TRACE-LEVEL METALS AND NATURAL ORGANIC MATTER INTERACTIONS: OXIDATIVE/ADSORPTIVE REMOVAL PATHWAYS

الأرافة المتوجعة ويراد والعرين

by

CEYDA SENEM UYGUNER

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ABSTRACT

The destructive removal of humic acids in natural waters has gained increased attention, because these substances are known to be major precursors of carcinogenic disinfection byproducts which are produced during chlorination. Since the conventional treatment methods are expensive and complicated, heterogeneous photocatalytic degradation processes using TiO_2 have been applied as an alternative treatment for the destruction of humic acid.

This study was conducted to investigate the effects of chromium and manganese ions on the photocatalytic degradation of humic acid (10 mg L^{-1}) in aqueous medium at neutral pH conditions (pH≃6.7). Bench scale experiments were carried out using titanium dioxide (0.25 mg mL⁻¹) as the photocatalyst and Black Light Fluorescent Lamp as the irradiation source. For comparison purposes, the photocatalytic degradation of humic acid was performed both in the presence and absence of metal ions. The degradation was followed by pseudo first order and Langmuir-Hinshelwood kinetics in terms of Color436, Color400, UV280 and UV₂₅₄. The presence of chromium and manganese ions resulted in decreased removal rates on the photocatalytic degradation of humic acid compared to the baseline rate of humic acid alone. Pseudo first order reaction rate constants for Color₄₃₆ and UV₂₅₄ were found to be 3.86×10^{-2} min⁻¹ and 2.73×10^{-2} min⁻¹ in the absence of metal ions. Color₄₃₆ removal rate constant decreased to 3.13×10^{-2} min⁻¹ in the presence of 0.10 mg L⁻¹ chromium ion and in the presence of 0.05 mg L^{-1} manganese ion, a value of 3.37×10^{-2} min⁻¹ was attained. On the other hand, a similar trend was observed for UV254, the removal rate constant in the presence of chromium was calculated to be the lowest with a value of 2.06×10^{-2} min⁻¹ whereas, in the presence of manganese it was found to be 2.31×10^{-2} min⁻¹. The decrease in the photocatalytic oxidation rate might be explained by the formation of a weak complex between humic acid and the metal ion which might have blocked the active sites on the TiO₂ surface. Complimentary adsorption experiments were also performed to evaluate the effect of adsorption intensity on the photocatalytic degradation rates. The results indicated that no significant difference was observed with the adsorption capacity (K_F) values, but compared to the other two, the humic acid + manganese system exhibited the highest values.

ÖZET

Doğal sularda bulunan humik asitlerin giderimi son zamanlarda önem kazanmıştır, çünkü bu maddelerin klorlama sırasında, kanserojen dezenfeksiyon yan ürünlerinin oluşumuna neden olduğu bilinmektedir. Geleneksel arıtma yöntemleri pahalı ve komplike olduğundan, titandioksit kullanılarak yürütülen heterojen fotokatalitik parçalanma prosesleri, humik asit giderimi için alternatif yöntem olarak uygulanmaktadır.

Bu çalışmada, nötr pH koşullarında (pH≃6.7) krom ve mangan iyonlarının, humik asidin (10 mg L^{-1}) fotokatalitik olarak parçalanması üzerine olan etkisi incelenmiştir. Fotokatalizör olarak titandioksit ve ışık kaynağı olarak da siyah ışıklı flurasan lamba kullanılarak laboratuvar ölçekli deneyler yapılmıştır. Karşılaştırma yapabilmek için, humik asidin fotokatalitik degradasyonu ortamda metal varken ve metal yok iken incelenmiştir. Humik asidin degradasyonu Langmuir-Hinshelwood ve birinci dereceden reaksiyon kinetiği ile Renk₄₃₆, Renk₄₀₀, UV₂₈₀ ve UV₂₅₄ parametreleri cinsinden incelenmiştir. Ortamda krom ve mangan iyonlarının bulunması humik asidin fotokatalitik degradasyon hızının azalmasına sebep olmuştur. Metal iyonları bulunmazken, Renk436 ve UV254 için birinci derece hız sabitleri sırasıyla 3.86x10⁻² min⁻¹ and 2.73x10⁻² min⁻¹ olarak bulunmuştur. Ortama 0.10 mg L^{-1} krom iyonu eklendiğinde Renk₄₃₆ giderim hız sabiti 3.13×10^{-2} min⁻¹ ve 0.05 mg L^{-1} mangan eklendiğinde ise 3.37×10^{-2} min⁻¹ olarak hesaplanmıştır. Diğer taraftan UV₂₅₄ gideriminde de Renk436'da gözlendiği gibi azalma görülmektedir. En düşük değerdeki hız sabiti ortamda krom varken UV_{254} için 2.06x10⁻² min⁻¹ olarak hesaplanmıştır, diğer taraftan ortamda mangan varken bu değer 2.31x10⁻² min⁻¹ bulunmuştur. Fotokatalitik oksidasyon gideriminde gözlenen bu düşüşler, humik asit ile metal iyonları arasında oluşan ve titandioksit yüzeyindeki reaktif merkezlerin örtülmesine sebep olan zayıf bir kompleks oluşumuyla açıklanabilir. Adsorpsiyonun fotokatalitik degradasyon hızına olan etkisini anlayabilmek için tamamlayıcı adsorpsiyon deneyleri de yapılmıştır. Elde edilen sonuçlara göre adsorpsiyon kapasite değerlerinde (K_F) çok önemli farklılıklar gözlenmemiştir, fakat diğer ikisiyle kıyaslandığında humik asit + mangan sisteminin en yüksek K_F değerini gösterdiği saptanmıştır.

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1. INTRODUCTION

Trace metals such as iron, copper, chromium, cadmium, lead, mercury, manganese and zinc are the major constituents of most of the aquatic systems. They originate from the natural interactions of water, sediments and the atmosphere. It is frequently desirable to measure and control the concentrations of these substances, because the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water because of their toxicity. Their impact on aquatic life and reactivity in aquatic system depends on the species formed due to association with other dissolved or suspended components of the system.

Humic substances are the dominant type of organic matter naturally present in ground and surface waters. Their role in aquatic environment received importance because of their interactions with other species in the environment. They are known to complex with metals and organic pollutants such as pesticides, and most significantly they are the precursors of trihalomethanes (THMs) which are mutagenic, halogenated compounds in water formed after chlorination.

The destructive removal of humic acids in natural waters has gained increased attention, because these substances are known to play an important role in the fate of organic pollutants Recent publications on the oxidative destruction of the humic acids in natural waters cover the application of advanced oxidation methods such as UV, $UV + H_2O_2$, ozone and radiation + ozone (Arai *et al.*, 1986; Gilbert, 1988; Backlund, 1992). Since these conventional treatment methods are expensive and complicated, heterogeneous photocatalytic processes using irradiated dispersions of TiO₂ have been applied as an alternative treatment for the destruction of humic acid. Recently, the photocatalytic degradation of humic acids in aqueous TiO₂ suspensions have been extensively studied (Bekbölet 1996; Bekbölet and Balcioğlu, 1996; Bekbölet and Özkösemen, 1996; Bekbölet *et al.*, 1998). The impact of natural water conditions on the photocatalytic degradation of humic acids in the presence of hardness causing calcium and magnesium ions and common counter ions such as chloride, nitrate, sulfate and phosphate and the results were also

investigated and the results were explained in terms of pseudo first order and Langmuir-Hinshelwood rates (Bekbölet,1999).

In this study, the photocatalytic degradation of humic acid in aqueous medium was carried out in the presence of chromium and manganese ions. The effects of the trace metal ions on the adsorptive properties of the photocatalyst and the photocatalytic oxidation rate of humic acid were investigated. Pseudo first order and Langmuir-Hinshelwood kinetics were applied to the obtained data and the applicability of the Freundlich adsorption constants were investigated in relation to the photocatalytic removal rates.

2. THEORETICAL BACKGROUND

2.1. Humic Substances

Humic substances, products of chemical and biological degradation of plant and animal residues and of synthetic activities of microorganisms, are the predominant type of organic matter naturally present in ground and surface waters. Their size, molecular weight, elemental composition, structure, and the number and position of functional groups vary, depending on the origin and the age of the material. They have been studied extensively for more than 200 years; however, much remains unknown about their structure and properties. (Gaffney *et al.*, 1996)

In general humic substances are described as a mixture of naturally occurring, polydisperse, heterogeneous polyelectrolytes. They can be divided into three fractions; fulvic acid, humic acid and humin. Fulvic acids are those organic materials that are soluble in water at all pH values. Humic acids are those materials that are insoluble at acidic pH values (pH < 2) but are soluble at higher pH values. Humin is the fraction of natural organic materials that is insoluble in water at all pH values. On the basis of their solubilities at different pH, these fractions can be differentiated from each other (Aiken *et al.*, 1985).

The humic content of soil varies from 0 to almost 10 %. In surface waters, the humic content which is expressed as dissolved organic carbon (DOC), varies from 0.1 to 50 ppm in dark-water swamps. In ocean waters, the DOC varies from 0.5 to 1.2 ppm at the surface, and the DOC in samples from deep groundwaters varies from 0.1 to 10 ppm. In addition about 10% of the DOC in surface waters is found in suspended matter, either as organic or organically coated inorganic particulates.

Humic substances are significant in aquatic systems for several reasons. They are natural high molecular weight constituents of surface waters which give the water a yellow-brownish color, they can complex with metals and organic pollutants such as pesticides, and

most significantly they are the precursors of mutagenic halogenated compounds in water formed after chlorination.

Humic substances (HS), their water-soluble subfractions humic (HA) and fulvic acids (FA) are the main sink for refractory organic carbon in the environment, acting as beneficial buffers for pollutants (e.g. metals, pesticides). HS generally consist of polydisperse, hardly separable mixtures of related organic macromolecules exhibiting a broad spectrum of (sub)structures, molecular weights, and functionalities. Due to this complexity the characterization of HS and their manifold environmental processes (e.g. metal binding) requires analytical tools consisting of efficient fractionation and spectroscopic methods.

2.1.1. Structure and Composition of Humic Substances

Humic substances have a wide range of molecular weights and sizes, ranging from a few hundred for fulvic acid to tens of thousands for humic acid and humin fractions. Humic materials vary in composition depending on their source, location, and method of extraction. Differences between humic acids and fulvic acids, can be explained by variations in molecular weight, numbers of functional groups (carboxyl, phenolic OH) and extent of polymerization. Humic acids contain more hydrogen, carbon, nitrogen, and sulfur and less oxygen than fulvic acids. The range of elemental composition of humic materials is approximately 40-60 % carbon, 30-50 % oxygen, 4-5 % hydrogen, 1-4 % nitrogen, 1-2 % sulfur, and 0-0.3 % phosphorus. 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 (Gaffney *et al.*, 1996).

Chemical properties of humic substances are shown in Figure 2.1. As can be seen from the figure, carbon and oxygen contents, acidity and degree of polymerization all change systematically with increasing molecular weight. The low-molecular-weight fulvic acids have higher oxygen but lower carbon contents than the high-molecular-weight humic acids. The total acidities of fulvic acids (900 - 1400 meq/100g) are considerably higher than that of humic acids (400 - 870 meq/100g).



Figure 2.1. Chemical Properties of Humic Substances (Stevenson, 1982)

Humic substances are complex aromatic macromolecules with amino acids, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups. They consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with major functional groups such as carboxylic acid, phenolic and alcoholic hydroxyls, ketone and quinone groups. The hypothetical structure for humic acid contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings. A possible model structure of humic acid which was suggested by Stevenson (1982) is given below in Figure 2.2.



Figure 2.2. The Model Structure of Humic Acid (Stevenson, 1982)

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The structures of fulvic acids are more aliphatic and less aromatic than humic acids; and fulvic acids are richer in carboxylic acid, phenolic, and ketonic groups. This is responsible for their higher solubility in water at all pH values. The presence of both polar and nonpolar substituents in their molecular structures allows the humic materials to function as surfactants, with the ability to bind both hydrophobic and hydrophilic materials. This property in combination with their colloidal properties, give humic and fulvic materials the ability to play important roles in transporting both water soluble and insoluble species in the environment. Humic acids are generally more hydrophobic than the fulvic acids, thus the speciation of hydrophobic pollutants may be related to that of the humic acid fraction. Adsorption of the humic acids will thus also immobilise the hydrophobic pollutants. Further it is also known that metal ions form complexes mainly with the functional groups of humic acids, and that the adsorbed humic matter plays an important role in contaminant binding to mineral particles.

Humic materials have a high content of radicals, probably of the semiquinone type, which are more dominant in humic acids than in fulvic acids. These free radicals can be found as permanent components or as transient species, that are generated by solar irradiation, pH changes or chemical reduction with lifetimes of minutes to hours. They also play important roles in polymerization or oxidation-reduction reactions. Humic materials can reduce metals with estimated reduction potentials of 0.5-0.7 V leading to an important effect on the migration of reducible cations.

Aquatic humic acid exhibits an absorbance spectrum that the absorbance values generally decrease with increasing wavelength with no absorption above about 550 nm. As can be seen from Figure 2.3., the humic materials absorb most of the solar energy between the region 300 and 500 nm in which a number of photochemical processes can be initiated. This light absorption can produce peroxy radicals and hydroxyl radicals as well as hydrated electrons, hydrogen peroxide, singlet oxygen, and superoxide. These species can also promote redox reactions. In addition, humic acids can photosensitize nonpolar organics such as herbicides and possibly accelerate their decomposition and detoxification (Gaffney *et al.*, 1996)



Figure 2.3. Absorption Spectrum of Humic Acid (Gaffney et al., 1996)

According to Chen and Schnitzer (1976), fulvic and humic acids behave like flexible, linear, synthetic polyelectrolytes. It was concluded that the humic materials are composed of condensed rings and numerous linkages about which relatively free rotation occurs.

Cameron *et al.* (1972) visualized the humic acid molecules in solution as a series of charged and branched strands which coil and wind randomly with respect to both space and time. The mean distribution of molecular mass is explained to be spherical and Gaussian about the center. Branching results in an increased coil density within the molecule and leads to the formation of more compact spheres. The humic acid molecules were also described as a structure which are able to exchange with bulk solvent molecules. It was pointed out that humic substances are negatively charged due to the abundance of carboxylic and phenolic type of groups. According to Cameron *et al.* (1972) the dissolved humic substances can be described by an extended conformation which adjusts itself due to changes in the environmental conditions. This results in a reduction or an increase of the electrostatic repulsion and formation of a more tightly or respectively loosely coiled configuration. The factors that are important in controlling the molecular conformation of humic materials are pH, concentration of the humic, and ionic strength of the system. The humic materials are rigid uncharged colloidal particles at high sample concentrations (>3.5 g/L), low pH (<3.5) and high electrolyte concentrations (> 0.05 M). On the other hand at low sample concentrations, high pH, and low electrolyte concentrations, humics and fulvics exist as flexible linear polyelectrolytes. In fresh waters, where both humic acid concentration and ionic strength would be expected to be low, and the pH is greater than 3.0, humic materials should exist as linear polyelectrolytes (Ghosh and Schnitzer, 1980).

Hayes *et al.* (1989) in a recent study, have made a comprehensive review of the different analytical techniques which can be used to characterize humic substances found in literature. The first method to differentiate between the humics in the different ecosystems is based on the elemental content as shown in Table 2.1 below.

Table 2.1. Mean elemental compositions of different humic substances from different origin expressed as weight percentage. (All values are on ash-free and moisture free basis) (Rice and MacCarty, 1991).

		Humic	Acid			Fulvic	Acid	
Element	Soil	Fresh-water	Marine	Peat	Soil	Fresh-water	Marine	Peat
С	55.4	51.2	56.3	57.1	45.3	46.7	45	54.2
Н	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
0	36.0	40.4	31.7	35.2	46.2	45.9	45.1	37.8

As can be seen from Table 2.1, humic acids and fulvic acids vary in elemental composition depending on their origin. The carbon content of humic acid is higher than that of fulvic acid whereas the oxygen content exhibits a lower weight percent. On the avarage humic acids contain more hydrogen, nitrogen, and sulfur and less oxygen than fulvic acids.

Another convenient method to study the relation between the elemental content and the

origin of the humic material is based on the graphical method, developed by Van Krevelen (1961) in which the atomic hydrogen to carbon ratio was plotted as a function of the atomic oxygen to carbon ratio. These diagrams have been frequently used by Visser (1983) to illustrate compositional differences between fulvic acid, humic acid and humin, and to show variations in humic substances from different origins, e.g. from fresh water, marine water, soil or peat (Rice and MacCarty, 1991).

