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**TITANIUM DIOXIDE BASED NOVEL ADVANCED OXIDATION PROCESSES
IN WATER TREATMENT AND BY-PRODUCT FORMATION**

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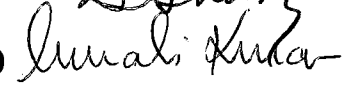
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LISTS OF ABBREVIATIONS

CD	: Conduction band
DO	: Dissolved oxygen
DOC	: Dissolved organic carbon
GAC	: Granular activated carbon
HA	: Humic acid
HSB	: Hoigne, Staehelin, and Dader model
GTF	: Gordon, Tomiyasu, and Fukutomi model
NOM	: Natural organic matter
NMR	: Nuclear magnetic resonance
PC	: Photocatalytic
PEC	: Photoelectrocatalytic
PAC	: Powdered activated carbon
SCE	: Saturated calomel electrode
SHE	: Standard hydrogen electrode
THM	: Trihalomethanes
TSA	: Total surface area
TIC	: Total inorganic carbon
TOC	: Total organic carbon
TO₃	: Transferred ozone
UV₂₅₄	: Absorbance at 254 nm wave length
Vis₄₀₀	: Absorbance at 254 nm wave length
VB	: Valance band

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LIST OF SYMBOLS

E_{bg}	: Band gap energy
E_f	: Fermi level
E_v	: The edge of the valence band
E_c	: The edge of the conduction band
E_{rdx}^0	: Standard potential
E_{rdx}	: Nernst potential
e_{CB}^-	: Photogenerated electron at the conduction band
F	: Faraday constant
V_{fb}	: Flat band potential
λ_{bg}	: The wavelength of the band gap
h	: Plank's constant
h_{VB}^+	: Photogenerated hole at the valance band
I	: Current
K	: Pseudo first order degradation constant
k_0	: Zero order degradation rate
k_1	: Pseudo first order degradation constant
α	: Optical absorption coefficient
N_c	: The effective density of energy levels at energy of E_c
N_v	: The effective density of energy levels at energy of E_v
pH_{pzc}	: Point of zero charge
R	: Pseudo first order degradation rate
T	: Temperature
$t_{1/2}$	: The half life for first order kinetic model
n	: The amount of the transferred electrons
q	: Electronic charge
ϵ_s	: The static dielectric constant of semiconductor
N_D	: Semiconductor parameters (between 10^{16} and 10^{18} cm^{-3})
ν	: The frequency of light
W	: Depletion layer

ÖZET

SU ARITIMINDA TİTANYUM DİOKSİT BAZLI YENİ İLERİ OKSİDASYON METODLARI VE YAN ÜRÜN OLUŞUMU

Bu çalışmada iki yeni ileri oksidasyon prosesi olan Fotoelektrokatalitik (FEK) ve katalitik ozonlama proseslerinde humik asit giderimi ve bromat oluşumu incelenmiştir.

İlk olarak, FEK arıtma yöntemi humik asit (HA) giderimi için kullanılmıştır. Humik asit giderimi 254 nm de absorbans değeri (UV_{254}) ve toplam organik madde ölçümleri ile izlenmiştir. Elde edilen sonuçlar FEK UV_{254} gideriminin sıfırıncı derece toplam organik karbon (TOK) gideriminin ise birinci derece kinetik modele uyduğu göstermiştir. Arıtma koşullarına göre FEK arıtma ile %90'ın üzerinde UV_{254} ve %58-80 TOK giderimi elde edilmiştir. Fotokatalitik arıtma yöntemi aynı koşullarda HA giderimi için kullanılmış ve FEK arıtma yönteminin fotokatalitik arıtma metoduna göre çok daha verimli olduğu tespit edilmiştir.

