technology*, Vol. 33, No. 6, pp. 189-194, 1996.

Bekbölet, M., Süphandağ, S.A., and Uyguner, C.S., "An Investigation of the Photocatalytic Efficiencies of TiO₂ Powders on the Decolorization of Humic Acids", *Journal of Photochemistry and Photobiology A: Chemistry*, Vol.148, pp. 121-128, 2002.

Benfield, L.D., Judkins, J.F. and Weand, B.I., "*Process Chemistry for Water and Wastewater Treatment*", pp. 211-238, Prentice-Hall, Inc., New Jersey, 1982.

Black, A.P., Singley, J.E., Whittle, G.P. and Maudling, J.S., "Stoichiometry of the Coagulation of Color-Causing Organic Compounds with Ferric Sulphate", *Journal of American Water Works Association*, Vol. 55, pp. 1347-1366, 1963.

Bolto, B., Abbt-Braun, G., Dixon, D., Eldridge, R., Frimmel, F., Hesse, S., King, S., and Toifl, M., "Experimental Evaluation of Cationic Polyelectrolytes for Removing Natural Organic Matter from Water", *Water Science and Technology*, Vol. 40, No. 9, pp. 71-79, 1999

Bolto, B., Dixon, D., Eldridge, R., and King, S., "Cationic Polymer and Clay or Metal Oxide Combinations for Natural Organic Matter Removal", *Water Research*, Vol. 35, No. 11, pp. 2669-2676, 2001.

Bolto, B., Dixon, D., Eldridge, R., and King, S., "Removal of THM precursors by Coagulation or Ion Exchange", *Water Research*, Vol. 36, pp. 5066-5073, 2002.

Boyacıoğlu, Z., "Photocatalytic Degradation of Humic Acid in Aqueous Solutions", M.S. Thesis, Bogaziçi University, 1997.

Camel, V., Bermond, A., "The Use of Ozone and Associated Oxidation Processes In Drinking Water Treatment", *Water Research*, Vol. 32, No. 11, pp. 3208-3222; 1998.

Chang, C., Ma, Y., and Zing, F., "Reducing the Formation of Disinfection By-products by Pre-ozonation", *Chemosphere*, Vol. 46, pp. 21-30, 2002.

Cheng, W.P., "Comparison of Hydrolysis/Coagulation Behavior of Polymeric and Monomeric Iron Coagulation in Humic Acid Solution", *Chemosphere*, Vol. 47, pp. 963-969, 2002.

Chiang, P.C., Chang, E.E., and Liang, C.H., "NOM Characteristics and Treatabilities of Ozonation Processes", *Chemosphere*, Vol. 46, pp. 929-936, 2002.

Choudry, G.G., "Interaction of Humic Substances with Environmental Chemicals", *The Handbook of Environmental Chemistry*, Vol. 2, pp. 103-128, Springer Verlag Berlin, 1982.

Diaper, E. W., "Disinfection of Water and Wastewater Using Ozone" Johnson, J. D. (Eds), *Disinfection; Water and Wastewater*, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, pp. 211-231, 1977.

Dincer, B., "Comparison of Photocatalytic Efficiency of Various Forms of Titanium Dioxide by Using Humic Acid as a Model Compound", M.S. Thesis, Bogaziçi University, 1998.

Droste, R. L., *Theory and Practice of Water and Wastewater Treatment*, John Wiley & Sons, Inc., USA, 1997.

Duan, J. and Gregory, J., "Influence of Soluble Silica on Coagulation by Aluminium Sulphate", *Colloids and Surfaces*, Vol. 107, pp. 309-319, 1996.

Duan, J. and Gregory, J., "Coagulation by Hydrolysing Metal Salts", *Advances in Colloid and Interface Science*, pp. 475-502, 2003

Edwards, M., Boller, M., Benjamin, M.M., "Effect of Pre-ozonation on Removal of Organic Matter During Water Treatment Plant Operations", *Water Science and Technology*, Vol.27, pp.37-45, 1992.

Edzwald, J.K., "Coagulation in Drinking Water Treatment Particles, Organics and Coagulants", *Water Science and Technology*, Vol.27, No.11, pp.21-35, 1993.