Other useful analytical techniques are for example; fluorescence spectroscopy, UV-visual spectrophotometry, infra-red spectroscopy, NMR and potentiometric titrations. Based on these techniques a sample of a specific humic substance can be characterized and classified. To study the interactions of a certain humic acid sample with other species present in the system, soil type or ecosystem it represents should be known.

2.1.2. Formation of Humic Substances

The formation of humic substances is one of the least understood aspects of humus chemistry. Figure 2.4 shows the natural synthesis of humic materials (Stevenson, 1982).



Figure 2.4. Natural Synthesis of Humus (Stevenson, 1982)

The synthesis is based on the condensation of quinones or phenolic compounds, which are formed in the biological transformation of plant residues, and the most important compounds involved in this respect are lignin, carbohydrates, and proteins. 50-60 % carbohydrates, 1-3 % proteins, 10-30 % lignin, and some phenolic compounds participate in the humification process. Lignin is considered to be the most important among this group of organics. This is due to the fact that carbohydrates and proteins are more available for the soil organisms and they have a higher chemical decomposition rate compared to that of lignin.

Several pathways exist for the formation of humic substances during the decay of plant and animal residues in soil. The classical theory is that humic substances represent modified lignins, but the majority of present day investigators favor a mechanism involving quinones. In practice all pathways might be considered as likely mechanisms for the synthesis of humic and fulvic acids in nature. They might operate in all soils, but not to the same extent or in the same order of importance.

The formation of humus depends on factors such as population and activity of microorganisms, vegetation, and on the hydrothermal conditions. The physical and chemical properties of the soil are also of great importance, both with regard to the rate of the humification process and to the composition of the humus products.

2.1.3. Environmental Effects of Humic Substances

Humic substances play an important role in the behaviour and mobility of metal ions in the natural environment. They interact with metal ions by complexation and ion-exchange mechanisms. Depending on the environmental conditions, this interaction may lead to solubilization or immobilization of the metal. Thereby, humic substances can control metal ion concentrations in soils and natural waters and affect the mobility of metals through soils and aquifers. Soil and peat humic substances found in the different terrestrial systems may leach into the groundwater and can be transported until they settle in one of the sediments. The composition of the different ecosystems is mainly controlled by a net balance of formation, degradation, and transfer of the humics.

Humic substances can neutralize hazardous chemicals by complexation with toxic metals or by association with toxic organic chemicals. This association may contribute to a greater persistence of the contaminants and to a decreased toxicity to plants and living organisms in the environment. (Benedetti *et al.*, 1995)

The presence of humic substances in a water supply can effect water quality adversely in several ways. They contribute an undesirable, yellow to brown color to drinking water which is an esthetical problem. In addition, humic substances have an environmental impact on water and wastewater treatment processes. It is known that humic substances serve as precursors of potentially carcinogenic trihalomethanes (THM) and other chlorinated byproducts which are produced during chlorination process in drinking water treatment. The ozonation of the biologically refractory humic substances can produce biodegradable byproducts and promote microbial growth of these components. They can stabilize dispersed and colloidal particles during coagulation processes. They can also precipitate in the distribution system which may lead to deterioration of tap water quality and increase the need for interior cleaning of pipes. Therefore, it is desirable to minimize the concentration of humic substances in drinking water supplies. An understanding of the mechanisms by which humic substances interfere with treatment processes, has considerable economic advantage (Suffet and MacCarty, 1989).

2.2. Trace Metals

2.2.1. Trace Metals in Aquatic Systems

Trace metals such as iron, copper, chromium, cadmium, lead, mercury, manganese and zinc are the major constituents of most of the aquatic systems. They originate from the natural interactions of water, sediments and the atmosphere. The range of trace metal concentrations in environmental freshwaters is given in Table 2.2. Their impact on aquatic life and reactivity in aquatic system depends on the species formed due to association with other dissolved or suspended components of the system. Many of these are organic species namely humic substances which have the capacity to bind metals.

Element	River and lake upstream	Surface water	Groundwater	All types
Iron	1-3925	150-5000	0.15	0.15-5000
Copper	0.11-200	14-110	3.7	0.11-200
Chromium	0.05-23	0.2-180	1.0	0.05-180
Cadmium	0.03-5	4-130	100-2600	0.03-2600
Lead	0.13-60	17-42	-	0.13-60
Mercury	0.009-1.3	-	-	0.009-1.3
Manganese	0.97-1835	70-500	3.2	0.97-1835
Zinc	0.86-630	2.5-250	8.9	0.86-630

Table 2.2. Range of Trace Metal Concentrations in Environmental Freshwaters ($\mu g L^{-1}$) (Crompton, 1997)

Manganese is one of the trace elements in the earth's crust. It turns into a soluble form in groundwaters due to reducing conditions of soil and rocks. Once it is exposed to air, it is oxidized and accumulates in sediments as manganese dioxide. The quantity of manganese has great importance for drinking and process waters. It causes undesirable taste and

aesthetic problems in drinking waters. For this reason, the presence of manganese content is limited by 0.05 mg L^{-1} in drinking waters and by 0.2 mg L^{-1} or less in industrial waters.

Chromium is an element found in many minerals widely distributed in the earth's crust. It occurs in nature in two common oxidation states, Cr (III) and Cr (VI). Trivalent forms are hydrolyzed completely in natural waters leading to a hydroxide precipitate formation. Chromium (VI) compounds, especially chromates are generated and used in industries, therefore chromium contaminated wastes from many sources are usually discharged to the environment as hexavalent chromium in the form of chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$). Hexavalent Cr is toxic and carcinogenic. For this reason, the permissible level for chromium in drinking waters has been restricted to 0.10 mg L⁻¹ (Sawyer *et al.*, 1994).

2.2.1.1. Manganese in Water

Manganese in natural waters usually exist in either of the +2, +3, +4, +6 or +7 oxidation states; in dissolved, colloidal and suspended forms. The +2 oxidation state which is faint pink in color is stable. The Mn^{2+} ion is a labile metal ion and a poor reducing agent. On the other hand, the Mn^{3+} ion is a strong oxidant. In acidic solution, it can be created from MnO_4^- and Mn^{2+} . The Mn^{4+} oxidation state is not very common, but in a reaction involving this ion, MnO_2 is readily precipitated. Not much information was given on the Mn^{5+} oxidation state, except that MnO_4^{2-} is reduced by e^-_{aq} in base to yield MnO_4^{3-} . MnO_4^{2-} is stable in basic solution. The +7 oxidation state is stable, and can be hydrolyzed to MnO_4^- which is a useful oxidant for organic substrates, such as hydrocarbons, aldehydes and alcohols.

The removal of manganese from aqueous solution (pH=9) by oxidation with dissolved molecular oxygen was shown to be autocatalytic in nature (Stumm and Morgan, 1996). The oxidation of manganese (II) could be explained by the following reactions:

$$Mn(II) + O_2 \longrightarrow MnO_{2(s)} \qquad slow \qquad (1)$$

$$Mn(II) + MnO_{2 (s)} \longrightarrow Mn(II).MnO_{2 (s)} \quad rapid \qquad (2)$$

$$Mn(II) MnO_{2(s)} + O_2 \longrightarrow 2MnO_2 \qquad \text{very slow} \qquad (3)$$

Stumm and Morgan (1996) showed that in waters containing dissolved oxygen, Mn (IV) is the only stable oxidation state for manganese and suggested the kinetics of the autocatalytic rate expression as follows:

$$\frac{-d\left[\mathrm{Mn}(\mathrm{II})\right]}{dt} = k_0 \left[\mathrm{Mn}(\mathrm{II})\right] + k \left[\mathrm{Mn}(\mathrm{II})\right] \left[\mathrm{MnO}_2\right]$$
(4)

In solution, manganese ion exists as the hydrated ion in the form of $Mn(H_2O)_6^{2^+}$. But it hydrolyzes and forms hydroxo species. Reactions of complex ion formation which increase the solubility of manganese (II) hydroxide are:

$$Mn^{2+} + OH^{-} \longleftrightarrow MnOH^{+} \qquad K_{1} = 10^{3.9} \qquad (5)$$
$$Mn^{2+} + 3OH^{-} \longleftrightarrow Mn(OH)_{3}^{-} \qquad K_{2} = 10^{8.3} \qquad (6)$$

Given below are the reduction potentials of manganese in acidic and basic solutions:

Acidic solution

- $Mn^{2^+} + 2e^- \longleftrightarrow Mn$ $E_o = -1.18 V$ (7)
- $Mn^{3+} + e^- \longleftrightarrow Mn^{2+} \qquad E_o = 1.50 V \qquad (8)$

$$MnO_2 + e^- + 4H^+ \longleftrightarrow Mn^{3+} + 2H_2O \qquad E_0 = 0.95 V \qquad (9)$$

$$MnO_4^- + e^- + H^+ \longleftrightarrow HMnO_4^- \qquad E_o = 0.90 V \qquad (10)$$

Basic Solution

$Mn(OH)_2 + 2e^-$	\leftrightarrow Mn + 20H ⁻	$E_{o} = -1.56 V$		(11)
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$$Mn_2O_3 + 3H_2O + 2e^- \longleftrightarrow 2Mn(OH)_2 + 2OH^- \qquad E_o = -0.234 V$$
(12)

$$2MnO_2 + H_2O + 2e^- \longleftrightarrow Mn_2O_3 + 2OH^- \qquad E_o = 0.146 V$$
(13)

$$MnO_4^{3-} + 2H_2O + e^- \longleftrightarrow MnO_2 + 4OH^- \qquad E_0 = 0.93 V$$
(14)

$$MnO_4^{2-} + e^- \longleftrightarrow MnO_4^{3-} \qquad E_o = 0.27 V \qquad (15)$$

$$MnO_4^- + e^- \iff MnO_4^{2-}$$
 $E_0 = 0.56 V$ (16)

In natural waters the following redox reaction takes place;

Oxidation:

$$\frac{1}{2}\operatorname{MnCO}_{3}(s) + \operatorname{H}_{2}O \longleftrightarrow \frac{1}{2}\operatorname{MnO}_{2}(s) + \frac{1}{2}\operatorname{HCO}_{3}^{-} + \frac{3}{2}\operatorname{H}^{+} + e^{-} \log \operatorname{K} = -8.9 \quad (17)$$

Reduction:

$$\frac{1}{4}O_2(g) + H^+ + e^- \longleftrightarrow \frac{1}{2}H_2O \qquad \log K = +13.75 \qquad (18)$$

The overall reaction is obtained by combining the two reactions:

$$\frac{1}{2}MnCO_{3} + \frac{1}{4}O_{2} + \frac{1}{2}H_{2}O \longleftrightarrow \frac{1}{2}MnO_{2} + \frac{1}{2}HCO_{3}^{-} + \frac{1}{2}H^{+} \qquad \log K = +4.85$$
(19)

where log K is the equilibrium constant for the redox reaction in neutral water, pH=7.00 at $25^{\circ}C$.

Since log K is positive, $\Delta G ^{\circ} < 0$ leading to a negative free energy change ($\Delta G^{\circ} = -RT \ln K$), the reaction is thermodynamically possible in neutral aqueous solutions at standard concentrations indicating that soluble manganese (II) can be oxidized to manganese (IV) in natural waters (Stumm and Morgan, 1996).

2.2.1.2. Chromium in Water

Chromium exists in a number of different oxidation states. These species differ in their solubility and tendency to be adsorbed by soil or other materials in natural waters.

$$CrO_{4}^{2-} \xrightarrow{\leq 1.0 \text{ V}} CrO_{4}^{3-} \xrightarrow{> 1.2 \text{ V}} Cr(IV) \xrightarrow{> 1.5 \text{ V}} Cr(III) \xrightarrow{-0.41 \text{ V}} Cr(III) \xrightarrow{-0.91 \text{ V}} Cr(III) \xrightarrow{-$$

The concentration and mobility of chromium depends strongly on its speciation characteristics.



Figure 2.5. Speciation of Chromium (Nriagu and Nieboer, 1988)

Chromium speciation in natural waters is affected by pE (redox) and pH conditions (Figure 2.5). Most of the soluble chromium in surface waters may be present as Cr (VI), which

predominates under oxidizing conditions and a small amount may be present as Cr (III) organic complexes under more reducing conditions. Chromium (VI) is extensively hydrolyzed in water.

$$H_2CrO_4 \longleftrightarrow H^+ + HCrO_4^- \qquad K_{a1} = 10^{0.6}$$
 (20)

$$HCrO_4^{-} \longleftrightarrow CrO_4^{2-} + H^{+} \qquad K_{a2} = 10^{-5.9}$$
(21)

The equilibrium between $HCrO_4^-$ and CrO_4^{2-} is pH dependent. At low pH, the reaction shifts to the left and favors the formation of $HCrO_4^-$. At high pH, where the H⁺ concentration is lower, the reaction shifts to the right, and CrO_4^{2-} predominates. In natural waters, the pH is between 6 and 8, so CrO_4^{2-} ion is the dominant species (Fig. 2.5). At Cr (VI) concentrations above 500 mg L⁻¹ (0.01 M), the $HCrO_4^-$ ion dimerizes to give $Cr_2O_7^{2-}$ ion in acidic environments.

$$2HCrO_4^- \longleftrightarrow Cr_2O_7^{2-} + H_2O \qquad K = 10^{2.2}$$
(22)

The dominant Cr (III) species occurring in groundwater are Cr^{3+} , $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$ and $Cr(OH)_4^-$. The speciation of Cr (III) is known to be pH dependent and the related reactions are given below:

$$Cr^{3+} + H_2O \longleftrightarrow CrOH^{2+} + H^+$$
 (23)

$$CrOH^{2+} + H_2O \longleftrightarrow Cr(OH)_2^{+} + H^{+}$$
(24)

$$Cr(OH)_3 + H_2O \longleftrightarrow Cr(OH)_4^- + H^+$$
 (25)

In natural groundwaters with a pH between 6 and 8, $Cr(OH)_2^+$ is the dominant species. $CrOH^{2+}$ and Cr^{3+} predominate in more acidic waters (pH<6), on the other hand $Cr(OH)_3$ and $Cr(OH)_4^-$ predominate in more alkaline waters (pH>8) (Nriagu and Nieboer, 1988).

According to Hem (1977), the low solubility of Cr (III) solid phases Cr_2O_3 and $Cr(OH)_3$, is the major reason why Cr (III) generally makes up a small percentage of the total chromium concentration in natural or polluted groundwaters.

Positively charged ions such as Cr (III), which is the dominant species below a pH of 4, are generally adsorbed by clay minerals that have high cation exchange capacities and low pH_{pzc} in the order of 2-2.5. In the anionic form, $HCrO_4^-$ and CrO_4^{2-} , Cr (VI) is attracted to positively charged surfaces, such as iron, manganese, aluminum oxides and hydroxides. These substances commonly coat aquatic materials and have a high pH_{pzc} of 6.7-8.5 (Stumm and Morgan, 1981). Adsorption of Cr (VI) characteristically decreases with increasing pH due to the decrease in positive surface charge of the adsorbing medium.

2.2.2. Humic Acid-Trace Metal Interactions

Humic substances are complex molecules whose structure and reactions are not fully understood. They contain a variety of functional groups which provide a range of possible metal binding sites. The strength and the ease of the interaction of metals with humic acids mostly depends on; the affinity of the metal ion for that type of site, stereochemical factors such as the position of the site within the humic acid molecule and the nature of the functional groups. Chelation by neighboring carboxyl and phenolic groups is the major mode of metal complexation. By blocking certain functional groups on the humic substances and exposing the modified humic material to metals in solution, it is possible to understand the functional groups involved in the complexation of metals. The order of decreasing affinity of metal ions to chelating is roughly as follows (Livens, 1991):

 $Fe^{+3} > Cu^{+2} > Ni^{+2} > Co^{+2} > Zn^{+2} > Fe^{+2} > Mn^{+2}$

Puchalski and Morra (1992) explained that humic acids can form a micelle-like cage structure by metal ion-bridging interactions. Depending on the pH of the aqueous solution, the polyelectrolytic nature of the humic acid will result in dissociation of the carboxyl and hydroxyl groups due to electrostatic interactions.

Lu *et al.* (1997) investigated the reactions of humic substances with manganese (VII) and chromium (VI). As a result it was reported that manganese (II) interacts directly with carboxylate anionic groups forming weak, outer-sphere complexes with humic substances. This was in accordance with the findings of Gamble *et al.* (1975) who had pointed out for

binding of manganese (II) with fulvic acid. On the other hand, the stability constant determined by the cation-exchange method gave a log K value of 2.0 (± 0.1) (Lu *et al.*, 1997).