İkinci olarak, FEK prosesinde ince TiO_2 film tabakası ile kaplı anot ve platinyum katot elektrotlar kullanılarak anot kompartımanında aktif brom ve bromat oluşumu araştırılmıştır. Anodik aktif brom oluşumu FEK prosesi içerisinde zamanla artmış ve belli bir reaksiyon süresi sonunda sabit konsantrasyona ulaşmıştır. Bromat oluşumunda kararlılık durumu gözlenmemiş ve zamana bağlı olarak bromat konsantrasyonu sürekli olarak artmıştır. Etkili parametrelere bağlı olarak proseste 25 mgL^{-1} ve 212 mgL^{-1} konsantrasyonları arasında aktif brom oluştuğu gözlenmiştir. Bromat oluşumu ise 5.5 den büyük pH değerlerinde gözlenmiş ve artan pH değerleri ile artmış fakat $pH > 9$ değerlerinde aktif brom oluşumundaki azalma nedeniyle tekrar azalmıştır. Çalışmada ayrıca çeşitli değişkenlerin HA giderimine, aktif brom üretimine ve bromat oluşumuna etkileride incelenmiştir.

Son olarak, katalitik ozonlama (TiO_2/O_3) sistemi bromür içeren sulara tatbik edilmiş ve katalitik ozonlamanın bromat oluşumuna etkisi incelenmiştir. Katalitik ozonlama ile katalitik yüzey alanına bağlı olarak bromat oluşumu %60-100 oranında azalmıştır. Ayrıca çalışmada katalitik ozonlama ve ozonlama işlemleri Büyükçekmece içme sularının arıtımı için tatbik edilmiş ve $10\text{ }\mu\text{gL}^{-1}$ konsantrasyonunun üzerinde bromat oluşumu katalitik ozonlama işleminde 1.25 mgmg^{-1} ve ozonlama işleminde ise 0.75 mgmg^{-1} üzerindeki transfer edilen ozon (TrO_3)/TOK oranlarında tespit edilmiştir.

SUMMARY

TITANIUM DIOXIDE BASED NOVEL ADVANCED OXIDATION PROCESSES IN WATER TREATMENT AND BY-PRODUCT FORMATION

In this study, two novel advanced oxidation processes (AOPs), photoelectrocatalytic (PEC) and catalytic ozonation, were performed to understand the processes with respect to the humic acid (HA) degradation and bromate formation.

Firstly, PEC method was applied for the degradation of HA in water. HA degradation was followed by measuring absorbance at 254 nm (UV_{254}) and total organic carbon (TOC). Results showed that the degradation of HA obeys zero order reaction kinetic model while TOC degradation followed a first order kinetic model. According to the treatment conditions, over 90% UV_{254} removal and 58% -80% TOC removals were obtained in the PEC system. Photocatalytic (PC) and PEC experiments were carried out under same condition and results showed that the PEC system was much more effective than the PC method.

Secondly, PEC method using titanium dioxide (TiO_2) thin-film electrodes as an anode was carried out for monitoring of PEC bromine generation and bromate formation in the photoanode side. Bromine production increased over time and finally reached a steady-state concentration of 25 mgL^{-1} . On the other hand, no steady-state concentration for bromate formation could be achieved and bromate concentration was observed with respect to time. According to the primary parameters, bromine concentrations between 25 mgL^{-1} and 212 mgL^{-1} were gained in the PEC process. No bromate formation was observed up to pH values of 6.0 while the bromate increased as pH increased up to 9 and decreased again due to the lower bromine generation at higher pH values. The influences of variables on the HA degradation, bromine generation and bromate formation in the PEC system were also investigated.

Finally, catalytic ozonation (TiO_2/O_3) was carried out to investigate its effect on the formation of bromate during ozonation of bromide-containing water. It was found that bromate formation reduced by 60-100% according to the used surface area of the catalyst. Complementary ozonation and catalytic ozonation experiments were also performed for the treatment of Büyükçekmece lake water. Transferred ozone (TO_3)/TOC ratio of 1.25 mg/mg was determined in the catalytic ozonation system for the appearance of bromate concentration higher than $10\text{ }\mu\text{gL}^{-1}$ while it was found to be 0.75 mg/mg in the ozonation process.