Eggins, B.R., Palmer, F.L., and Byrne, J.A., "Photocatalytic Treatment of Humic Substances in Drinking Water", *Water Research*, Vol.31, No. 5, pp. 1223-1226, 1997.

EPA, Alternative Disinfectants and Oxidants Guidance Manual, EPA/815/R-99/014, USA, 1999.

Gaffney, J. S., Marley, N. A., and Clark, S. B., "Humic and Fulvic Acids and Organic Colloidal Materials in the Environment" Gaffney, J. S., Marley, N. A., Clark, S. B., (Eds.), *Humic and Fulvic Acids: Isolation, Structure, and Environmental Role*, ACS Symposium Series 651, American Chemical Society, Washington DC, pp. 2-16, 1996.

Gamble D.S. and Schnitzer, M., "The Chemistry of Fulvic Acids and Its Reaction with Metal Ions" in Singer, P. (Eds.), *Trace Metals and Metal-Organic Interactions*, 225-302, Ann Arbor Science, Ann Arbor, M.I, 1974 reference in Rebut, M. and Lurie, M., "Control of Organic Matter by Coagulation and Flocculation", *Water Science and Technology*, 24 pp. 1-20, 1993.

Gao, B.Y., Hahn, H.H., and Hoffmann, E., "Evaluation of Aluminum-Silicate Polymer Composite as a Coagulant for Water Treatment", *Water Research*, Vol. 36, pp. 3573-3581, 2002.

Gjessing, E. T., *Physical and Chemical Characteristics of Aquatic Humus*, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, 1976.

Gjessing, E.T., 1981 reference in Josephson, J., "Humic Substances," *Environmental Science and Technology*, Vol. 16, No. 1, pp. 20 A-24A, 1982.

Glaze, W. H., *Oxidation of Water Supply Refractory Species by Ozone with Ultraviolet Radiation*, EPA-600/2-80-110, USEPA Cincinnati, Ohio, 1980.

Gracia, R, Aragües, J.L., and Ovelleiro, J.L., "Study of the Catalytic Ozonation of Humic Substances in Water and Their Ozonation Byproducts", *Ozone Science & Engineering*, Vol. 18, pp.195-208, 1996.

Gregor, J.E., Nokes, C.J., and Fenton, E., "Optimising Natural Organic Matter Removal from Low Turbidity Waters by Controlled pH Adjustment of Aluminum Coagulation", *Water Research*, Vol.31, pp.2949-2958, 1997.

Hall, E.S. and Packham, R.F., "Coagulation of Organic Color with Hydrolyzing Coagulants", *Journal of American Water Works Association*, Vol. 57, pp. 1149-1166, 1965.

Hayes, M. H. B., "Humic Substances: Progress Towards More realistic Concepts of Structures" in Davies G., Ghabbour E. A. (Eds.), *Humic Substances: Structures, Properties and Uses*, Royal Society of Chemistry, pp. 1-27. 1998.

Huang, P.M., "Adsorption Processes in Soil" in Hutzinger, O. (Eds.), *The Hand Book of Environmental Chemistry*, Volume 2, Part A, pp. 54-65, Springer-Verlag Berlin, 1980.

Hu,Z., Chandran,K., Smets,B.F., and Grasso,D., "Evaluation of a Rapid Physical-Chemical Method for the Determination of Extant Soluble COD", *Water Research*, Vol.36, pp.617-624, 2002.

Huang, W., Chen, L., and Peng, H., "Effect of NOM Characteristics on Brominated Organics Formation by Ozonation", *Environment International*, Article in Press, 2003.

Hunca, G., "Competitive Interactions Among Natural Organic Matter and Metal Ions In Photocatalytic Oxidation Systems," M. S. Thesis, Boğaziçi University, 1999.

Hundt, T.R. and O'Melia, C.R., "Aluminum-Fulvic Acid Interactions: Mechanisms and Applications", *Journal of American Water Works Association*, Vol. 80, pp. 176-186, 1988.

Kaastrup, E. and Halmo, T.M., "Removal of Aquatic Humus by Ozonation and Activated Carbon Adsorption" in McCarthy, P., Suffet, I. H. (Eds.), *Aquatic Humic Substances, Influences on Fate and Treatment of Pollutants*, American Chemical Society, Washington DC, pp. 697-727, 1989.