The reduction of Cr (VI) in the presence of humic substances was studied and the rate of reduction was related to humic acid concentration, pH, temperature and UV-vis radiation. The reaction of chromium (VI) and humic substances with UV-visible spectroscopy was followed by measuring the absorbance of mixtures over time and the mechanism of reaction was explained in two steps. The first step was the formation of chromium (VI) complex with diol, carboxylic acid and polyphenol groups in humic substances. The next step was a redox process occurring under acidic conditions, in which humic substances were detected to reduce chromium (VI) to chromium (V) as an intermediate, and then to chromium (III) which was complexed by humic substances (Lu et al., 1997). In accordance with this, Nakayama et al. (1981) found that naturally organic matter could bind chromium (III) in sea water. It was observed that some amino acids and polyhydric organic acids formed complexes with chromium (III) under conditions prevalent in natural sea water. On the other hand, it was also explained by Lu et al. (1997) that chromium (V) is a highly stable intermediate at room temperature and neutral pH, which may result from a complex with ligands such as carboxylic acid and/or polyphenol groups in the humic substances. The possible structures of the chromium (V) complex with humic substances are shown in Figure 2.6.



Figure 2.6. Possible Structures of Chromium (V) Complex with Humic Substances (Lu et al., 1997)

Bidoglio *et al.* (1997) also studied humic acid binding of chromium (III) by different fluorescence methods. In the analysis of low concentration metal ion-HA interactions only the binding of predominant ions; aqua ion Cr^{3+} and the first hydroxo complex $Cr(OH)^{2+}$ were taken into account.

Goodgame *et al.* (1984) studied the interaction of Cr (VI) with humic acid in aqueous solution in the pH range 4 to 9. The reduction of chromium (VI) with organic compounds revealed chromium (V) compounds that were relatively persistent at a pH of 5.6. At lower pH values solids containing chromium (III) were formed.

2.3. Advanced Oxidation Processes

Oxidation is a chemical treatment of organic pollutants in water which destroys hazardous contaminants by converting them to nontoxic or less hazardous compounds. Highly reactive species such as superoxide (O_2^{\bullet}) and the hydroxide radical ($^{\bullet}OH$) which are generated as a result of electron transfer processes can be used to decompose a pollutant into harmless end-products even to CO_2 and H_2O by complete mineralization. In order to improve the oxidation process, chemical reactants with high oxidation potentials are used. According to Table 2.3, hydroxyl radical is the most powerful oxidizing agent followed by holes (h^+) generated on TiO₂ by irradiation.

Species	Standard reduction potential vs.	
	normal hydrogen electrode (V)	
e ⁻ (TiO ₂)	-0.50	
h^+ (TiO ₂)	2.70	
Superoxide radical	-0.33	-
Hydrogen peroxide	1.77	
Ozone	2.07	
Hydroxyl radical	2.80	

 Table 2.3. Redox Power of Agents for Pollution Abatement (Rajeshwar, 1996)

Recent developments in oxidative degradation procedures in applying catalytic and photochemical methods for organic compounds were an improvement in chemical water treatment. Advanced oxidation processes (AOP's) have recently gained attention as an important class of these technologies for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water and air. Potential application of AOP's include decontamination and deodorization. The basic principle of these processes is the generation of highly potent chemical oxidants such as the hydroxyl radical (e.g., OH^{*}) (Legrini *et al.*, 1993).

Advanced oxidation processes cover the following:

- 1. Ultraviolet Photolysis / Direct Photooxidation
- 2. Ultraviolet Photolysis in the Presence of Oxidizing Species such as H₂O₂/O₃
- 3. Heterogeneous Photocatalytic Oxidation (TiO₂/UV Process)

2.3.1. Ultraviolet Photolysis / Direct Photooxidation

Light can have a significant effect on an organic molecule leading to the breakage of the bonds photolytically within the pollutant molecule. This is especially feasible when the pollutant contains chromophoric groups, for example carbonyls. In direct photochemical transformations the light-absorbing substance is changed due to the electronic excitation of the molecule and its ability to lose or gain electrons is often altered. Photooxidation reactions upon electronic excitation of the organic substrate imply in most cases an electron transfer from the excited state (C^*) to ground state molecular oxygen (O_2), with subsequent homolysis to form radicals. The free radicals generated can then react with dissolved oxygen in water:

$C + hv \longrightarrow C$		(26)	ļ
• • • •	-	· ·	

$$C^* + O_2 \longrightarrow C^{\bullet +} + O_2^{\bullet -}$$
(27)

$$\mathbf{R} \cdot \mathbf{X} + h\mathbf{v} \longrightarrow \mathbf{R}^{\bullet} + \mathbf{X}^{\bullet}$$
(28)

$$\mathbf{R}^{\bullet} + \mathbf{O}_2 \longrightarrow \mathbf{RO}_2 \tag{29}$$

The absorption cross section of the organic molecule, the quantum yield of the process, the photon rate at the wavelength of excitation and the concentration of dissolved molecular oxygen are important parameters in determining the rate of photooxidation (Legrini *et al.* 1993).

In practice, treatment of contaminated waters by UV alone is not widely used. Ultraviolet photolysis procedures are generally of low efficiency when compared to the procedures involving hydroxyl radical formation. Also degradation of organic compounds to new

organic molecules and inorganic products may be a disadvantage. This is due to the fact that the products formed may be more toxic and more resistant to biodegradation. Another limitation for ultraviolet photolysis is the absorption of light by the target molecule in competition with other absorbers in solution. This creates a real problem in highly polluted wastewaters. Most contaminated waters contain a variety of pollutants to be destroyed and their removal by photodegradation is not always cost effective in terms of process economics.

2.3.2. Ultraviolet Photolysis in the Presence of Oxidizing Agents Such as H₂O₂/O₃

The fundamental aspects of UV/H_2O_2 process appear to be fairly well understood at present. The most commonly accepted mechanism of hydroxyl radical generation, is the cleavage of hydrogen peroxide with UV light below 300 nm, where two hydroxyl radicals are formed per quantum of radiation absorbed. Photolysis of H_2O_2 occurs via the initial step:

$$H_2O_2 \xrightarrow{h\nu < 300nm} 2 ^{\circ}OH$$
(30)

The 'OH are subsequently involved in a chain reaction often with quantum yields in excess of unity. These radicals attack organic molecules by abstracting hydrogen atoms or by adding to double bonds. In the literature, three different mechanisms were stated for the reactions of hydroxyl radicals in the presence of an organic substrate:

1. Hydrogen Abstraction:

 $HO^{\bullet} + RH \longrightarrow R^{\bullet} + H_2O \tag{31}$

2. Electrophilic Addition:

 $HO^{\bullet} + PhX \longrightarrow HOPhX^{\bullet}$ (32)

3. Electron Transfer:

 $HO^{\bullet} + RX \longrightarrow RX^{\bullet} + HO^{-}$ (33)

When compared to other chemical and photochemical water treatment methods, the use of hydrogen peroxide as an oxidant has a number of advantages like; commercial availability, thermal stability and storage on site, infinite solubility in water, minimal capital investment etc. On the other hand, the rate of chemical oxidation of the contaminant is limited by the rate of formation hydroxyl radicals. The trapping of hydroxyl radicals by bicarbonate and carbonate ions is considered to be the main disadvantage of the reaction.

$$HO^{\bullet} + HCO_3^{-} \longrightarrow H_2O + CO_3^{\bullet-}$$
(34)

$$HO^{\bullet} + CO_3^{2-} \longrightarrow HO^{-} + CO_3^{\bullet}$$
(35)

Another disadvantage of UV/H₂O₂ photolysis is that the process is only efficient at lower wavelengths, this is due to the fact that hydrogen peroxide absorbs only weakly in the range 200-300 nm and does not absorb beyond 300 nm. Therefore the UV/H₂O₂ process is not suitable for the treatment of polluted water with a high UV absorbance and/or a high background total organic carbon concentration. The low molar extinction coefficient of H₂O₂ means that in turbid waters or waters containing strong UV absorbers (e.g. aromatic organic compounds), the fraction of light absorbed by H₂O₂ will be low unless very high concentrations are used with an increase in process costs (Rajeshwar, 1996).

The O_3/UV process is another advanced water treatment method for the effective oxidation and destruction of toxic and refractory organics in water. The O_3/UV process provides an enhancement of both the rate of complete destruction achievable and the range of compounds attacked, due to the greater oxidation power of hydroxyl radical vs. ozone. Legrini *et al.* (1993) reviewed the O_3/UV process which was proposed as a two-step process involving the light induced homolysis of O_3 and production of HO[•] radicals by the reaction of O (¹D) with water.

$$O_3 \xrightarrow{h\nu < 310nm} O(^1D) + O_2$$
(36)

$$O(^{1}D) + H_{2}O \longrightarrow H_{2}O_{2}$$
(37)

Since the net result of ozone photolysis is the conversion of ozone into hydrogen peroxide, O_3/UV becomes a rather expensive method to make hydrogen peroxide.

2.3.3. Heterogeneous Photocatalysis (TiO₂/UV Process)

Photocatalysis can be defined as "acceleration of a photoreaction by the presence of a catalyst". The most significant advantage of photocatalysis over current water treatment technologies is its ability to achieve complete mineralization by degrading many compounds to CO_2 , H_2O and mineral acids such as HCl, instead of simply transferring them to another medium. Therefore electron transfer processes involving the excited state and the contacting medium (for example water) can generate highly reactive species like the hydroxide ('OH) and the superoxide (O_2^{-}) radicals which can be used to decompose a pollutant chemically into harmless end products.

Photocatalytic processes using a variety of semiconductor materials have been intensively studied in the area of photochemical conversion and light harvesting (Matthews, 1992). The degradation of organic pollutants present in wastewaters using irradiated dispersions of titanium dioxide is a fast growing field in basic and applied research. TiO₂ has been most frequently investigated for the degradation of a variety environmentally harmful organic molecules including halogenated and non-halogenated compounds. Other semiconductors such as ZnO, SiO₂, SnO₂, Fe₂O₃ etc. have also been used but none of them have matched its attributes in terms of stability, performance, ready availability, low toxicity and low cost. In this regard it is a semiconductor generally preferred for use in commercial advanced oxidation applications.

TiO₂ exhibits photoconductivity when illuminated by photons having an energy level that exceeds the TiO₂ band gap energy level of 3.2 electron volts. This photon energy which is required to overcome the band gap energy and excite an electron from the valence to the conduction band can be provided by UV radiation with a wavelength between 200 and 385 nanometers (nm). However, the semiconductor band energies are slightly different for anatase (E_{bg} =3.2 eV) and rutile (E_{bg} =3.1 eV) modifications of TiO₂. The anatase form is superior to rutile for photocatalytic applications. This is due to the fact that the conduction band location for anatase is more favorable for driving conjugate reactions involving electrons. On the other hand, the poorer photocatalytic activity of rutile was attributed to its high e⁻-h⁺ recombination rate and its lower oxygen photoadsorption capacity (Rajeshwar, 1995).
A simplified TiO_2 photocatalytic mechanism is summarized in Figure 2.7. The mechanism is being researched and published research indicates that the primary photocatalytic mechanism is believed to proceed as follows:



Figure 2.7. A simplified TiO₂ Photocatalytic Mechanism (EPA, 1997)

The combination of the electron in the conduction band and the hole in the valence band is referred to as an electron-hole pair. The excitation of the anatase TiO₂ by UV radiation of wavelength 385 nm or less produces electron-hole pairs. Many of the photogenerated e^-h^+ pairs simply recombine. Since, the electron is in an unstable, excited state, the electron-hole pairs within a semiconductor tend to reverse to a stage where the electron-hole pair no longer exists. This is a practical problem of semiconductor photoconductivity which results in the generation of photons or heat instead of ^{*}OH. This leads to a significant decrease in the photocatalytic activity of the semiconductor. However, the band gap inhibits this reversal so long enough that excited electrons and holes near the surface of the semiconductor participates in reactions at the surface of the semiconductor. A fraction of the photogenerated $e^- - h^+$ pairs escape to the TiO₂ surface, and then react with the solution species or with the hydroxyl groups invariably present at oxide surfaces. Thus, species such as O₂^{•-} and ^{*}OH are generated which can be used to break down the pollutant.

When an electron in the valence band is excited into the conduction band, a vacancy or a hole is left in the valence band. These holes have the effect of a positive charge and react subsequently with the adsorbed species in oxidative reactions.

$$\mathrm{TiO}_2 \xrightarrow{h\nu} \mathrm{h}^+ + \mathrm{e}^- \tag{38}$$

The most important of these reactions is the oxidation of adsorbed water or hydroxide ions by holes to produce hydroxyl radicals. In the presence of an organic pollutant in aqueous media, the electron transfer from adsorbed substrate RX and electron transfer from adsorbed solvent molecules (H_2O , OH⁻) can be described by:

$$\mathbf{h}^{+} + \mathbf{R}\mathbf{X}_{(\mathrm{ads})} \longrightarrow \mathbf{R}\mathbf{X}_{(\mathrm{ads})}^{+}$$
(39)

$$\mathbf{h}^{+} + \mathbf{H}_{2}\mathbf{O}_{(ads)} \longrightarrow \mathbf{O}\mathbf{H}_{(ads)} + \mathbf{H}^{+}$$

$$\tag{40}$$

$$\mathbf{h}^{+} + 2\mathbf{OH}^{-}_{(ads)} \longrightarrow \mathbf{OH}_{(ads)} + \mathbf{OH}^{-}$$
(41)

An additional reaction may occur where the electron in the conduction band reacts with dissolved oxygen (O_2) in water to form superoxide ions (O_2^{-}) or hydrogen peroxide as follows:

$$e^{-} + O_2 \longrightarrow O_2^{*-}$$
 (42)

$$2e^{-} + O_2 + 2H^{+} \longrightarrow H_2O_2$$
(43)

These O_2^{\bullet} can then react with H_2O to provide additional $^{\bullet}OH$, OH^{-} , and O_2° :

$$2 O_2 + 2 H_2 O \longrightarrow 2^{\circ} OH + 2 OH + O_2$$

$$(44)$$

On the other hand photogenerated H_2O_2 has been reported to promote the generation of hydroxyl radicals in TiO₂ activated photocatalytic systems.

$$H_2O_2 + O_2 \longrightarrow OH + OH^- + O_2$$
(45)

One possible method of increasing the photocatalytic activity of a semiconductor is to add irreversible electron acceptors. It has been shown by Al-Ekabi *et al.* (1993) that the addition of hydrogen peroxide considerably enhances the rate of photodegradation. H_2O_2 not only inhibits the electron-hole reversal process and prolongs the life time of the photogenerated hole, but it also generates additional OH.

$$H_2O_2 + e^- \longrightarrow OH^- + OH$$
 (46)

A crucial advantage with UV/TiO₂ (unlike UV/H₂O₂ and UV/O₃) is that the conductionband electrons have considerable reducing power and can be used to reduce the pollutant directly. As a result of the quantized nature of the UV/TiO₂ process, there is a threshold wavelength beyond which photon absorption will be negligible.

Heterogeneous photocatalytic oxidation processes (HPCO) using titanium dioxide have been shown capable of destroying a wide range of anthropogenic organic compounds, yet to date there has been no widespread commercial application of this technology. The process has found its technical applications only in small to medium sized units for the treatment of contaminated groundwaters especially with the TOC determination (Matthews, 1992) and for the production of ultrapure water for microelectronic and pharmaceutical industries (Legrini *et al.*, 1993).

2.3.4. Photocatalysis in the Presence of Trace Metals

Munoz and Domenech (1990) found that the ultraviolet illumination of Cr (VI) solutions containing TiO_2 in suspension caused the reduction of Cr (VI) to Cr (III) at neutral pH. It was reported that the percentage of Cr (VI) photoreduced decreased with increasing initial pH. On the other hand, the amount of photoreduction was also found to decrease slightly with decreasing initial Cr (VI) concentration. The decrease in the photoreduction yield was explained with the migration of the photogenerated electron-hole pairs to the surface of the catalyst. It was assumed that the electrons reduced Cr (VI) to Cr (III) and the holes oxidized water. But the presence of oxygen competed with Cr (VI) for the photogenerated TiO_2 electrons and therefore resulted in a decrease of the photoreduction yield. Related equations were given as:

$$TiO_2 \xrightarrow{h\nu} TiO_2 (e^-, h^+)$$
(47)

$$8H^{+} + CrO_{4}^{2-} + 3 e^{-} \longrightarrow Cr^{3+} + 4H_{2}O$$
(48)

$$H_2O + 2h^+ \longrightarrow \frac{1}{2}O_2 + 2H^+$$
(49)

In another study of Domenech and Munoz (1990), the photocatalytic reduction of Cr(VI) to Cr(III) from aqueous solutions at neutral and low alkaline pH was investigated using ZnO powder as the catalyst. At pH 7, maximum Cr (VI) elimination was reported. But the yield of Cr (VI) elimination decreased falling off at lower and higher pH values in the range pH 6-9. It was also verified that the photocatalytic elimination of Cr (VI) proceeded via reduction to Cr (III) by the electrons photogenerated in the ZnO conduction band.