1. INTRODUCTION

Humic substances (HS), namely humic acids (HA), are naturally occurring dissolved organic materials that represent major problem in drinking water due to the complex nature of their heterogeneous molecules that give yellow-brown color to the water (Bennett and Darikas, 1993), form complexes with pesticides (Hiraide, 1992), cause plugging and fouling problems on membranes (Yuan and Zydney, 2000), and, most significantly, act as precursors of hazardous trihalomethanes (Rook, 1974). Therefore, any attempt to lower the level of total organic carbon (TOC) that would also accomplish the removal of HA species is beneficial for minimizing the formation of chlorinated species.

On the other hand, bromide plays an important role in disinfection processes. Bromide acts more efficiently than chlorine as a biocide, being five times more active than chlorine. Thus, bromide can be added to water during chlorination and ozone disinfection to produce bromine (Daniel et al., 1999; von Gunten, 2003). Due to the health effects of brominated by-products such as brominated trihalomethanes (THMs) and bromate (Rook, 1974; Kurokawa et al., 1986; Krashner et al., 1993), a great deal of attention has been focused on the behavior of bromide and brominated by-products in a disinfection processes (Haag and Hoigne, 1984; von Gunten and Hoigne, 1994).

In recent years, many researches were focused on advanced oxidation processes (AOPs) in order to increase their oxidative capacity for the purification and disinfection of waters. The oxidative species mainly used in AOPs are hydroxyl radicals ($\text{HO}\bullet$), which can be generated in aqueous medium by using Fe^{2+} - H_2O_2 (Fenton process), UV/catalyst, $\text{H}_2\text{O}_2/\text{O}_3$, $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$, $\text{O}_3/\text{catalyst}$, $\text{H}_2\text{O}_2/\text{catalyst}$, UV/ $\text{O}_3/\text{catalyst}$, UV/ $\text{H}_2\text{O}_2/\text{catalyst}$ couples (Al-Hayek et al., 1989, 1990; Allemane et al., 1993; Adams et al., 1997; Legube and Leitner, 1999).

Interest in the use of ozone has been increasing steadily, because ozone can control taste and odor (Glaze et al., 1990 and 1993), oxidize synthetic organic pollutants and natural organic matter (NOM), remove color (Flogstad and Odegaard, 1995), and enhance coagulation-flocculation (Reckow et al., 1986). As a result, it reduces the formation of chlorinated disinfection by-products (DBPs) such as trihalomethanes (THMs), and most significantly, inactivates certain microorganism such as *Giardia lamblia* cysts and *crystosporidium oocysts* which chlorine is less effective. Thus, ozonation is one of the most powerful treatment options to enhance water quality. There are three basic disadvantages of ozone utilization in water treatment (Cavanagh, 1991). First of all, ozone react with NOM to form assimilable organic carbon (AOC) that is easy biodegradable, and promotes biological growth in the distribution system. Secondly, ozone is not stable to provide a sufficient residual for the preservation of water in distribution system. Most importantly, ozonation of bromide containing water can produce brominated disinfection by-products (BDBPs) that some of them such as bromoform and bromate are known to be possible carcinogens (Song, 1996). Thus, USEPA has set $10 \mu\text{gL}^{-1}$ and $80 \mu\text{gL}^{-1}$ maximum contaminant levels for bromate and THMs, respectively.

Heterogeneous Catalytic Ozonation is a novel ozonation method, which combines ozone with the oxidative and adsorptive properties of solid phase metal oxide catalysts in aqueous phase to enhance mineralization of dissolved organics. Due to the stability of TiO_2 , recently many researchers have focused on TiO_2 based catalytic ozonation process for treatment of NOM in drinking water (Paillard et al., 1991; Logemann and Annee, 1997; Volk et al., 1997; Gracia et al., 2000). All studies show that NOM removal in the TiO_2 based catalytic ozonation process was better than that in merely ozonation process.