Kam, S.K., and Gregory, J., "The Interaction of Humic Substances with Cationic Polyelectrolyte", *Water Research*, Vol. 35, No. 15, pp. 3557-3566, 2001.

Karabacakoğlu, E., "Photocatalytic Oxidation Efficiency of Titanium Dioxide in Hard Waters", M.S. Thesis, Boğaziçi University, 1998.

Kerç, A., "Oxidation of Aqueous Humic Substances by Ozonation", Ph.D. Dissertation, Boğaziçi University, 2002.

Kerç, A., Bekbölet, M., and Saatci, A., "Effect of Partial Oxidation by Ozonation on the Photocatalytic Degradation of Humic Acids", *International Journal of Photoenergy*, Accepted for Publication, 2003.

Kim, J.S., Chian, E.S.K., Saunders, F.M., Perdue, E.M., and Giabbai, M.F., "Characteristics of Humic Substances and their Removal Behavior in Water Treatment," in McCarthy, P., Suffet, I. H. (Eds.), *Aquatic Humic Substances, Influences on Fate and Treatment of Pollutants*, American Chemical Society, Washington DC, pp. 727-748, 1989.

Kruithof, C. J., van der Gaag, M. A., and Van Der Kooy, D., "Effect of Ozonation and Chlorination on Humic Substances in Water" in McCarthy, P., Suffet, I. H. (Eds.), *Aquatic Humic Substances, Influences on Fate and Treatment of Pollutants*, American Chemical Society, Washington DC, pp. 663-679, 1989.

Kusakabe, K., Aso, S., Hayashi, J. I., Isomura, and K., Morooka, S., "Decomposition of Humic Acid and Reduction of Trihalomethane Formation Potential in Water by Ozone with UV Irradiation", *Water Research*, Vol. 24, No. 6, pp. 781-785, 1990.

Lagaly, G., and Ziesmer, S., "Colloid Chemistry of Clay minerals: The Coagulation of Montmorillonite Dispersion", *Advances in Colloid and Interface Science*, Vol 101, pp. 105-128, 2003.

Langlais, B., Reckhow, D. A., and Brink D., *Ozone in Water Treatment Application and Engineering*, Lewis Publishers, Inc., USA, 1991.

Legrini, O., Oliveros, E., and Braun, A. M., "Photocatalytic Processes for Water Treatment," *Chemical Reviews*, Vol. 93, pp. 671-698, 1993.

Li, X.Z., Fan, C.M., and Sun, Y.P., "Enhancement of Photocatalytic Oxidation of Humic Acid in TiO₂ Suspensions by Increasing Ionic Strength", *Chemosphere*, Vol. 48, pp. 453-460, 2002.

Lu, X., Chen, Z., and Yang, X., "Spectroscopic Study of Aluminum Speciation in Removing Humic Substances by Al Coagulation", *Water Research*, Vol. 33, pp. 3271-3280, 1999.

MacCarthy, P. and Suffet, I. H., *Aquatic Humic Substances, Influences on Fate and Treatment of Pollutants*, American Chemical Society, Washington DC, 1989.

Manahan, S.E., "Interactions of Hazardous-Waste Chemicals with Humic Substances," in McCarthy, P., Suffet, I. H. (Eds), *Aquatic Humic substances, Influences on Fate and Treatment of Pollutants*, American Chemical Society, Washington DC, pp. 83-92, 1989.

McCoy, M. C., "Minimizing the Economic Impact of Organics on Ion Exchange Systems", *International Water Conference*, 1996.

Mao, J., Hu, W., Schmidt-Rohr, K., Davies, G., Ghabbour, E. A., and Xing, B., "Structure and Elemental Composition of Humic Acids: Comparison of Solid-State ^{13}C NMR Calculations and Chemical Analysis" in Davies, G., Ghabbour, E. A., (Eds.), *Humic Substances: Structures, Properties and Uses*, Royal Society of Chemistry, pp. 1-27, 1998.