Xu and Chen (1990) reinvestigated the photocatalytic reduction of dichromate over semiconductor catalysts and reported rutile titanium dioxide to be the most efficient. It was indicated that the photocatalytic reduction of dichromate was pH dependent, being more favorable at low pH.

Prairie *et al.* (1993) studied the photocatalytic oxidation of Cr (VI) to Cr (III) for different pH values using TiO_2 as the photocatalyst and a variety of organics as the organic substrate (methanol, formic acid, salicylic acid, EDTA, phenol and nitrobenzene). It was reported that the photocatalytic conversion of Cr (VI) to Cr (III) for different pH values (pH 1 to pH 6) using salicylic acid as the organic substrate followed first order reaction kinetics. Rapid reduction of Cr(VI) was also observed with EDTA, mandelic acid and citric acid. The organics capable of donating electrons to the valence band of TiO_2 resulted in high oxidation rates whereas those that are only oxidized by hydroxyl radicals resulted in slow reduction by indirect effect.

Lin *et al.* (1993) studied the photocatalytic reduction of Cr (VI) on TiO₂ surface for pH 0 and pH 10 in aqueous media. It was shown that the photocorrosion of TiO₂ was thermodynamically less favorable in basic media. On excitation of light, the photogenerated holes were assumed to oxidize the hydroxyl ions to O_2 while the electrons reduced the Cr (VI) to Cr (III).

Lozano *et al.*(1992) investigated the photocatalytic oxidation of manganese (II) to MnO_2 in aqueous suspensions of TiO₂ at pH 5.2. It was concluded that at the point of zero charge of TiO₂, the adsorption of manganese (II) increased sharply favoring the charge-transfer reactions at the semiconductor-electrolyte interface. The oxidation of manganese (II) to MnO_2 with UV irradiation was explained by the following reaction:

$$Mn^{2+} + \frac{1}{2}O_2 + H_2O \longrightarrow MnO_2 + 2H^+$$
(50)

The formation of insoluble MnO_2 was also observed by the appearance of a slight dark coloration on the semiconductor surface. The results obtained from manganese (II) solutions at neutral pH were discussed in terms of Langmuir-Hinshelwood kinetics. The adsorption constants, k and K were found to be $6.0x10^{-5}$ mol L⁻¹ min⁻¹ and $3.6x10^3$ L mol⁻¹ respectively with the high value of K indicating that manganese (II) is strongly adsorbed on TiO₂ particles.

Butler and Davis (1993) investigated the effect of transition metal ions on the photocatalytic oxidation of toluene in aqueous TiO₂ suspensions. A significant increase in the removal rate of toluene was observed at low pH (between 3 and 5) values with the addition of Mn (II) to the system but at higher pH values the reaction rates decreased. The oxidation of Mn (II) to Mn (III) was observed on the TiO₂ surface at pH 5 and pH 8. In the presence of dissolved ions, rate increase in the photocatalytic removal was suggested to be through a homogeneous pathway rather than through a TiO₂ surface reaction. Negligible adsorption of metals on TiO₂ surface at optimum concentration was observed therefore a mechanism involving formation of a ternary complex between the metal organic substrate and an oxygen containing species such as H_2O_2 or O_2 was proposed.

2.3.5. Humic Acid Treatment by Advanced Oxidation Processes

Application of the advanced oxidation processes for the destructive removal of humic acids was investigated as homogeneous and heterogeneous processes.

2.3.5.1. Homogeneous Processes

Backlund (1992) studied the degradation of aquatic humic material by UV light. At high UV doses, part of the dissolved organic matter (DOM) was observed to precipitate as a result of polymerization, but no change was detected with the dissolved organic carbon (DOC) content whereas in the presence of H_2O_2 , the formation of the same acidic degradation products which accounted for 80% of the dissolved organic matter was enhanced. UV_{254} and DOC value were found to decrease after 30 minutes of irradiation. But no significant change was observed from 30 to 60 minutes.

Arai *et al.* (1986) investigated the combined effect of radiation and ozone on degradation of humic acid in water. Humic acid solution (5 mgL⁻¹) was irradiated with Co γ -rays at room temperature in the presence of ozone of different concentrations (2.9, 6.3, and 17 mgL⁻¹). The total organic carbon (TOC) reduction rate was found to increase both with the ozone concentration at the constant dose rate and with the dose rate at constant ozone concentration.

Gilbert (1988) later studied the effects of ozonation on the biodegradability of the oxidation products of humic acids following COD-, DOC-elimination, decrease of UV-absorbance and ozone consumption. Unlike to the aromatic compounds, a quick decolorization and a decrease of the absorbance at 254 nm was observed with the ozonation. The oxidation products of humic acids were well biologically degraded after a high ozone consumption (3-4 mg O₃ per mg initial DOC). With this ozone consumption complete decolorization of the solutions was achieved. At this time 60% of the COD-value and 30% of the DOC-value were eliminated and the value of UV/DOC decreased from 4 to 0.8 m² g⁻¹.

2.3.5.2. Heterogeneous Processes (TiO₂/UV Process)

Bekbölet (1996) studied the destructive removal of humic acids in aqueous media by TiO₂/UV process. The effects of initial concentration of humic acid and titanium dioxide loadings were investigated. The degradation was followed in terms of UV-vis spectra and TOC. For 50 mgL⁻¹ humic acid solution with TiO₂ concentration of 1 mgL⁻¹, 40% of TOC and 75% of Color₄₀₀ were removed after 60 minutes of irradiation and the apparent quantum yield was found to be 0.221. Bekbölet *et al.* (1996) also reported that the BOD₅/COD ratio for humic acid solution increased with irradiation time and more biodegradable substances have been formed. The biodegradability (BOD₅/COD) for humic acid solution was found to be 0.66 after 2 hours of irradiation.

Bekbölet and Araz (1996) studied the inactivation of Escherichia coli in presterilized surface water sample using titanium dioxide as the photocatalyst under irradiation of BLF Fluorescent lamps. Inactivation of E. coli was achieved in 60 minutes in the presence of 1.0 mg mL⁻¹ TiO₂.

Bekbölet and Balcioğlu (1996) later investigated the influence of hydrogen peroxide and bicarbonate ion on the photocatalytic degradation of humic acid in aqueous TiO_2 dispersions. The kinetics of photocatalytic degradation was followed in terms of TOC, COD and UV-vis spectra. The degradation rate constants for 50 mgL⁻¹ humic acid were found to increase in the presence of 1×10^{-2} M H₂O₂. It was also explained that bicarbonate ions slowed down the degradation rate by scavenging the hydroxyl radicals.

Bekbölet and Özkösemen (1996) later determined the trihalomethane potentials (THMFP) of the photocatalytically treated humic acid solutions. They concluded that the destructive removal of humic acid in aqueous medium by TiO_2/UV process was an effective method to keep the THM levels below the maximum contaminant level of 100 µgL⁻¹ (USEPA).

Özkaraova (1996) examined the photocatalytic degradation of humic acid in the presence of nitrate and chloride ions. It was reported that nitrate ions and chloride ions caused approximately 40% and 45% adsorption respectively. Following the adsorption,

photocatalytic degradation took place and the degradation rate was observed to decrease with an increasing chloride concentration.

Boyacioğlu (1997) studied the influence of pH dependent phosphate species on the photocatalytic degradation of 10 mgL⁻¹ humic acid in aqueous medium. At low pH values, irradiation with 0.25 mg/mL TiO₂ for 1 hour resulted in 95% Color₄₃₆ and 62% TOC removal. Increasing the phosphate concentration up to five fold was reported to inhibit the degradation rate of humic acid.

Eggins *et al.* (1997) investigated the semiconductor photocatalysis for the treatment of humic substances in drinking water using 0.1% suspension of titanium dioxide. Degradation was followed over time by measuring color in Hazen units, 254/400 nm absorbance, fluorescence and size exclusion high performance chromatography. It was reported that the half-life of photodegradation was 12 minutes but in order to achieve 50% complete mineralization 60 minutes of irradiation was required. In the absence of oxygen, light or titanium dioxide no significant degradation was observed.

Bekbölet *et al.* (1998) reported the photocatalytic color removal of humic acid in the presence of common anions such as chloride, nitrate, sulfate and phosphate at pH 6.8. It was concluded that both Color_{436} and Color_{400} could be used as parameters to follow the decolorization of humic acids in natural waters. The first order decolorization rates for the anions were found to be decreasing in the order of nitrate, sulfate and chloride. The presence of phosphate ions was found to inhibit the color removal rate strongly.

Gönenç (1998) found that the photocatalytic degradation of humic acid was affected in the presence of chlorinated oxyanions; ClO_3^- , ClO_4^- , OCl^- , but the overall reaction rate was not influenced. It was also observed that humic acid strongly complexes with iron until precipitation of an insoluble complex occurs. The photocatalytic degradation of humic acid was significantly masked by this precipitation.

The photocatalytic efficiencies of two crystal forms of titanium dioxide; anatase and rutile were compared by Dincer (1998) using humic acid as a model compound. Relatively higher

removal rates were observed with Anatase Degussa P-25 photocatalyst and its efficiency on the photocatalytic degradation of humic acid was concluded.

Karabacakoğlu (1998) investigated the influence of hardness cations such as calcium and magnesium on the photocatalytic degradation of humic acid. It was found that Color_{436} and UV_{254} removal rates increased in the presence of 50 mg L⁻¹ calcium and 5 mg L⁻¹ magnesium hardness. The increase in the removal rates was explained by the changes of the humic acid structure in the presence of divalent cations.

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 whereas the presence of copper caused a decrease both in $Color_{436}$ and UV_{254} removal rates.

Cloete *et al.* (1999) has recently proposed photocatalytic oxidation as an alternative for the destruction and removal of humic substances in drinking water. The photocatalytic oxidation was followed in terms of TOC analysis, UV absorbance at 254 nm and THM formation potential. A significant reduction was observed in all three responses which confirmed the removal of humic substances from the water samples via photocatalytic oxidation.

Bekbölet (1999) recently reviewed the impact of natural water conditions on the photocatalytic degradation of humic acids. Reactions were carried out in the presence of hardness causing calcium and magnesium ions and common counter ions such as chloride, nitrate, sulfate and phosphate and the results were explained in terms of pseudo first order and Langmuir-Hinshelwood rates. Chloride and phosphate ions were reported to decrease the photocatalytic degradation rate whereas nitrate ions caused an increase. Langmuir-Hinshelwood rates were found to differ significantly from the first order reaction rates. The pseudo-first order reaction rate constant for Color₄₃₆ was found to be 4.18×10^{-2} min⁻¹ for humic acid whereas the Langmuir-Hinshelwood kinetics revealed the rate constant to be $0.427 \text{ min}^{-1} \text{ m}^{-1}$. The presence of divalent cations separately and in combination increased the pseudo first order reaction rates for Color₄₃₆ due to the combined effect of adsorption and coagulation acting simultaneously.

2.4. Kinetics of Chemical Processes

2.4.1. Kinetics of Photocatalytic Degradation

In heterogeneous photocatalysis the presence of TiO_2 particulates brings about the interaction of the surface with the solvent and the substrates. The substrate and water molecules could adsorb on the surface and their competition for the same active sites cannot be ignored. These simultaneous adsorptions influence the observed reaction kinetics. In such a case, modified forms of the Langmuir-Hinshelwood equation has been successful as a qualitative model to describe solid-liquid interactions. The general expression describing the rate is:

$$\frac{-dC}{dt} = k \frac{K[C_0]}{1+K[C_0]}$$
(52)

where k is the reactivity constant, K is the adsorption equilibrium constant and C_0 is the initial concentration of the substrate. The expression on integration gives the following equation for the half-life (t_{1/2}) of the reaction:

$$t_{1/2} = \frac{0.693}{kK} \ln \left[\frac{[C_0]}{[C_t]} + \frac{1}{k} ([C_0] - [C_t]) \right]$$
(53)

It follows that:

$$t_{1/2} = \frac{0.693}{kK} + \frac{0.5 \left[C_0\right]}{k}$$
(54)

The rate of oxidation, R in mg L^{-1} min⁻¹ can also be calculated by the expression given below:

$$\mathbf{R} = k \frac{K \left[C_0 \right]}{1 + K \left[C_0 \right]} \tag{55}$$

Langmuir-Hinshelwood (L-H) kinetics have been useful in many studies of photocatalytic degradation rates in reducing the concentration dependence of the data to a minimum number of numerical parameters. The rate of destruction is not directly proportional to concentration and comparisons of destruction rates between different compounds cannot be made at single concentrations. To estimate the destruction rate at any particular concentration, a knowledge of the Langmuir-Hinshelwood kinetics for the compound is required.

The simple rate law may be modified to give the equation:

$$\frac{-dC}{dt} = k \frac{K[C_0]}{1+K[C_0]+K_s[C_s]}$$
(56)

where K_s is the adsorption coefficient and C_s is the concentration of the solvent.

The part of TiO₂ surface covered by the solvent is approximately unchanged at all reactant concentrations used, to the extent that $C_s > C_0$ and C_s remains constant.

Integration of the above equation gives:

$$\ln \frac{C_0}{C} + \frac{K}{1 + K_s C_s} (C_0 - C) = \frac{kK}{1 + K_s C_s} t$$
(57)

This equation is the sum of zero order and first order reaction rate equations, their contribution to the overall reaction depends on the initial concentration C. When C is very small, the equation turns out to be:

$$\ln\left(C_0/C\right) = \mathbf{k}'\mathbf{t} \tag{58}$$

The reactions approximate first-order reaction kinetics to a high degree of degradation. Plots of natural logarithm of normalized concentrations of solutes versus irradiation time give a straight line whose slope is the apparent first-order rate constant, k'.

It has been extensively explained in the literature that the photocatalytic degradation of various organic compounds at low concentrations obeys pseudo first-order kinetics (Ollis *et al.*, 1989):

$$\frac{-dC}{dt} = \mathbf{k} \left[C \right] \tag{59}$$

where k is the pseudo first-order degradation constant (time⁻¹) and [C] is the concentration of the substrate. The expression on integration gives:

$$\ln\left[C_{1}\right] = \ln\left[C_{0}\right] - \mathrm{kt} \tag{60}$$

where $[C_t]$ and $[C_0]$ are the concentrations of solute at time t and 0 respectively.

The half-life of the reaction, $t_{1/2}$ is calculated as follows:

$$t_{1/2} = \frac{0.693}{k} \tag{61}$$

2.4.2. Kinetics of Adsorption

Adsorption isotherms describe the equilibrium conditions for an adsorbate (that which is adsorbing) onto the surface of an adsorbent. The adsorption of molecules on to a surface is a necessary prerequisite to any surface mediated chemical process. Usually the amount of material adsorbed is some complex function of the concentration of the adsorbate. Different solutes show different behaviors on the adsorbent, so their adsorption isotherms can be named according to their shapes resembling the letters, such as L type, S type, C type, etc.

The Freundlich Isotherm

The Freundlich isotherms is the most widely used nonlinear adsorption equilibrium model. It describes adsorption events occurring on heterogeneous surfaces composed of different adsorption sites, with adsorption on each site following the Langmuir isotherm. The model has the general form:

$$q_A = K_F C_e^{1/n} \tag{62}$$

where;

\mathbf{q}_{A}	: The amount of solute adsorbed per unit weight of solid adsorbent
Ce	: The concentration of the solute remaining in the solution at equilibrium
K _F	: The constant which relates to adsorption capacity
1/n	: The constant which relates to adsorption intensity

Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation as follows:

$$\log q_{\rm A} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{63}$$

A plot of log q_A versus log C_e should yield a straight line whose slope is $\frac{1}{n}$ and whose intercept is log K_F . The intercept is roughly an indicator of adsorption capacity and the slope of adsorption intensity.