Photocatalysis is another promising advanced oxidation technology and already has been successfully applied for disinfection and purification of waters in the USA and Europe. Among many kinds of semiconductors, TiO_2 is the most used photocatalyst due to its low cost, chemical and physical stability and ability to mineralize chlorinated by-products precursors such as HA or their by-products to CO_2

(Bekbolet, 1996; Eggins et al., 1997; Dunlop et al., 2002), and eliminates pathogens in the water (XI et al., 2001, Bekbölet, 2002).

Fujishima and Honda in 1972 introduced the photoelectrocatalytic (PEC) process for splitting of water. Subsequent studies improved the process by applying a biasing potential to decrease the recombination rate of electron and hole (Kim and Anderson, 1994). Then, some researchers applied PEC process for the treatment and disinfection of water, and all related studies demonstrated that PEC process was much more effective than TiO_2/UV process alone (Candal et al., 1998; Pelegrini et al., 2000; Herper et al., 2001). More recently, some developments have made it possible to separate electron and hole reactions in the PEC system (Vinodgopal et al., 1994; Zaroni et al., 2002), providing great advantage to hinder their interaction and to improve the efficiency of TiO_2 .



2. SCOPE OF THE STUDY

PEC and catalytic ozonation are newly developed advanced oxidation methods and there are many questions to be solved before the application of these processes for the treatment of waters. Since novel treatment methods, photocatalytic and catalytic ozonation are developed, it is necessary to research disinfection by-products formation and scale up these methods for purification of waters. The specific objectives of this research are:

1. PEC treatment of humic acid

- Anodic HA degradation
- Kinetics of HA degradation
- Effect of variables on PEC HA degradation
- Effect of Experimental conditions
- Application of PEC in treatment of river water
- Comparison of photocatalytic and PEC methods

2. Behavior of bromide in the PEC process

- Bromine formation
- Bromate formation
- Effect of variables
- Effect of experimental conditions

3. Catalytic ozonation

- Bromate formation
- Comparison of ozonation and catalytic ozonation
- Effect of some variables on bromate formation
- Application of catalytic ozonation in drinking water

The overall goal of this study is to develop an understanding of novel PEC and catalytic ozonation processes for possible application in disinfection and treatment of waters. The study also presents tools for understanding how water characteristics and water treatment variables affect bromate formation and natural organic matter (NOM) removal, evaluating potential bromate minimization strategies in both processes and comparing ozone-catalytic ozone and photocatalytic-PEC processes.

3. THEORETICAL BACKGROUND

3.1. Advanced Oxidation Processes

In recent years, many researches were focused on Advanced Oxidation Processes (AOPs), in order to increase their oxidative capacity to purify drinking water and wastewater. The oxidative species mainly used in AOPs are hydroxyl radicals ($\text{HO}\bullet$), which can be generated in aqueous medium by using Fe^{2+} - H_2O_2 (Fenton process), UV/catalyst, $\text{H}_2\text{O}_2/\text{O}_3$, $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$, $\text{O}_3/\text{catalyst}$, $\text{H}_2\text{O}_2/\text{catalyst}$, UV/ $\text{O}_3/\text{catalyst}$, UV/ $\text{H}_2\text{O}_2/\text{catalyst}$ couples (Al-Hayek et al., 1989, 1990; Allemane et al., 1993; Adams et al., 1997; Legube et al., 1999).

Ozonation and TiO_2 photocatalytic processes and/or their combination are the most used AOPs processes for the inactivation of microorganism, taste/odor control and treatment of NOM in drinking water. Due to the restricted drinking water standards especially about disinfection by-products, innovative advanced oxidation processes, namely catalytic ozonation and photoelectrocatalytic treatments have been performed as alternative methods for purification and disinfection of waters.