Matthews, R. W., "Environment: Photochemical and Photocatalytic Processes. Degradation of Organic Compounds" in Pelizzetti, E., Schiavello, M., (Eds.), *Photochemical Conversion and Storage of Solar Energy*, pp.427-449, Kluwer Academic Publishers, The Netherlands, 1991.

Matsui, Y., Yuasa, Akira, and Li, F., "Pretreatment Effects on Activated Carbon Adsorption of Humic Substances: Distributed fictive Component Analysis", *Water Science and Technology*, Vol.40, No. 9, pp. 223-230, 1999.

Myllykangas, T., Nissinen, T. K., Rantakokko, P., Martikainen, P. J., and Vartiainen, T., "Molecular Size Fractions of Treated Aquatic Humus", *Water Research*, Vol. 36, pp., 3045-3053, 2002.

Nishijima, W., Mukaidami, F.T., and Okada, M., "DOC Removal by Multi-Stage Ozonation-Biological Treatment", *Water Research*, Vol. 37, pp. 150-154, 2003.

Oepen, B., Von, Kordel, W., and Klein, W., "Sorption of Nonpolar and Polar Compounds to Soils: Processes, Measurements and Experience with the Applicability of the Modified OECD-Guideline 106", *Chemosphere*, Vol. 22, No. 3-4, pp. 285-304, 1991.

O'Melia, C.R., Becker, W.C., and Au, K.K., "Removal of Humic Substances by Coagulation", *Water Science and Technology*, Vol. 40, pp. 47-54, 1999.

O'Melia, C.R., "Coagulation and Flocculation" in Weber, Jr., W.J., *Physicochemical Processes for Water Quality Control*, pp. 1-109, John Wiley & Sons, Inc, USA, 1990.

O'Melia, C.R., "Particle-Particle Interactions," in Stumm, W. (Eds.), *Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface*, pp. 385-403, John Wiley & Sons, Inc., USA, 1987.

Overbeek, J.Th.G. and Verveij, E.J.W., *Theory of the Stability of Hydrophobic Colloids*, Elsevier Scientific Publishing Company, Amsterdam, 1948.

Oxenford, J. L., "Disinfection By-Products: Current Practices and Future Directions" in Minear, R. A., Amy, G. L., (Eds), *Disinfection By-Products in Water Treatment: The Chemistry of Their Formation and Control*, CRC Press Inc., Boca Raton, pp. 3-14, 1996.

Özkaraova, E. B., "Effects of Nitrate and Chloride Ions on the Photocatalytic Degradation of Humic Acid," M.S. Thesis, Boğaziçi University, 1996.

Rebun, M. and Lurie, M., "Control of Organic Matter by Coagulation and Floc Separation," *Water Science and Technology*, Vol. 27, pp. 1-20, 1993.

Schneider, O.D., and Tobiasson, J.E., "Preozonation Effects on Coagulation", *Journal of American Water Works Association*, Vol. 92, No. 10, pp. 74-87, 2000.

Stephenson, R.J. and Duff, S.J.B., "Coagulation and Precipitation of a Mechanical Pulping Effluent-I. Removal of Carbon, Color and Turbidity," *Water Research*, vol. 30, pp. 781-792, 1996.

Stevenson, F. J., *Humus Chemistry, Genesis, Composition, Reactions*, John Wiley & Sons, New York, 1982.

Stumm, W., and Morgan, J.J. (Editors), *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, pp. 726-871, 3rd Edition, John Wiley & Sons, Inc., USA, 1996.

Stumm, W., and O'Melia, C.R., "Stoichiometry of Coagulation," *Journal of American Water Works Association*, Vol. 60, pp. 514-539, 1968

Stumm, W., *Chemistry of Solid Water Interface*, John Wiley & Sons, Inc., New York, 1992.

Takahashi, N., Nakai, T., Satoh, Y., and Katoh, Y., "Ozonolysis of Humic Acid and Its Effect on Decoloration and Biodegradability," *Ozone Science & Engineering*, Vol. 17, pp. 511-525, 1995.

Tchobanoglous, G. and Burton, F. L., *Wastewater Engineering : Treatment, Disposal and Reuse*, McGraw-Hill, Inc., Singapore, 1991.