The Freundlich equation generally agrees well with the Langmuir equation and with the experimental data over a moderate range of concentrations. However, unlike the Langmuir equation, it does not reduce to a linear adsorption expression at very low concentrations. And at high concentrations, it does not agree well with the Langmuir equation, since n must reach some limit when the surface is fully covered.

Langmuir Isotherm

The initial fractional adsorption of a reactant is described with the Langmuir isotherm:

$$\theta = \frac{\mathrm{KC}}{1 + \mathrm{KC}} \tag{64}$$

where θ is the surface coverage of the reactant, K the adsorption equilibrium constant, and C the initial concentration of the reactant in solution in contact with the solid adsorbent.

Langmuir isotherm involves the three following assumptions:

- 1. The surface is uniform and all sites are equivalent.
- 2. The adsorbed molecules form a monolayer coverage. When the surface has achieved saturation, no further adsorption can occur.
- 3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

It is used as a starting point for kinetic modeling of various competing mechanisms that may occur after the primary photochemical event. It can also be used to characterize the surface smoothness, because the Langmuir model derives from the assumption that a smooth surface is involved in which adsorption is not dependent on preliminary surface coverage by other reagents (Langmuir, 1918).

BET Isotherm

The BET (Brunauer, Emmett and Teller) isotherm differs from the Langmuir isotherm in that it allows more than one layer of adsorbate molecules to form on the surface. When multilayer adsorption occurs, the heat of adsorption of an adsorbate molecule adsorbing on a bare surface will differ considerably from the heat of adsorption on to another layer of adsorbate. The assumptions used in the BET isotherm are:

- Adsorption of the first layer is on a uniform array of surface sites of equal energy (i.e. Langmuir)
- Second layer adsorption can only take place on top of first, third on top of second, etc. When the pressure equals the saturated vapor pressure of the adsorbate, an infinite number of layers will form.
- 3. At equilibrium, the rates of condensation and evaporation are the same for each individual layer.

Adsorption is a significant phenomenon in most natural, physical, biological and chemical processes. Examples include removal of taste and odor producing organic materials and other trace organic contaminants such as trihalomethanes, pesticides and chlorinated organic compounds, removal of residual organic contaminants from treated wastewater effluents, and the treatment of leachates, industrial wastewaters, and hazardous wastes. Sorption of solids, particularly active carbon, has become a widely used operation for purification of waters and wastewaters. All three of the adsorption isotherms have been widely used to analyze adsorption data from wastewater studies. In general, the Langmuir and BET equations do not apply to dilute solutions or mixed solutes as well as the Freundlich equation. Therefore, Freundlich equation finds its wide application in environmental engineering; it is commonly used for comparison of powdered carbons for water treatment. Sigh (1984) compared five adsorption equations and found that the Freundlich equation was the most accurate in describing the adsorption of SO_4^{-2} by soils. Polyzopoulos et al. (1985) compared four adsorption equations in a study concerned with phosphate adsorption by soil. They found that Langmuir-type or Freundlich expressions described the data with comparable success.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Humic Acid

Humic acid was supplied from Roth. Stock humic acid solution (1000 mg L^{-1}) was prepared according to the procedure outlined by Urano *et al.* (1983). Appropriate dilutions were prepared weekly from the stock solution using distilled deionized water. Stock humic acid solution was stored in a dark glass container and was protected from light to prevent decomposition.

3.1.2. Titanium Dioxide Powder

Degussa P-25 TiO₂ was used as the photocatalyst. The primary particle size was 20-30 nm, and BET surface area was $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$. Crystal form was 70% anatase and 30% rutile. Homogeneous slurry of TiO₂ was obtained by sonicating the solution for 3 minutes.

3.1.3. Standard Manganese Solution

Standard manganese solution was prepared according to Standard Methods using distilled deionized water (APHA/AWWA/WPCF, 1989).

3.1.4. Standard Chromium Solution

Standard chromium solution was prepared according to Standard Methods using distilled deionized water.

3.1.5. Laboratory Equipment

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

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

<u>Memmert Top-Shaker</u>: the adsorption experiments of chromium and manganese containing humic acid and TiO_2 suspensions were carried out on the Memmert water-bath shaker.

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 weighing certain amounts of titanium dioxide.

<u>Ultra Sonic Waterbath LC30</u>: The homogeneous suspension was provided by sonification of the slurry.

<u>Framo-Geraetechnik M21/1 Magnetic Stirrer:</u> It was used for the continuous mixing of the suspensions throughout the reaction time during photocatalytic treatment.

<u>WTW pH Meter-pH 526</u>: The pH values of photodegraded suspensions were measured to observe pH changes. The pH meter was calibrated with pH 4 and pH 7 buffer solutions.

Memmert Oven: It was used to dry the glassware.

<u>Sterile Millex -HA Millipore Filter</u>: The suspensions were filtered through 45µm Millipore syringe filter to remove the residual photocatalyst after centrifuging.

3.2. Methods

3.2.1. Photocatalytic Degradation

3.2.1.1. Experimental Set-Up

125 W Black Light Fluorescent Lamp (BLF) which had an output spectrum ranging between 320-440 nm, was used as the light source. The lamp exhibited a maximum emission at 365 nm and no emission below 300 nm and above 500 nm. The intensity of incident light, measured using ferrioxalate actinometery, was 2.854x10¹⁶ quanta sec⁻¹. A cylindrical pyrex reaction vessel with a diameter of 7.5 cm, a height of 3.5 cm was used as the photoreactor. Volume of the reaction mixture was 50 mL. Continuous stirring of the suspension was provided by means of a magnetic stirrer throughout the duration of the experiments. The photoreactor was enclosed by a mirror casing and the whole system was placed in a box. The inner walls of the box were covered with Al-foil.

3.2.1.2. Experimental Procedure

All experiments were conducted under neutral pH conditions (pH = 6.7). Dark reactions were carried out to evaluate the probable initial adsorption of humic acid onto TiO_2 both in the presence and absence of metal ions. In order to assess the direct interaction of light with humic acid, control reactions were performed in the absence of the photocatalyst.

10 mg L⁻¹ humic acid solution was prepared by dilution from the stock solution. 50 mL of 10 mg L⁻¹ humic acid solution containing 0.10 mg L⁻¹ chromium and 0.05 mg L⁻¹ manganese concentration was added directly to the reaction vessel containing 0.25 mg mL⁻¹ TiO₂. The slurry was sonicated for 3 minutes to ensure a homogeneous mixture and then placed on a magnetic stirrer to be irradiated for certain reaction periods. Volume corrections were made with distilled deionized water in all of the experiments to compensate the volume loss due to the evaporation of water observed at longer irradiation periods. Prior to analysis, TiO₂

was removed from the suspension by filtering through a 0.45μ Millipore syringe filter. The clear solution obtained was analyzed with the spectrophotometer for residual absorbance at 436, 400, 280 and 254 nm (Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄).

3.2.1.3. Parameters Studied

For monitoring color (Color₄₃₆ and Color₄₀₀), aromaticity (UV₂₈₀) and organic matter content (UV₂₅₄) of humic acid solution, absorbance values of the samples were recorded at 436 nm, 400 nm, 280 nm and 254 nm wavelengths. Color₄₃₆ and Color₄₀₀ values were expressed as color units, per meter (C.U., m⁻¹), whereas UV₂₈₀ and UV₂₅₄ were given as absorbance units, per meter (A.U., m⁻¹).

3.2.2. Adsorption Experimental Procedure

Batch adsorption experiments were carried out using flasks filled with 25 mL humic acid solution containing chromium or manganese ions. TiO_2 ranging from 0.1 mg mL⁻¹ to 1.0 mg mL⁻¹ was added into each flask. Then the samples were sonicated for an evenly distribution of TiO_2 in the slurry. One blank solution containing only humic acid and chromium or manganese ion was also prepared for control purposes. The stoppered flasks were immersed into the water-bath and shaken for 24 hours at room temperature. The contents were then filtered through 0.45 μ Millipore syringe filters and analyzed for residual absorbance at 436, 400, 280 and 254 nm to monitor the same parameters used in photocatalytic degradation.

4. RESULTS AND DISCUSSION

4.1. Photocatalytic Degradation of Humic Acid

In order to assess the effects of chromium and manganese ions on the photocatalytic degradation of humic acid, reactions were carried out in the absence of these ions.

10 mg L^{-1} humic acid solution containing 0.25 mg m L^{-1} TiO₂ was photocatalytically degraded for certain reaction periods up to 60 minutes. The reaction was carried out under neutral pH conditions. Control reactions without irradiation (dark reactions) in the presence of catalyst and preliminary experiments without TiO₂ in the presence of light were also performed under identical experimental conditions.

The data obtained from dark reactions of humic acid for Color_{436} , Color_{400} , UV_{280} and UV_{254} were given in Figure 4.1. It can be seen from the graph that TiO_2 and humic acid interaction resulted in an initial adsorptive removal of approximately 40%. Adsorption-desorption processes were observed in 20 minutes. In extended period, after 60 minutes, 48% removal was achieved.

In the absence of TiO_2 , dark control reactions were also carried out and no significant change was observed in the humic acid concentration, but irradiation in the absence of the photocatalyst resulted in <5% removal after 60 minutes.

The data obtained from the photocatalytic removal of humic acid for $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} removals were demonstrated in Figure 4.2.

As can be seen from the figure, 57% of $Color_{436}$ was removed after 10 minutes of irradiation. 72% removal was attained in 30 minutes and only 8% $Color_{436}$ was detected after 60 minutes of irradiation. On the other hand, by dark reaction 48% $Color_{436}$ removal was achieved in 60 minutes (Figure 4.1). $Color_{400}$ removal showed a similar trend to

Color₄₃₆ removal both in dark and photocatalytic reactions. For UV_{280} almost 50% removal was observed in 10 minutes. Further irradiation upto 60 minutes resulted in 85% removal. UV_{254} removal followed a similar trend to UV_{280} removal.

The photocatalytic degradation of humic acid in terms of Color_{436} , Color_{400} , UV_{280} and UV_{254} can be explained by pseudo first order kinetics. According to the data obtained, pseudo first order reaction rate constants, half-life values and related correlation coefficients of photocatalytic degradation are calculated and given in Table 4.1.

Table 4.1. Pseudo First Order Reaction Rate Constants (k, min⁻¹), Half-life Values ($t_{1/2}$, min) and Related Correlation Coefficients (R) of Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid

Parameter	k (min ⁻¹)	t _{1/2} (min)	\mathbf{R}^2
Color ₄₃₆	3.86x10 ⁻²	18	0.970
Color ₄₀₀	3.72×10^{-2}	19	0.968
UV_{280}	2.91×10^{-2}	24	0.955
UV ₂₅₄	2.73x10 ⁻²	25	0.951

According to Table 4.1, Color_{436} and Color_{400} removal rate constants were almost equal to each other ($\cong 4 \times 10^{-2} \text{ min}^{-1}$) and the corresponding half-life values were 18 and 19 minutes. The removal rate for Color_{436} was calculated to be 0.278 min⁻¹ m⁻¹ whereas Color_{400} removal rate was found to differ by 25% with a reaction rate of 0.368 min⁻¹ m⁻¹.

 UV_{280} removal rate constant was calculated as 2.91×10^{-2} min⁻¹ with a half-life value of 24 minutes. The removal rates calculated for UV_{280} and UV_{254} were close to each other with a difference < 10%. A removal rate of 0.994 min⁻¹ m⁻¹ was determined for UV_{254} . The trends observed in the reaction rates were also reflected in the corresponding half-life values.

The reaction rate constants for the color forming centers ($Color_{436}$ and $Color_{400}$) were almost 1.5 folds of the UV absorbing centers (UV_{280} and UV_{254}).



Figure 4.1. Normalized Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ Values with Respect to Time in the Presence of 10 mg L^{-1} Humic Acid and 0.25 mg m L^{-1} TiO₂



Figure 4.2. Normalized Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ Values with Respect to Irradiation Time in the Presence of 10 mg L^{-1} Humic Acid and 0.25 mg m L^{-1} TiO₂

During the photocatalytic oxidation, humic acids which are aromatic compounds are converted to simpler, less aromatic compounds with a reduction in the UV absorbance. After the photocatalytic oxidation, decolorization of the humic acid was observed. The decrease in absorption at 400 nm was also an indicative of decolorization. On the other hand, the decrease in absorption at 280 and 254 nm indicated the degradation of the aromatic sites of the humic acid.

4.2. Effect of Chromium Ion on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of humic acid was carried out in the presence of chromium ion. The effect of chromium ion concentration on the photocatalytic oxidation of humic acid was investigated in the range of 0.05 to 0.20 mg L^{-1} .

The comparison of pseudo first order decay parameters and related correlation coefficients of Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ removals for the photocatalytic degradation of 10 mg L⁻¹ humic acid, in the presence of different chromium concentrations were given in Appendix A in Tables A.1-A.4. The data obtained from the photocatalytic removal of humic acid for Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ removals, in the presence of different chromium concentrations were also demonstrated in Figures A.1-A.4 in Appendix A.

The data of the preliminary experiments which were obtained during 60 minutes of irradiation in the absence of the photocatalyst, were carried out using 0.10 mg L⁻¹ chromium and 10 mg L⁻¹ humic acid and given in Figure 4.3 as a representative example. The initial absorbance difference between humic acid and humic acid + chromium solution was negligible ($\Delta Abs \leq 0.003$) indicating that no reaction occurred between humic acid and the chromium ion. After 60 minutes of irradiation, no significant removal was observed.

4.2.1. Effect of 0.05 mg L⁻¹ Cr on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of 10 mg L^{-1} humic acid with 0.25 mg m L^{-1} TiO₂ was carried out in the presence of 0.05 mg L^{-1} chromium ion and the data was presented in Figure 4.4.

Photocatalytic oxidation of humic acid in the presence of chromium followed a first order reaction profile. Almost 85% degradation was achieved in 60 minutes for $Color_{436}$ and $Color_{400}$. On the other hand, for UV₂₅₄, almost 76% removal was attained after 60 minutes, and UV₂₈₀ removal reflected almost the same trend with a 78% removal in 60 minutes. The

data was evaluated in terms of pseudo first order reaction kinetics and the results were given in Table 4.2.

Table 4.2. Pseudo First Order Reaction Rate Constants (k, min⁻¹), Half-life Values ($t_{1/2}$, min) and Related Correlation Coefficients (R) of Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of 0.05 mg L⁻¹ Chromium

Parameter	k (min ⁻¹)	t _{1/2} (min)	\mathbf{R}^2
Color ₄₃₆	2.51x10 ⁻²	28	0.861
Color ₄₀₀	2.72x10 ⁻²	25	0.893
UV ₂₈₀	2.12×10^{-2}	33	0.869
UV ₂₅₄	2.02×10^{-2}	34	0.859

According to the evaluated data, the removal rate constants for Color_{436} and Color_{400} were close to each other. The removal rate for Color_{436} was found to be 0.176 min⁻¹ m⁻¹ whereas Color_{400} removal rate was 0.266 min⁻¹ m⁻¹. Almost 34% difference was obtained in the removal rates. The half-life values for Color_{436} and Color_{400} were calculated as 28 minutes and 25 minutes, respectively.

As can be seen from the table, almost the same rate constant were obtained from UV_{280} and UV_{254} data. The difference between the rate constants was $\leq 5\%$. The removal rate constant for UV_{280} was calculated as 2.12×10^{-2} min⁻¹ with a corresponding half-life value of 33 minutes. The removal rate constant for UV_{254} was 2.02×10^{-2} min⁻¹ with a half-life of 34 minutes. A removal rate of 0.723 min⁻¹ m⁻¹ was calculated for UV_{254} . On the other hand, the removal rate for UV_{280} was found to be 11% slower with a reaction rate of 0.642 min⁻¹ m⁻¹.

It can be concluded that the presence of chromium ion has a retarding effect on the photocatalytic degradation rate of humic acid. The removal rate of humic acid in the absence of metal ions was calculated to be $0.278 \text{ min}^{-1} \text{ m}^{-1}$ for Color₄₃₆. On the other hand, in the presence of 0.05 mg L⁻¹ chromium ion the rate was found to be 0.176 min⁻¹ m⁻¹. Almost 37% decrease was detected in the photocatalytic removal rate of humic acid.



Figure 4.3. Normalized Color_{436} , Color_{400} , UV_{280} and UV_{254} Values with Respect to Irradiation Time in the Presence of 0.10 mg L⁻¹ Cr without TiO₂



Figure 4.4. Normalized $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} Values with Respect to Irradiation Time in the Presence of 0.05 mg L⁻¹ Cr

4.2.2. Effect of 0.10 mg L^{-1} Cr on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of 10 mg L⁻¹ humic acid with 0.25 mg mL⁻¹ TiO₂ was carried out in the presence of 0.10 mg L⁻¹ chromium ion. According to the data obtained, Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ removals were presented in Figure 4.6.