3.1.1. Ozonation

3.1.1.1. Ozone decomposition

Molecular ozone is a powerful oxidant and can oxidize various numbers of inorganic and organic compounds in aqueous media. As ozone decays in water, it reacts a great number compounds via both direct molecular ozone or OH radical reactions.

Ozone decomposition has been very well studied in literature (Gurol and Singer, 1982). Considering drinking water conditions (near neutral pH), there are the two most known models for the ozone decomposition. The first model, HSB model was developed by Hoigne, Staehelin and Bader and second model, GTF model was based

on the work by Gordon, Tomiyasu, and Fukutomi (Staehelin and Hoigne, 1985; Song, 1996).

Table 3.1. HSB ozone decomposition model (Song, 1996).

Reaction type	Reaction	Rate constant
Initiation	$O_3 + OH^- \rightarrow HO_2^\bullet + O_2^\bullet$	$k = 70 \text{ M}^{-1}\text{s}^{-1}$
Propagation	$O_3 + O_2^\bullet \rightarrow O_2 + O_3^\bullet$ $O_3^\bullet + H^+ \leftrightarrow HO_3^\bullet$ $HO_3^\bullet \rightarrow OH^\bullet + O_2$ $O_3 + OH^\bullet \rightarrow HO_4^\bullet$ $HO_4^\bullet \rightarrow O_2 + HO_2^\bullet$	$k = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ <pka=10.3 </pka=10.3 $k = 1.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ $k = 2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k = 2.8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
Termination	$2HO_4^\bullet \rightarrow H_2O_2 + 2O_3$ $HO_4^\bullet + HO_3^\bullet \rightarrow H_2O_2 + O_2 + O_3$	$k = 5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k = 5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$

Table 3.2 GTF ozone decomposition model (Song, 1996).

Reaction type	Reaction	Rate constant
Initiation	$O_3 + OH^- \rightarrow HO_2^- + O_2^-$	$k = 40 \text{ M}^{-1}\text{s}^{-1}$
Propagation	$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^\bullet$ $HO_2^\bullet \leftrightarrow O_2^\bullet + H^+$ $O_2^\bullet + O_3 \rightarrow O_3^\bullet + O_2$ $O_3^\bullet + H_2O \rightarrow OH^\bullet + O_2 + OH^-$ $O_3^\bullet + OH^\bullet \rightarrow O_2^\bullet + HO_2^\bullet$ $O_3 + OH^\bullet \rightarrow O_2 + HO_2^\bullet$	$k = 2.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ pKa=4.8 $k = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k = 25 \text{ M}^{-1}\text{s}^{-1}$ $k = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
Termination	$O_3^\bullet + OH^\bullet \rightarrow O_3 + OH^-$	$k = 2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$

Both models described ozone decomposition via a series of chain reactions and the overall ozone decomposition reactions by first-order kinetics. As presented in Tables 3.1 and 3.2, although there are some similarities, obviously some differences exist. In the scheme of the HSB model, the initiation step is characterized by either an oxygen atom transfer or oxygen radical transfer from ozone to hydroxide. On the other hand, the GTF model involves just oxygen atom transfer from ozone to hydroxide. Finally, one hypothesized in the HSB model, $\text{HO}_4^\bullet$, is not included in the GTF mechanism (Song, 1996).

Aside from these two models, also ozone decomposition kinetics is well studied in the literature. Gurol and Singer (1982) developed an ozone decomposition kinetics and its rate equation ($d[\text{O}_3]/dt = -k_0[\text{OH}^-]^{0.55}[\text{O}_3]^2$) gives a very good correlation ($r^2=0.9997$) with the HSB model ($d[\text{O}_3]/dt = -k_0[\text{OH}^-][\text{O}_3]$).