Tobiason, J.E., Reckhow, D.A., and Edzwald, J.K., "Effects of Ozonation on Optimal Coagulant Dosing in Drinking Water Treatment", *Journal Water SRT Aqua*, Vol. 44, No. 3, pp. 142, 1995.

USEPA, UV Disinfection Process Design Manual, U. S. Environmental Protection Agency, Washington, DC, 1992.

Van Benschoten, J.E. and Edzwald, J.K., "Chemical Aspects of Coagulation Using Aluminum Salts-II. Coagulation of Fulvic Acid Using Alum and Polyaluminum Chloride", *Water Research*, Vol. 24, pp. 1527-1535, 1990.

VanLoon, G. W. and Duffy, S: J., *Environmental Chemistry*, Oxford University Press, Oxford, 2000.

Vik, E.A. and Eikebrokk, B., "Coagulation Process for Removal of Humic Substances from Drinking Water," in McCarthy, P., Suffet, I. H. (Eds.), *Aquatic Humic substances, Influences on Fate and Treatment of Pollutants*, American Chemical Society, Washington DC, pp. 385-408, 1989.

Vilge-Ritter, A., Masion, A., Boulange, T., Rybacki, D. and Bottero, J.Y., "Removal of Natural Organic Matter by Coagulation-Flocculation: A Pyrolysis-GC-MS Study", *Environmental Science and Technology*, Vol. 33, pp. 3027-3032, 1999.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G., and Lechevallier, M., "Impact of Enhanced and Optimized Coagulation on Removal of Organic Matter and Its Biodegradable Fraction in Drinking Water", *Water Research*, Vol. 34, No. 12, pp. 3247-3257, 2000.

Von Gunten, U., "Ozonation of Drinking Water: Part I. Oxidation Kinetics and Product Formation," *Water Research*, Vol.37, pp. 1443-1467, 2003.

Walker, H.W., and BOB, M. M., "Stability of Particle Floccs upon Addition of Natural Organic Matter under Quiquent Conditions," *Water Research*, Vol. 35, No. 4, pp. 875-882, 2000.

Wang, D., and Tang, H., "Modified Inorganic Polymer Flocculant-PFSi: Its Preparation, Characterization and Coagulation Behavior", *Water Research*, Vol. 35, No. 14, pp. 3418-3428, 2001.

Weber, W. J., *Physicochemical Processes for Water Quality Control*, John Wiley & Sons, New York, pp. 199-259, 1972.

Weinberg, H. S. And Glaze, W. H., "An Overview of Ozonation disinfection By-Products" in Minear, R. A., Amy, G. L., (Eds), *Disinfection By-Products in Water Treatment: The Chemistry of Their Formation and Control*, CRC Press Inc., Boca Raton, pp. 165-186, 1996.

Wigrd, D.L., Gray, K.A., and McAuliffe, K., "Removal of Algal-Derived Organic Material by Preozonation and Coagulation: Monitoring Changes in Organic Quality by Pyrolysis-GC-MS", *Water Research*, Vol. 30, No. 11, pp. 2621-2632, 1996.

Zhou, H. and Smith, D.W., "Advanced Technologies In Water and Wastewater Treatment," *Journal of Engineering Science*, Vol.1, pp. 247-264, 2002.

REFERENCES NOT CITED

Crittenden, J. C., Hu, S., Hand, D.W., and Green, S.A., "A Kinetic Model for H₂O₂/UV Process In a Completely Mixed Batch Reactor", *Water Research*, Vol.33, No. 10, pp. 2315-2328, 1999.

Hites R. A., Eisenreich S. J., *Sources and Fates of Aquatic Pollutants*, American Chemical Society, Washington DC, 1987.

Mill, T., "Chemical and Photooxidation" in Hutzinger, O. (Eds.), *The Hand Book of Environmental Chemistry*, Volume 2, Part A, pp. 77-99, Springer-Verlag Berlin, 1980.

Volk, C., Roche, P., Joret, J., and Paillard, H., "Comparison of the Effect of Ozone, Ozone-Hydrogen Peroxide System and Catalytic Ozone on the Biodegradable Organic Matter of a Fulvic Acid Solution", *Water Research*, Vol.31, No. 3, pp. 650-656, 1997.