Control reactions without irradiation (dark reactions) in the presence of catalyst were also performed under identical experimental conditions. The data obtained from dark reactions for $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} were demonstrated in Figure 4.5.

According to Figure 4.5, TiO_2 and humic acid interaction in the presence of chromium ion resulted in an initial adsorptive removal of approximately 40%. Adsorption-desorption processes were observed upto 30 minutes. In extended period after 60 minutes, 60% Color₄₃₆ and 50% UV₂₅₄ removals could be achieved.

On the other hand, as can be seen from Figure 4.6, a decreasing trend was observed upon irradiation. In the presence of 0.10 mg L⁻¹ Cr, 82% Color₄₃₆ and 64% UV₂₅₄ removals were attained after 60 minutes. The obtained results were evaluated in terms of pseudo-first order kinetics and given in Table 4.3 accordingly.

Table 4.3. Pseudo First Order Reaction Rate Constants (k, min⁻¹), Half-life Values ($t_{1/2}$, min) and Related Correlation Coefficients (R) of Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of 0.10 mg L⁻¹ Chromium

Parameter	k (min ⁻¹)	t _{1/2} (min)	\mathbf{R}^2
Color ₄₃₆	3.13x10 ⁻²	22	0.976
Color ₄₀₀	2.93×10^{-2}	24	0.984
UV ₂₈₀	2.20×10^{-2}	32	0.978
UV ₂₅₄	2.06x10 ⁻²	34	0.980

The reaction rate constant for Color_{436} was calculated to be $3.13 \times 10^{-2} \text{ min}^{-1}$ with a half-life value of 22 minutes. The removal rate constant for Color_{400} was $2.93 \times 10^{-2} \text{ min}^{-1}$.



Figure 4.5. Normalized $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} Values with Respect to Time in the Presence of 0.10 mg L⁻¹ Cr



Figure 4.6. Normalized Color_{436} , Color_{400} , UV_{280} and UV_{254} Values with Respect to Irradiation Time in the Presence of 0.10 mg L⁻¹ Cr

A comparison between the reaction rate constants of Color_{436} and Color_{400} indicated that the difference was $\leq 7\%$. On the other hand, the photocatalytic degradation rate of Color_{436} was determined to be 0.232 min⁻¹ m⁻¹ which is $\leq 22\%$ of the reaction rate of Color_{400} . The reaction rates of the UV absorbing centers were found to be higher than the color forming centers. UV₂₈₀ and UV₂₅₄ reaction rate constants were calculated to be 2.20x10⁻² min⁻¹ and 2.06x10⁻² min⁻¹ with half-life values of 32 and 34 minutes, respectively.

4.2.3. Effect of 0.15 mg L⁻¹ Cr on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of 10 mg L^{-1} humic acid with 0.25 mg m L^{-1} TiO₂ was carried out in the presence of 0.15 mg L^{-1} chromium ion and the results obtained were presented in Table 4.4 below.

Table 4.4. Pseudo First Order Reaction Rate Constants (k, min⁻¹), Half-life Values ($t_{1/2}$, min) and Related Correlation Coefficients (R) of Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of 0.15 mg L⁻¹ Chromium

Parameter	k (min ⁻¹)	t _{1/2} (min)	\mathbb{R}^2
Color ₄₃₆	3.14x10 ⁻²	22	0.980
Color ₄₀₀	2.98×10^{-2}	23	0.976
UV ₂₈₀	2.11x10 ⁻²	33	0.922
UV ₂₅₄	2.05x10 ⁻²	34	0.922

The removal rate constants for Color_{436} and Color_{400} were found to be close to each other; 3.14x10⁻² min⁻¹and 2.98x10⁻² min⁻¹ respectively. The trend observed in the reaction rates was also reflected in the corresponding half-life values. The photocatalytic degradation rate of Color_{436} was determined to be 0.220 min⁻¹ m⁻¹ which is $\leq 25\%$ of the reaction rate of Color_{400} . The reaction rate for UV₂₅₄ was determined as 0.734 min⁻¹ m⁻¹ whereas it was 0.652 min⁻¹ m⁻¹. The half-life values were calculated as 33 and 34 minutes for UV₂₈₀ and UV₂₅₄, respectively.



Figure 4.7. Normalized Color_{436} , Color_{400} , UV_{280} and UV_{254} Values with Respect to Irradiation Time in the Presence of 0.15 mg L⁻¹ Cr



Figure 4.8. Normalized $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} Values with Respect to Irradiation Time in the Presence of 0.20 mg L⁻¹ Cr

The normalized Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ values for humic acid in the presence of 0.15 mg L⁻¹ chromium ion were shown in Figure 4.7. According to the figure, initially 50% of Color₄₃₆ removal was achieved for humic acid. After 60 minutes of irradiation, almost 84% of Color₄₃₆ was removed. Color₄₀₀ removal showed a similar trend to Color₄₃₆ and almost the same removal was attained after 60 minutes. On the other hand, UV₂₈₀ and UV₂₅₄ removals followed a similar trend, almost the same removal (70%) was achieved after 60 minutes of irradiation.

4.2.4. Effect of 0.20 mg L⁻¹ Cr on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of 10 mg L⁻¹ humic acid with 0.25 mg mL⁻¹ TiO₂ was carried out in the presence of 0.20 mg L⁻¹ chromium ion. The normalized Color₄₃₆, Color₄₀₀,UV₂₈₀ and UV₂₅₄ values for humic acid in the presence of 0.20 mg L⁻¹ chromium ion were shown in Figure 4.8. As can be seen from the figure, initially almost 30% removal was observed. After 60 minutes of irradiation almost 85% Color₄₃₆ and 70% UV₂₅₄ removals were attained.

The obtained results were evaluated in terms of pseudo-first order reaction kinetics and presented in Table 4.5 accordingly.

Table 4.5. Pseudo First Order Reaction Rate Constants (k, min⁻¹), Half-life Values ($t_{1/2}$, min) and Related Correlation Coefficients (R) of Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of 0.20 mg L⁻¹ Chromium

Parameter	k (min ⁻¹)	t _{1/2} (min)	\mathbf{R}^2
Color ₄₃₆	3.15x10 ⁻²	22	0.941
Color ₄₀₀	2.94x10 ⁻²	24	0.929
UV_{280}	2.18x10 ⁻²	32	0.865
UV ₂₅₄	2.07x10 ⁻²	34	0.859

According to Table 4.5, a decreasing trend was observed in the reaction rate constants, with

increasing half-life values. First order reaction rate constants calculated for humic acid in the presence of 0.20 mg L⁻¹ chromium ion varied between 3.15×10^{-2} min⁻¹ and 2.07×10^{-2} min⁻¹. The reaction rate for Color₄₃₆ was found to be 0.221 min⁻¹ m⁻¹ with a half-life value of 22 minutes. The removal rate for Color₄₀₀ was calculated as 0.291 min⁻¹ m⁻¹ with an almost 25% increase compared to the removal rate of Color₄₃₆. On the other hand, UV₂₅₄ removal was achieved with a reaction rate of 0.756 min⁻¹ m⁻¹. The half-life value for UV₂₅₄ was 34 minutes. Compared to the removal rate of UV₂₅₄, almost 10% decrease was detected for UV₂₈₀. The removal rate for UV₂₈₀ was calculated to be 0.674 min⁻¹ m⁻¹ with a half-life value of 32 minutes.

4.2.5. Comparison of the Effects of Different Chromium Concentrations on the Photocatalytic Degradation of Humic Acid

The photocatalytic degradation rate of humic acid was investigated in the presence of 0.05 mg L^{-1} , 0.10 mg L^{-1} , 0.15 mg L^{-1} and 0.20 mg L^{-1} chromium ions in order to compare the effects of different chromium ion concentrations. The data were evaluated in terms of pseudo first order reaction kinetics. The changes in reaction rates and the half-life values with respect to chromium ion concentration were given in graphs in Figure 4.9 and Figure 4.10.

The comparison of pseudo first order decay parameters and related correlation coefficients of $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} removals were given in Appendix A in Tables A.1-A.4. The data obtained from the photocatalytic removal of humic acid in the presence of different chromium concentrations were also demonstrated in Figures A.1-A.4 in Appendix A.

In Figure 4.9, the rate of the reaction was plotted against chromium ion concentration. It can be seen from the figure that the reaction rates calculated for different chromium ion concentrations were smaller than the baseline rate of humic acid which is the rate obtained in the absence of the metal ions. A significant decrease in the reaction rate was detected in the presence of 0.05 mg L^{-1} chromium ion. Further increase in the chromium ion concentration did not cause any change in the reaction rate.



Figure 4.9. Rate vs. Chromium Concentration for the Photocatalytic Degradation of 10 mg L^{-1} Humic Acid



Figure 4.10. Half-life vs. Chromium Concentration for the Photocatalytic Degradation of 10 mg L^{-1} Humic Acid

The removal rate of humic acid was calculated as 0.278 min⁻¹ m⁻¹. In the presence of 0.05 mg L⁻¹ chromium ion, almost 35% decrease was observed in the rate of Color₄₃₆. However, compared to the photocatalytic degradation of humic acid, a two fold increase in the concentration yielded 15% decrease in the Color₄₃₆ removal efficiency. But further increase in the chromium ion concentration did not cause any significant change in reaction rates. UV₂₅₄ removal rate for humic acid was calculated to be 0.994 min⁻¹ m⁻¹, whereas it was found to be 0.738 min⁻¹ m⁻¹ in the presence of 0.10 mg L⁻¹ chromium ion.

So, it can be concluded that the presence of chromium had a retarding effect on the photocatalytic removal of humic acid, and the rate of the reaction did not depend on the chromium ion concentration. Therefore, Langmuir-Hinshelwood kinetics could be applied successfully by increasing the humic acid concentration and keeping the chromium ion concentration constant at 0.10 mg L^{-1} .

In Figure 4.10, the reaction rates for chromium ion concentrations in range of 0.05 mg L⁻¹ to 0.20 mg L⁻¹ were plotted against the half-life values. It can be seen that the half-life values correlated well with the reaction rates. In accordance with decreasing reaction rates, increasing half-life values were encountered. The half-life values calculated for different chromium ion concentrations were larger than the half-life values of humic acid alone. The most significant change was observed in the presence of 0.05 mg L⁻¹ chromium ion. The half-life of the reaction was calculated to be 28 minutes for Color₄₃₆, whereas it was 18 minutes for humic acid alone. Doubling the chromium ion concentration had an effect of decreasing the half-life to 22 minutes, but further increase in the chromium ion concentration did not cause any significant change in the half-life values.

4.3. Effect of Manganese Ion on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of humic acid was carried out in the presence of manganese ion. The effect of 0.05 mg L^{-1} manganese ion concentration on the photocatalytic oxidation of 10 mg L^{-1} humic acid was investigated.

Control experiments were also performed in the absence of light and the data were presented in Figure 4.11. The initial absorbance difference between humic acid and humic acid + manganese solution was negligible ($\Delta Abs \leq 0.003$) indicating that no reaction occurred between humic acid and the manganese ion.

4.3.1. Effect of 0.05 mg L⁻¹ Mn on the Photocatalytic Degradation of Humic Acid

Photocatalytic degradation of humic acid in the presence of 0.05 mg L^{-1} manganese ion followed a first order reaction profile. The data obtained for $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} removals were demonstrated in Figure 4.12. As can be seen from the figure, in the presence of 0.05 mg L^{-1} manganese ion, 82% $Color_{436}$ and 74% UV_{254} removals were attained after 60 minutes of irradiation.

Control reactions without irradiation (dark reactions) in the presence of catalyst were also performed under identical experimental conditions. The data obtained from dark reactions for $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} were demonstrated in Figure 4.11.

According to Figure 4.11, TiO₂ and humic acid interaction in the presence of manganese ion resulted in an initial adsorptive removal of approximately 35%. Adsorption-desorption processes were observed up to 30 minutes and in extended period after 60 minutes, approximately 65% Color₄₃₆ and 70% UV₂₅₄ removals could be achieved. The data was evaluated in terms of pseudo first order reaction kinetics and the results were given in Table 4.6.

Table 4.6. Pseudo First Order Reaction Rate Constants (k, min⁻¹), Half-life Values ($t_{1/2}$, min) and Related Correlation Coefficients (R) of Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of 0.05 mg mL⁻¹ Manganese

Parameter	k (min ⁻¹)	t _{1/2} (min)	\mathbf{R}^2
Color ₄₃₆	3.37x10 ⁻²	20.5	0.966
Color ₄₀₀	3.27×10^{-2}	21	0.962
UV ₂₈₀	2.40×10^{-2}	29	0.912
UV ₂₅₄	2.31x10 ⁻²	30	0.908

According to Table 4.6, the removal rate constant for Color_{436} was calculated to be $3.37 \times 10^{-2} \text{ min}^{-1}$. The rate constant of Color_{400} was 3.27×10^{-2} with a half-life of 21 minutes. A comparison between the reaction rate constants of Color_{436} and Color_{400} indicated that the difference was $\leq 3\%$. The reaction rate constant for UV_{280} was found to be $2.40 \times 10^{-2} \text{ min}^{-1} \text{ m}^{-1}$ with a half-life value of 29 minutes. The removal rate constant for UV_{254} was calculated as $2.31 \times 10^{-2} \text{ min}^{-1} \text{ m}^{-1}$ with an almost 3% decrease compared to the UV_{280} removal rate constant.

The photocatalytic degradation rate of 10 mg L⁻¹ humic acid for Color_{436} , in the presence of 0.05 mg L⁻¹ manganese ion was found to be 0.236 min⁻¹ m⁻¹. On the other hand, in the presence of 0.10 mg L⁻¹ chromium ion the reaction rate was calculated as 0.232 min⁻¹ m⁻¹. In the absence of metal ions, the photocatalytic degradation of humic acid alone was found to be the fastest with a reaction rate of 0.278 min⁻¹ m⁻¹. In the presence of manganese ion, almost 15% retardation was detected in the photocatalytic degradation rate of humic acid for the color forming centers.

The removal rate of UV_{254} for humic acid in the presence of manganese ion, was calculated to be 0.843 min⁻¹ m⁻¹. Compared to the photocatalytic degradation rate of humic acid in the presence of 0.10 mg L⁻¹ chromium ion, almost 11% decrease was detected for UV_{254} . In the absence of metal ions, the photocatalytic degradation of humic acid alone was found to be the fastest with a reaction rate of 0.994 min⁻¹ m⁻¹.


Figure 4.11. Normalized $Color_{436}$, $Color_{400}$, UV_{280} and UV_{254} Values with Respect to Time in the Presence of 0.05 mg L⁻¹ Mn



Figure 4.12. Normalized Color₄₃₆, Color₄₀₀, UV₂₈₀ and UV₂₅₄ Values with Respect to Irradiation Time in the Presence of 0.05 mg L^{-1} Mn

4.4. Evaluation of the Results in Terms of Langmuir-Hinshelwood Kinetics

The results of the study show that the presence of chromium ion [Cr (VI) in the form of $Cr_2O_7^{-2}$] or manganese ion [in the form of Mn (II)] retards the photocatalytic removal rate provided that the removal rate is explained in terms of Langmuir-Hinshelwood (L-H) kinetics. Further details are given in Chapter 2.4, Kinetics of Chemical Processes.

The L-H kinetics were evaluated for humic acid in the concentration range of 5 mg L^{-1} to 20 mg L^{-1} . By the treatment of the kinetic data obtained for humic acid, the following k and K values were calculated. The data were presented in Table 4.7.

Table 4.7.	Summary of Langmuir-Hinshelwood (L-H)	Parameters	and Oxidation	Rates of
Humic Acid	ł			

			Rate (min ⁻¹ m ⁻¹)			
	k (min ⁻¹ m ⁻¹)	K (m)	5 mg L ⁻¹	10 mg L ⁻¹	15 mg L ⁻¹	20 mg L ⁻¹
Color ₄₃₆	0.124	0.600	0.0847	0.101	0.108	0.111
Color ₄₀₀	0.173	0.536	0.125	0.145	0.154	0.158
UV ₂₈₀	0.412	0.161	0.296	0.343	0.363	0.375
UV ₂₅₄	0.468	0.141	0.339	0.392	0.415	0.427
UV ₂₅₄	0.468	0.141	0.339	0.392	0.415	0.427

The results indicated that the reactivity constant k values, for UV_{280} and UV_{254} were higher than the values obtained for $Color_{436}$ and $Color_{400}$. Contrary to that, the adsorption equilibrium constants (K) of the UV absorbing centers were found to be lower than the color forming centers. This verified the fact that the UV absorbing centers were less adsorbed.