Gurol and Singer (1982) found that the rate of decomposition is insensitive to pH values. The primary decomposition of ozone results from a dissociation reaction:



Besides pH, ozone concentration, temperature, and some other parameters affect the ozone decomposition as initiator, promoter, and inhibitor. Initiators such as OH^- , H_2O_2 , Fe^{2+} , humics, and formate, are capable of forming a superoxide radical from reactions with ozone. Promoters are organic or inorganic solutes ($\text{R}_2\text{-C(H)OH}$, alkyl-R, O_3 , humics, formate etc.) producing a superoxide radical by reacting hydroxyl radical. Inhibitors (CH_3COO^- , alkyl-R, $\text{HCO}_3^-/\text{CO}_3^{2-}$, humics, tert-butanol etc.) use the generated hydroxyl radical without regenerating a superoxide radical (Song, 1996).

3.1.1.2. Hydroxyl radical ($\text{OH}^\bullet$) yield and concentration

In the literature, $\text{OH}^\bullet$ yield was calculated per ozone molecule. Both HSB and GTF models give a theoretical $\text{OH}^\bullet$ yield values of 0.67 for ozone decomposition by initiator of OH^- . It means that 2 $\text{OH}^\bullet$ can be generated by 3O_3 . But it is reported that OH radical generation is dependent on reactor type and solution composition. As a

result, $\text{OH}^\bullet$ yield could be as high as 1.0. For example, in the presence of hydrogen peroxide (H_2O_2), the $\text{OH}^\bullet$ yield can be increased up to 1.0 (Peyton and Bell, 1994) as described below;



From these reaction the total reaction can be written as follow;



3.1.1.3. Heterogeneous catalytic ozonation

It is well known that ozonation alone is not enough to obtain complete mineralization of the natural organic materials. Heterogeneous catalytic ozonation is a novel ozonation method, which combines ozone with the oxidative and adsorptive properties characteristic of metal oxide catalysts to enhance mineralization of dissolved organics in aqueous phase.

First time Chen et al. mentioned catalytic ozonation process to remove phenols by $\text{O}_3/\text{Fe}_2\text{O}_3$ process and it was found that the degradation of TOC in the $\text{O}_3/\text{Fe}_2\text{O}_3$ process is 2 times higher than that in merely ozone process (Chen et al., 1976). Later, Pailard et al. (1991) used O_3/TiO_2 process to oxidize oxalic acid and they reported that the O_3/TiO_2 catalytic ozonation process is far superior to $\text{O}_3/\text{H}_2\text{O}_2$. Recently many different catalysts such as Mn, Al_2O_3 , CuO, and etc. were performed together with ozone and catalytic effects have been reported in comparison to ozonation (Allemane et al., 1993; Andreozzi et al., 1998; Karpel et al., 1999; Cooper and Burch, 1999; Lagube and Leitner, 1999; Ni and Chen, 2000; Gracia et al., 2000).

More recently, many researchers have focused on various TiO_2 based catalytic ozonation process for treatment of NOM in drinking water (Paillard et al., 1991; Logemann and Annee, 1997; Volk et al., 1997; Gracia et al., 2000). All studies show that NOM removal in the TiO_2 based catalytic ozonation process is better than in the ozonation process, besides not causing any dissolution of the titanium in the treated water by ozonation (Gracia et al., 2000).

In this system there are three phases, gas, liquid and solid. First ozone should be transferred from gas into the liquid and then dissolved ozone may act with the organic by both direct molecular ozone and indirect radical reactions. There are still many questions about the mechanism of the catalytic ozonation however it is assumed that the oxidation in catalytic ozonation occurs in three parts (Langlais et al., 1991; Ni and Chen, 2000).

- (i) Simultaneous adsorption of ozone and organic molecules on the catalyst surface
- (ii) Conversion of ozone to more reactive radicals ($\text{O}_2^{\bullet-}$, $\text{O}_3^{\bullet-}$, $\text{O}^{\bullet-}$, $\text{OH}^{\bullet}$).
- (iii) Oxidation of adsorbed organics by direct O_3 , radicals and solid catalytic reactions.

3.1.2. Photocatalysis

The term of photocatalysis consists of the combination of photochemistry and catalysis that light and a catalyst are necessary to bring about or to accelerate a chemical transformation. Biasing of semiconductors by external potential under light illumination has created a new photocatalytic method, namely photoelectrocatalysis or photoelectrochemistry. Reactions that fulfill these simple requirements have been named by many terms such as catalysed, assisted, induced, accelerated, promoted, stimulated, applied, biased, etc.

3.1.2.1. Photoelectrocatalytic treatment

The main mechanism for the photocatalytic destruction of these molecules is the photogenerated electrons and holes generated at the photocatalyst surface. Upon illumination with photon energies in excess of the band-gap energy of the semiconductor photocatalyst, photogenerated electrons move from the valance band

to the conduction band and the holes migrate to the surface reacting adsorbed species on the valance band and conduction band (Figure 3.1). These photogenerated species take part in photocatalytic redox reactions (Eq 3.9-3.17). The holes react with the electron donors in the electrolyte to produce free radicals such as HO[•]. Free radicals are powerful oxidizing species and take part in oxidation reactions.

The simplified mechanism;



e_{CB}^- reactions;



h_{VB}^+ reactions;



However TiO₂/UV process exhibits some major disadvantages (Palmer et al., 2002; Shaphard et al., 2002):

- (i) The quantum efficiency (less than 10%) of TiO₂ is very low due to the fast rate of recombination of electrons and holes.
- (ii) The separation of TiO₂ particles from aqueous suspension is difficult after treatment. In recent years, many attempts have been done to immobilize TiO₂ on the solid surfaces.

- (iii) In addition in water treatment, TiO_2/UV photocatalytic process is still pH dependant.

The photoelectrocatalytic (PEC) process was introduced by Fujishima and Honda (1972) for splitting of water. Later, some researchers improved the process biasing external potential to decrease the recombination rate of electron and hole (Kim and Anderson, 1994). Then, PEC process was performed for the treatment and disinfection of water by many researchers (Candal et al., 1998; Candal et al., 2000; Pelegrini et al., 2000; Harper et al., 2001). All related studies demonstrated that PEC process was much more effective than TiO_2/UV process alone. In recent years, electron and hole reactions were separated in the PEC system (Vinodgopal et al., 1994; Zanoni et al., 2002). This provided great advantage for the disinfection and treatment of pollutants.

3.1.2.2. Fundamentals of photoelectrocatalysis

Energy Bands: If two atoms are bonded together, each atomic level is split in two molecular energy levels, which are grouped into energy bands. The energy bands consist of valance band (VB) and conduction band (CB). Each energy band also has upper and lower level, called the band edges. The upper edge of the valence band and the lower edge of the conduction band were marked E_v and E_c respectively. A solid is called as a metal if the highest occupied and lowest empty energy bands overlap. On the other hand, the solid is a semiconductor or insulator if the valance and the conduction bands edges are separated by an energy gap, which is commonly called as the band gap energy (E_{bg}). The magnitude of the band gap energy distinguishes semiconductors from insulators (Figure 3.3). In general, solids with E_{bg} less than 4 eV are known semiconductor while insulators have E_{bg} larger than 4 eV. Also, according to their hole or electron concentrations, they are called n-type and p-type semiconductors respectively (Table 3.3) (Kim, 1993, Rajeshwar, 2001).

Charge carrier generation: Electrical conductivity results from the mobility of electrons. Electrons must occupy a partially empty level within an energy band to be mobile in a solid. In metals, filled and empty are not separated, and the empty energy band are available above the filled energy band thus electrons easily jump up to the empty levels at room temperature and move under applied potential. But in semiconductor and insulator, the energy bands are separated from each other by the

band gap and conduction is not possible in simple condition. Basically, semiconductors can be conductive by putting extra electrons into the conduction band, or removing electron from valance band. Electron removal from valance band creates positive charged vacancy (hole), which is also mobile charge carrier. As a result, semiconductors can be mobile by either electrons or holes charge carriers (Finklea, 1983; Choi et al., 1994).