The increase in humic acid concentration caused a slight increase in the removal rates of both color forming and the UV absorbing centers. The removal rates of Color_{436} and UV_{254} for 10 mg L⁻¹ humic acid were calculated to be 0.101 min⁻¹ m⁻¹ and 0.392 min⁻¹ m⁻¹,

respectively. Increasing the humic acid concentration two folds, caused approximately 9% increase in the removal rates of $Color_{436}$ and UV_{254} .

The L-H kinetics evaluated for humic acid in the concentration range of 5 mg L^{-1} to 20 mg L^{-1} in the presence 0.10 mg L^{-1} chromium ion were also given below for comparison purposes. The data were presented in Table 4.8.

 Table 4.8.
 Summary of Langmuir-Hinshelwood (L-H) Parameters and Oxidation Rates of

 Humic Acid in the Presence of Chromium Ion

			Rate (min ⁻¹ m ⁻¹)			
	k (min ⁻¹ m ⁻¹)	K (m)	5 mg L ⁻¹	10 mg L ⁻¹	15 mg L ⁻¹	20 mg L ⁻¹
Color ₄₃₆	0.0625	0.401	0.0373	0.0461	0.0506	0.0532
Color ₄₀₀	0.0857	0.311	0.0428	0.0647	0.0705	0.0738
UV ₂₈₀	0.235	0.127	0.149	0.178	0.191	0.198
UV ₂₅₄	0.250	0.0958	0.161	0.195	0.210	0.219

The reaction rate of humic acid in the presence of chromium ion indicated an increasing trend, depending on the increasing humic acid concentration. UV absorbing sites reflected higher removal rates than the color absorbing sites. The reactivity constants (k) for UV_{280} and UV_{254} were found to be approximately three times faster than the reactivity constants obtained for $Color_{436}$ and $Color_{400}$. This was also in accordance with the decreased adsorption equilibrium constants (K) of UV absorbing centers. They were less adsorbed than the color absorbing centers.

Examination of the constants for humic acid alone and humic acid in the presence of chromium indicated that the values of the reactivity constant k were significantly lower in the presence of the metal ion. The decrease in the value of k might be due to absorbance of UV illumination by a complex between chromium (in the form of dichromate) and a humic acid oxidation intermediate.

According to the Table 4.8, approximately 55% decrease was observed in the rate of color

removal of humic acid in the presence of chromium ion. The removal rates of Color_{436} and Color_{400} for 10 mg L⁻¹ humic acid were calculated to be 0.101 min⁻¹ m⁻¹ and 0.145 min⁻¹ m⁻¹, respectively. With the addition of chromium ion, the given Color_{436} removal rate was decreased to 0.0461 min⁻¹ m⁻¹ whereas Color_{400} removal rate was found to be 0.0647 min⁻¹ m⁻¹. The difference between the rates of color removal can be explained by the different reactivities of the color forming chromophoric groups absorbing at 400 nm and 436 nm. Color_{436} removal rate was found to be 29% slower than Color_{400} in the presence of chromium ion. The reason for this might be the presence of reactive sites absorbing at 436 nm that are more susceptible to interact with chromium ions.

For UV₂₅₄ removal, the reaction rate for 10 mg L⁻¹ humic acid was calculated to be 0.392 min⁻¹ m⁻¹. With the addition of chromium ion, the removal rate was found to be 0.195 min⁻¹ m⁻¹ with a 50% reduction. The inhibition effect could be related to strong adsorption which could be explained by Freundlich adsorption constants.

The data of the L-H kinetics evaluated for humic acid in the concentration range of 5 mg L^{-1} to 20 mg L^{-1} in the presence 0.05 mg L^{-1} manganese ion were presented in Table 4.9.

Table 4.9. Summary of Langmuir-Hinshelwood (L-H) Parameters and Oxidation Rates of Humic Acid in the Presence of Manganese Ion

~	· · · · · · · · · · · · · · · · · · ·	0.0.0.em		Rate (m	in ⁻¹ m ⁻¹)	
	k (min ⁻¹ m ⁻¹)	K (m)	10 mg L ⁻¹	15 mg L ⁻¹	20 mg L ⁻¹	25 mg L ⁻¹
Color ₄₃₆	0.148	0.580	0.119	0.128	0.133	0.136
Color ₄₀₀	0.201	0.416	0.162	0.173	0.179	0.184
UV ₂₈₀	0.423	0.110	0.326	0.353	0.369	0.379
UV ₂₅₄	0.486	0.0965	0.379	0.409	0.426	0.437

The reaction rate of humic acid in the presence of manganese ion indicated an increasing trend with increasing humic acid concentration. UV absorbing sites reflected higher removal rates than the color absorbing sites. The reactivity constants (k) for UV_{280} and UV_{254} were calculated to be 0.423 min⁻¹ m⁻¹ and 0.486 min⁻¹ m⁻¹, respectively. On the other hand, the

reactivity constants obtained for Color_{436} and Color_{400} were 0.148 min⁻¹ m⁻¹ and 0.201 min⁻¹ m⁻¹. The adsorption equilibrium constants (K) indicated a decreasing trend with increasing reactivity constants (k). The UV absorbing centers were less adsorbed than the color absorbing sites.

Examination of the constants for humic acid and humic acid in the presence of manganese indicated that the values of the reactivity constant k were slightly higher in the presence of the metal ion. The reaction rates for the color forming centers were also found to be higher but the UV absorbing centers were lower in the presence of the manganese. For Color_{436} the reaction rate for 10 mg L⁻¹ humic acid was calculated to be 0.101 min m⁻¹. In the presence of manganese ion the reaction rate was detected to be the fastest with a value of 0.119 min⁻¹ m⁻¹ and the slowest reaction rate was achieved in the presence of chromium ion with a value of 0.0461 min⁻¹ m⁻¹.

The presence of chromium and manganese ions resulted in decreased removal rates on the photocatalytic degradation of humic acid compared to the baseline rate that is the rate obtained in the absence of the metal ions. The most pronounced retarding effect was observed in the presence of chromium ion with decrease (54% for Color₄₃₆ and 50% for UV₂₅₄) in the L-H reaction rate.

4.5. Evaluation of Metal Ion Effect

The presence of chromium and manganese ions resulted in decreased removal rates on the photocatalytic degradation of humic acid compared to the baseline rate that is the rate obtained in the absence of the metal ions. The most pronounced retarding effect was observed in the presence of chromium ion with decrease (19% for Color₄₃₆ and 25% for UV_{254}) in the pseudo first order reaction rate constants.

4.5.1. Manganese Ion Effect

In this study, the photocatalytic oxidation of 10 mg L⁻¹ humic acid was carried out in the presence of 0.05 mg L⁻¹ manganese (II) in the form of hydrated aqua complex, $Mn(H_2O)_6^{2+}$ at neutral pH in aqueous medium.

The visual examination of the reaction medium did not reveal any precipitate formation due to the oxidation of Mn (II) to MnO_2 .

$$Mn^{2+} + \frac{1}{2}O_2 + H_2O \longrightarrow MnO_2 + 2H^+ \qquad k_{ox} = 10^{-6} \text{ min}^{-1}$$
(65)

It is known that the photocatalytic oxidation of manganese (II) to insoluble MnO₂ is thermodynamically possible ($k_{ox}=10^{-6}$ min⁻¹) in neutral to acidic aqueous medium, followed by a pH decrease during the reaction ($\Delta pH=0.4$) (Lozano *et al.*, 1992).

According to the results of the experimental study, a pH drop ($\Delta pH=0.65$) was observed which might be either an indication of MnO₂ formation or be related with the possible degradation of humic acid to organic acids and/or CO₂. On the other hand, k_{ox} value of the reaction (k_{ox}=10⁻⁶ min⁻¹) is very slow compared to the photocatalytic degradation rate of humic acid (k_{pco}=3.86x10⁻² min⁻¹). Therefore, the photocatalytic oxidation of humic acid in the presence of manganese ion might be more favorable than the direct oxidation of Mn (II) to MnO_2 .

Aqueous manganese ion speciation studies indicate that Mn (II) ion is expected to be in the form of hydrated aqua complex, $Mn(H_2O)_6^{2+}$ at pH \cong 7. As reported by Gamble *et al.* (1977), hydrated manganese (II) ions and humic substances might form outer-sphere complexes in which manganese (II) ions remain partly hydrated at binding sites of humic acid. It is also shown by Lu et al. (1997) that manganese (II) interacts directly with carboxylate anionic groups in humic substances forming a weak complex with a log K value of 2.0 (± 0.1). The slightly lower value of the reaction rate constant in the presence of manganese ion, $(k_{PCO} \le 13\%$ for Color₄₃₆, $k_{PCO} \le 15\%$ for UV₂₅₄) compared to the rate constant k of humic acid, might be explained by the possible complex formation with humic acid. the weak complex formed might block the active sites on the TiO2 surface and hence, lead to a slight reduction in the photocatalytic removal rate of humic acid. In accordance with this, in the presence of manganese ions, high K_F values were obtained from the adsorption experiments for the UV-absorbing centers. This reveals that, the adsorption process is being favored by the aromatic moieties rather than the color forming centers where K_F values of humic acid and humic acid + manganese systems were not significantly different. The observed phenomenon could not be explained clearly due to the lack of the available literature knowledge.

The photocatalytic oxidation of toluene, a simple organic molecule, using TiO_2 as the photocatalyst was carried out in the presence of 10^{-5} M manganese (II) at pH 3 and a significant increase in the reaction rate was observed contrary to the findings of this study (Butler and Davis, 1993). The increase in the reaction rate was explained by the oxidation of metal ions by the photogenerated holes (reaction 66), proceeding in competition with reactions 40 and 41.

$$\mathbf{M}^{(\mathbf{n}-1)^{+}} + \mathbf{h}^{+} \longrightarrow \mathbf{M}^{\mathbf{n}^{+}} \tag{66}$$

$$h^+ + H_2O_{(ads)} \longrightarrow OH + H^+$$
 (40)

$$h^{+} + 2OH_{(ads)} \longrightarrow OH + OH$$
(41)

The consumption of holes (h^+) by the metal ion results in an increased rate of **•OH** radical formation through the reactions given above (Butler and Davis, 1993).

In this study neither aqueous manganese (II) ion oxidation to insoluble MnO_2 , nor an increase in the reaction rate was observed. This might be related to the complex structure of humic acid, comprising a variety of ligands. According to Ghosh and Schnitzer (1980), in the presence of metal ions, due to a possible complex formation with humic acid, rearrangement of the electrostatic forces takes place. The formation of a micelle-like cage structure by metal ion-bridging interactions might also be expected (Puchalski *et al.*, 1992).

On the other hand, the zero point of charge (ZPC) for TiO₂ Degussa P-25 was reported as $pH_{zpc} \cong 6.3$ (Bahnemann *et al.*, 1994). In acidic medium ($pH < pH_{zpc} \cong 6.3$) the particle surface is positively charged and the adsorption of anionic and polar substrates is enhanced; in basic medium ($pH > pH_{zpc} \cong 6.3$) the surface charge is negative and the adsorption of cationic species is favored.

In acidic medium:

 $TiOH + H_3O^+ \longrightarrow TiOH_2^+ + H_2O$ (67)

In basic medium:

 $TiOH + OH^{-} \longleftrightarrow TiO^{-} + H_2O$ (68)

It is also known that at neutral pH, the TiO_2 surface comprises of an equal number of positive and negative charges. As a result of this, repulsive and attractive forces of the same strength are generated on the surface. Due to electrostatic interactions, the negatively charged sites on TiO_2 might be expected to interact with the cationic manganese ions found in solution as $Mn(H_2O)_6^{2+}$.

Finally, as a result of the competitive reactions between metal ion, ligands of humic acid and the photocatalyst; the photocatalytic removal efficiency of humic acid in the presence of manganese ions might be altered with no significant change in oxidation rates.

4.5.2. Chromium Ion Effect

In this study, the photocatalytic oxidation of 10 mg L^{-1} humic acid was carried out in the presence of 0.10 mg L^{-1} chromium at neutral pH in aqueous medium.

Changing the chromium ion concentration in order to understand the concentration dependency indicated no significant change on the calculated removal rates. So it can be concluded that the photocatalytic removal of humic acid was not dependent on chromium ion concentration.

The oxyanions of chromium (VI) are known to exhibit complex equilibria in aqueous solution involving the species $CrO_4^{2^-}$, $HCrO_4^-$, H_2CrO_4 and $Cr_2O_7^{2^-}$ with an equilibrium between $HCrO_4^-$ and $Cr_2O_7^{2^-}$ (Cotton and Wilkinson, 1976).

$$2HCrO_4 \longleftrightarrow Cr_2O_7^{2^*} + H_2O$$
(22)

In medium to low pH, Cr (VI) exists in aqueous solution predominantly as the dichromate anion, $Cr_2O_7^{2-}$. Therefore, in this study, at the neutral pH of the solution, chromium was also expected to be in the form of dichromate oxyanion.

The results of the experimental study showed that, the photocatalytic degradation rate of humic acid decreased by 19% for Color₄₃₆ and 25% for UV₂₅₄ in the presence of chromium ion. The reduction in rate might be explained by the possible complex formation with humic acid, but chromium (VI) in the form of dichromate $(Cr_2O_7^{2^-})$ is unchelatable. Therefore reduction of chromium (VI) might be expected. The possible reduction of chromium might be achieved either directly by the humic acid or by the use of the photogenerated electrons in the presence of irradiated titanium dioxide powders. In the presence of humic acid reduction of $Cr_2O_7^{2^-}$ to chromium (III) is only possible in acidic medium but this study is carried out at neutral pH conditions (pH \cong 6.7) which is not sufficiently acidic to complete the reaction. Therefore, the reduction of $Cr_2O_7^{2^-}$ to chromium (III) is not the major pathway of oxidation.

As explained by Lu et al. (1997), the reaction of chromium (VI) and humic substances involved two steps. The first step was the formation of chromium (VI) complex with diol, carboxylic acid and polyphenol groups in humic substances. The next step was a redox process occurring under acidic conditions, in which humic substances were detected to reduce chromium (VI) to chromium (V) as an intermediate, and then to chromium (III) which was complexed by humic substances (Goodgame et al., 1984). Chromium (V) is known to be a stable intermediate at room temperature and neutral pH conditions. Possible structures of chromium (V) intermediate complex with ligands in humic substances proposed by Lu et al. (1997) were given in Figure 2.6. If chromium (V) species existed in solution, the whole complex would be negatively charged. On the other hand, at neutral pH of the solution (pH=6.7), the surface of titanium dioxide comprised of negative and positive charges (reactions 69,70). The positively charged sites might attract the negatively charged [Cr (V) HA]ⁿ⁻ complex, while the negatively charged sites repelled the complex but the results of the adsorption experiments showed that lower K_F values ($\leq 45\%$) were obtained for humic acid in the presence of chromium ion for the color forming centers (0.537 for humic acid, 0.298 for humic acid + chromium system). So, adsorption process was not favored by the color forming centers. According to Stumm and Morgan (1981), a metal must bind to the surface through its coordinate sphere by filling all of its available coordination sites with ligands so that it becomes nonadsorbable. Therefore, complex formation of chromium ion with humic acid might be expected to predominate over the adsorption process and block the active sites on the photocatalyst.

Davis and Leckie (1978) investigated three component adsorption systems and postulated a nonsymmetrical metal ligand system that allows the formation of three surface adsorbate configurations resulting in a "metal-like", "ligand-like" or both "metal-like and ligand-like" adsorptive behaviors. Accordingly, in this study a ligand-like adsorption behavior might be expected for the humic acid + chromium system. As verified by Stumm and Morgan (1981), available coordination sites of chromium would be filled by the ligands of humic acid and thereby adsorption of humic acid instead of the metal ion onto the surface of the photocatalyst would be favored. In the presence of metal ions, due to the possible complex formation between humic acid and the metal ions, rearrangement of the electrostatic forces

takes place, and formation of a micelle-like cage structure by metal ion-bridging interactions might be expected as stated by Puchalski and Morra (1992).

On the other hand, the ultraviolet illumination of Cr (VI) solutions containing TiO_2 in suspension was found to reduce Cr (VI) to Cr (III) at neutral pH (Munoz and Domenech, 1990; Xu and Chen, 1990). It was assumed that the electrons reduced Cr (VI) to Cr (III) and the holes oxidized water. The presence of oxygen competed with Cr (VI) for the photogenerated TiO_2 electrons and therefore resulted in a decrease of the photoreduction yield. Related equations were given as:

$$\mathrm{TiO}_2 \xrightarrow{h^{\nu}} \mathrm{h}^+ + \mathrm{e}^- \tag{38}$$

$$8H^{+} + CrO_{4}^{2^{-}} + 3 e^{-} \longrightarrow Cr^{3^{+}} + 4H_{2}O$$
(69)

$$H_2O + 2h^+ \longrightarrow \frac{1}{2}O_2 + 2H^+$$
(70)

Accordingly in this study, the photoreduction process might be expected to take place by electron transfer from illuminated TiO_2 to anionic Cr (VI) species. The retardation effect of chromium ion on the photocatalytic degradation rate of humic acid might be related to the use of the photogenerated titanium dioxide electrons for the possible reduction of Cr (VI), therefore leading to the decreased generation of hydroxyl radical and possible reduction in the removal rate of humic acid.

The photocatalytic oxidation of Cr (VI) to Cr (III) at different pH values using TiO₂ as the photocatalyst and a variety of organics as the organic substrate (methanol, formic acid, salicylic acid, EDTA, phenol and nitrobenzene) was investigated by Prairie *et al.*, (1993). It was reported that the photocatalytic conversion of Cr (VI) to Cr (III) in the presence of salicylic acid at different pH values (pH 1 to pH 6) followed first order reaction kinetics. Rapid reduction of Cr (VI) was also observed with EDTA, mandelic acid and citric acid. Since humic acids contain a variety of functional groups similar to those model compounds, reduction of Cr (VI) in the presence of humic acid might also be expected but unfortunately could not be determined due to the analytical difficulties.

4.6. Adsorption Effects in Photocatalysis

In heterogeneous catalysis, the reaction occurs in the adsorbed phase and the overall process can be decomposed into five independent steps (Serpone and Pelizzetti, 1989):

- 1. Transfer of the reactants in the fluid phase to the surface
- 2. Adsorption of at least one of the reactants
- 3. Reaction in the adsorbed phase
- 4. Desorption of the products
- 5. Removal of the products from the interface region

A heterogeneous photocatalytic reaction involves the interaction of photoproduced charge carriers with at least one adsorbed reactant. The reactant (R) should be adsorbed from the solution and should follow the simple reaction network as given below:

$$R \longleftrightarrow R_{ads} \longrightarrow product \tag{71}$$

$$\mathbf{R} \longleftrightarrow \mathbf{R}_{\mathsf{ads}} \longleftrightarrow (\mathbf{R}_1)_{\mathsf{ads}} \longleftrightarrow \cdots \longleftrightarrow (\mathbf{R}_n)_{\mathsf{ads}} \longrightarrow \mathsf{product}$$
(72)

Interpretation of solute adsorption onto the surface of the semiconductor and the influence of such adsorption upon the rate of photocatalytic degradation of the substrate is an important phenomena. In the analysis of heterogeneous kinetics of photocatalyzed reactions, a number of the earlier literature results were fitted to a simple rate equation as explained by Langmuir-Hinshelwood kinetics:

$$\frac{-dC}{dt} = k \frac{K[C_0]}{1+K[C_0]}$$
(52)

The Langmuir-Hinshelwood (L-H) kinetic model involves reactions between reactant species adsorbed onto the surface of the photocatalyst.

In literature, adsorption process was explained using models. The most frequently used ones

are Freundlich and Langmuir models. Langmuir model derives from the assumption that a smooth surface is involved in which all sites are equivalent and the adsorbed molecules form a monolayer coverage. When the surface has achieved saturation, no further adsorption can occur. On the other hand, Freundlich model describes adsorption events occurring on heterogeneous surfaces composed of different adsorption sites. The details of the adsorption models were given in Section 2.4.2.

In this study, batch adsorption experiments were carried out to evaluate the effect of the extent of adsorption of humic acids onto TiO_2 in the presence of a fixed concentration of 0.05 mg L⁻¹ manganese and 0.10 mg L⁻¹ chromium ions separately. The adsorption experiments were conducted according to the method outlined in Section 3.2.2. For comparison purposes, q_A versus C_e graphs were plotted for humic acid, humic acid + manganese and humic acid + chromium systems where, qA is the amount of solute adsorbed per unit weight of solid adsorbent, and Ce is the concentration of the solute remaining in the solution at equilibrium. The data for $Color_{436}$ and UV_{254} were presented in Figures 4.13 and 4.14.

According to Figure 4.13, humic acid, humic acid + manganese and humic acid + chromium systems followed a Langmuirian type behaviour for Color_{436} . On the other hand, as can be seen from Figure 4.14, UV_{254} data for humic acid of the same concentration showed a different profile other than Color_{436} . In the presence of metal ions a Langmuirian type behaviour was observed for UV_{254} .

The results of the adsorption experiments were fitted to the Freundlich adsorption equation which is the most commonly used nonlinear adsorption equilibrium model. Further discussion for the determination of the empirically derived coefficients were given in Section 2.4.2.

For comparison purposes the Freundlich parameters, K_F and 1/n values obtained from the adsorption experiments of humic acid in the presence of manganese or chromium ion and humic acid alone were given in Table 4.10.



Figure 4.13. Comparison of Color₄₃₆ Adsorption Isotherms of Humic Acid, Humic Acid + Manganese and Humic Acid + Chromium Systems



Figure 4.14. Comparison of UV_{254} Adsorption Isotherms of Humic Acid, Humic Acid + Manganese and Humic Acid + Chromium Systems

	\mathbf{K}_{F}	1/n	R ²
Color ₄₃₆			
Humic Acid	0.537	1.5	0.717
Humic Acid+Manganese	0.542	0.51	0.962
Humic Acid+Chromium	0.298	0.48	0.863
Color ₄₀₀			
Humic Acid	0.467	1.5	0.733
Humic Acid+Manganese	0.628	0.48	0.964
Humic Acid+Chromium	0.353	0.47	0.878
UV ₂₈₀			
Humic Acid	0.108	1.8	0.943
Humic Acid+Manganese	1.35	0.16	0.776
Humic Acid+Chromium	0.500	0.50	0.852
UV ₂₅₄			
Humic Acid	0.0738	1.9	0.935
Humic Acid+Manganese	1.59	0.18	0.808
Humic Acid+Chromium	0.498	0.53	0.863

Table 4.10. Freundlich Parameters, K_F , 1/n and Correlation Coefficients (R^2)

In the presence of chromium (VI) in the form of dichromate $(Cr_2O_7^{2-})$ and manganese (II) in the form of $Mn(H_2O)_6^{2+}$, the adsorption intensity (1/n) values were found to be lower than 1/n values of the humic acid/TiO₂ system. It can be seen that the color forming centers exhibited lower 1/n values than the UV absorbing centers for humic acid and higher values for humic acid + manganese systems. This might be due to different binding capacities of manganese ions on different sites of humic acid. On the other hand no significant change was observed for the adsorption intensity values of the chromium ion.

As can be seen from Table 4.10, no significant difference was observed with the Freundlich

 K_F constants, but compared to the other two, the humic acid + manganese system exhibited the highest values. This can be related to the formation of a weak complex between humic acid and manganese, which enables humic acid to be adsorbed on the photocatalyst surface, but in the presence of chromium ion the complex formed with humic acid might be assumed to block the active sites on the photocatalyst. Therefore a decreased adsorption trend was observed.

For the color forming centers, the lowest K_F constants were determined for humic acid in the presence of chromium ion. But for the UV absorbing centers, the lowest K_F values were determined for the humic acid alone.

Metal adsorption onto oxide surfaces has been extensively studied in literature (Petrovic *et al.*,1999). Davis and Leckie (1978) investigated three component adsorption systems and postulated a nonsymmetrical metal ligand system that allows the formation of three surface adsorbate configurations resulting in a "metal-like", "ligand-like" or both "metal-like and ligand-like" adsorptive behaviours.

Stumm and Morgan (1981) claimed that a metal must bind to the surface through its coordinate sphere by filling all of its available coordination sites with ligands so that it becomes nonadsorbable.

Accordingly, in this study a ligand-like adsorption behaviour might be expected for the humic acid + manganese and humic acid + chromium system. As verified by Stumm and Morgan (1981), available coordination sites of manganese and chromium would be filled by the ligands of humic acid and thereby adsorption of humic acid instead of the metal ion onto the surface of the photocatalyst would be favored.

5. CONCLUSION AND RECOMMENDATIONS

The aim of this study was to investigate the effects of chromium and manganese ions on the photocatalytic degradation of humic acid at neutral pH conditions (pH \cong 6.7). For comparison purposes, preliminary experiments were also carried out to follow the photocatalytic degradation of humic acid in the absence of metal ions.

The oxidative degradation of humic acid (10 mg L⁻¹) in the presence of chromium or manganese ion with 0.25 mg mL⁻¹ TiO₂, Degussa P-25 was followed by both pseudo first order and Langmuir-Hinshelwood kinetics. Complimentary adsorption experiments were also performed to evaluate the effect of adsorption intensity on the photocatalytic degradation rates and the results were expressed in terms of Freundlich constants. The results indicated that chromium ions in the range of 0.05-0.20 mg L⁻¹ exhibited a retardation effect on humic acid degradation. A significant decrease in the reaction rate was detected in the presence of 0.05 mg L⁻¹ chromium. Further increase in the chromium ion concentration did not cause any important change in the reaction rates for the parameters studied (reaction rate difference < 1%). The presence of 0.10 mg L⁻¹ chromium ion, which is the maximum allowable limit in natural waters, retarded the removal rates for all of the parameters when compared with the baseline rate of humic acid (for Color₄₃₆, $k_{PCO} \le 19\%$; for Color₄₀₀ $k_{PCO} \le 21\%$; for UV₂₈₀ $k_{PCO} \le 24\%$ and for UV₂₅₄, $k_{PCO} \le 25\%$).

The results of this study illustrated that the presence of chromium and manganese ions retarded the photocatalytic removal rate of humic acid. The retardation effect of chromium could be explained by the formation of a complex with humic acid, but chromium (VI) in the form of dichromate $(Cr_2O_7^{-2})$ is unchelatable. Therefore reduction of chromium (VI) to stable chromium (V) and then to chromium (III) might be expected. The possible reduction of chromium might be achieved either by the use of the photogenerated titanium dioxide electrons or directly by the humic acid in which humic substances are assumed to reduce chromium (VI) to chromium (V) as an intermediate, and then to chromium (III) which was complexed by humic substances (Goodgame *et al.*, 1984). In the former case, a photoreduction process might take place by electron transfer from illuminated TiO₂ to the

metal ion. Thereby the formation of reactive radical species on the photocatalyst, which compete with the reduction of the chromium ions probably complexed with the humic substances in the system might be slowed down resulting in retardation of the oxidation rate of humic acid.

The results of the adsorption experiments showed that the adsorption of humic acid was not favored in the presence of chromium ions since the obtained K_F values were relatively small compared to the K_F values of humic (0.537 for humic acid, 0.298 for humic acid + chromium for the color forming centers). So, adsorption process was not favored by the color forming centers. Therefore, complex formation of chromium ion with humic acid might be expected to predominate over the adsorption process and retard the degradation of the humic acid molecule. The competitive reactions between metal ions, humic acids and the photocatalyst might alter the photocatalytic removal efficiency of humic substances.

The effect of 0.05 mg L⁻¹ manganese ion on the photocatalytic degradation rate of humic acid was also studied. It was found that the presence of manganese ion caused a slight decrease in the removal rate of humic acid (for Color₄₃₆, $k_{PCO} \le 13\%$; for Color₄₀₀ $k_{PCO} \le 12\%$; for UV₂₈₀ $k_{PCO} \le 18\%$ and for UV₂₅₄, $k_{PCO} \le 15\%$). The reason for this might be explained by the formation of a weak complex with humic acid which might have blocked the active sites on the TiO₂ surface and hence, reduce the photocatalytic removal of humic acid.

As a result it can be said that, the complexity of the structure of humic acid molecule and the presence of metal ions in the system can ultimately change the profile of the photocatalytic oxidation through complex formation, oxidation-reduction and adsorption-desorption processes. Since the surface characteristics of TiO₂, the nature of functional groups of humic acid and the speciation of metals in solution are all pH dependent, the effect of pH can also be studied.

In this study, the determination of chromium and manganese ion concentrations in the presence of natural organic matter could not be performed with the spectrophotometric methods. Also possible amount of manganese and chromium ions adsorbed on the surface of the photocatalyst could not be determined. Therefore ion selective electrodes might be

used to determine the amount of trace metals in solution and to have a better idea of the amount of metal complexed with the humic acid and the amount of metal adsorbed on the surface of the photocatalyst. The use of a hole scavenger such as methyl alcohol might be helpful, in order to find an explanation for the reaction mechanism in relation to MnO_2 formation.

APPENDIX A

Table A.1. Pseudo First Order Decay Parameters and Related Correlation Coefficients of $Color_{436}$ Removal for the Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of Different Chromium Concentrations

Chromium Ion					
Concentration (mg L ⁻¹)	НА	0.05	0.10	0.15	0.20
Rate $(\min^{-1} m^{-1})$	0.278	0.176	0.232	0.220	0.221
t _{1/2} (min)	18	28	22	22	22
R ²	0.970	0.861	0.976	0.980	0.941

Table A.2. Pseudo First Order Decay Parameters and Related Correlation Coefficients of $Color_{400}$ Removal for the Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of Different Chromium Concentrations

Chromium					
concentration (mg L ⁻¹)	НА	0.05	0.10	0.15	0.20
Rate $(\min^{-1} m^{-1})$	0.368	0.266	0.287	0.295	0.291
t _{1/2} (min)	19	25	24	23	24
\mathbb{R}^2	0.968	0.893	0.984	0.976	0.929

Table A.3. Pseudo First Order Decay Parameters and Related Correlation Coefficients of UV_{280} Removal for the Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of Different Chromium Concentrations

Chromium					
concentration (mg L ⁻¹)	НА	0.05	0.10	0.15	0.20
Rate $(\min^{-1} m^{-1})$	0.899	0.642	0.667	0.652	0.674
t _{1/2} (min)	24	33	32	33	32
R ²	0.955	0.869	0.978	0.922	0.869

Table A.4. Pseudo First Order Decay Parameters and Related Correlation Coefficients of UV_{254} Removal for the Photocatalytic Degradation of 10 mg L⁻¹ Humic Acid in the Presence of Different Chromium Concentrations

Chromium					
concentration (mg L^{-1})	НА	0.05	0.10	0.15	0.20
Rate (min ⁻¹ m ⁻¹)	0.994	0.723	0.738	0.734	0.756
t _{1/2} (min)	25	34	34	34	34
R ²	0.951	0.859	0.980	0.922	0.859



Figure A.1. Normalized Color_{436} Values with Respect to Irradiation Time in the Presence of Different Chromium Ion Concentrations



Figure A.2. Normalized Color₄₀₀ Values with Respect to Irradiation Time in the Presence of Different Chromium Ion Concentrations



Figure A.3. Normalized UV_{280} Values with Respect to Irradiation Time in the Presence of Different Chromium Ion Concentrations



Figure A.4. Normalized UV_{254} Values with Respect to Irradiation Time in the Presence of Different Chromium Ion Concentrations

APPENDIX B

Pseudo First-Order Kinetics

The equation of the first-order kinetics is given as:

-dC / dt = k [C]

k : pseudo first-order reaction rate constant, (min⁻¹)

[C] : substrate concentration, $(mg L^{-1}, m^{-1})$

Upon integration, the following equation is obtained:

 $\ln \left[C_t / C_o \right] = -kt$

 $\begin{bmatrix} C_t \end{bmatrix}$: concentration at time t

 $\begin{bmatrix} C_o \end{bmatrix}$: concentration at time 0

When $\ln [C_t/C_o]$ versus time graph is plotted, the slope gives the reaction rate constant (k, min⁻¹). The half-life (t_{1/2}, min) of the reaction is calculated as follows:

 $t_{1/2} = 0.693 / k$

Example:

Photocatalytic degradation rate of Color₄₃₆ removal:

Time (min.)	[C _t] / [C _o]	ln [C _t / C _o]
0	1.000	0.000
10	0.431	-0.842
20	0.375	-0.981
30	0.278	-1.280
40	0.194	-1.828
50	0.111	-2.198
60	0.083	-2.489

 $k = 3.86 \times 10^{-2}$

 $t_{1/2} = 0.693 / 3.86 \times 10^{-2} = 18$

 $R^2 = 0.970$

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