Thermal excitation, doping and photo-excitation are known three methods to make semiconductor conductive. First, thermal excitation can be enough to excite an electron from the valence band to the conduction band if the band gap of the semiconductor is sufficiently small (<0.5 eV). Second, doping is to create new energy levels into the band gap, and semiconductor can act as a metal according to the doping level. The third mechanism to generate charge carriers is photoexcitation. If photon energy is bigger than the band gap energy ($h\nu > E_{bg}$), an electron can be excited from the valence band to the conduction band, leaving holes in the valance band (Figure 3.3a). Thus, the conversion of sunlight to usable energy form depends on the band gab energy, and the band gap sets the condition for photon absorption. According to the band gap energy a semiconductor can absorb a limited wavelengths. The wavelength of the band gap (λ_{bg}) is defined with the following equation

$$\lambda_{bg} \text{ (nm)} = 1240/E_{bg} \text{ (eV)} \quad (3.18)$$

A semiconductor cannot absorb the wavelengths greater than its λ_{bg} value. Table 3.3 lists λ_{bg} and E_{bg} values for some important semiconductors. Considering sunlight maximum solar energy conversion can be obtained for $E_{bg} = 1.5 \pm 0.5$ eV ($600\text{nm} < \lambda_{bg} < 1100\text{nm}$) (Finklea, 1983; Rajeshwar, 2001). In the photocatalytic process, electron-hole transitions are of two types; direct and indirect transitions. The optical absorption coefficient (α) for such transitions in semiconductor is given by;

$$\alpha \cdot h\nu = A(h\nu - E_{bg})^n \quad (3.19)$$

In eq. 3.19, A, constant; h, the Plank's constant; ν , the frequency of light; α , the optical absorption coefficient; E_{bg} , the band gap energy; $n=1/2$ for a direct transitions and $n=2$ for indirect one (Rajeshwar et al., 1997; Lindgren, 2001).

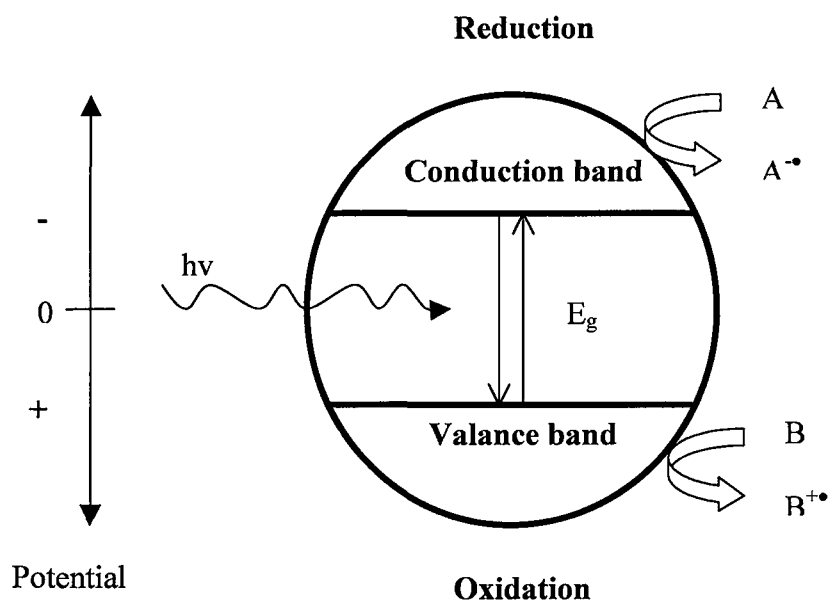


Figure 3.1. Oxidation and reduction in the photocatalytic process (A, reducible and B, oxidizable species).

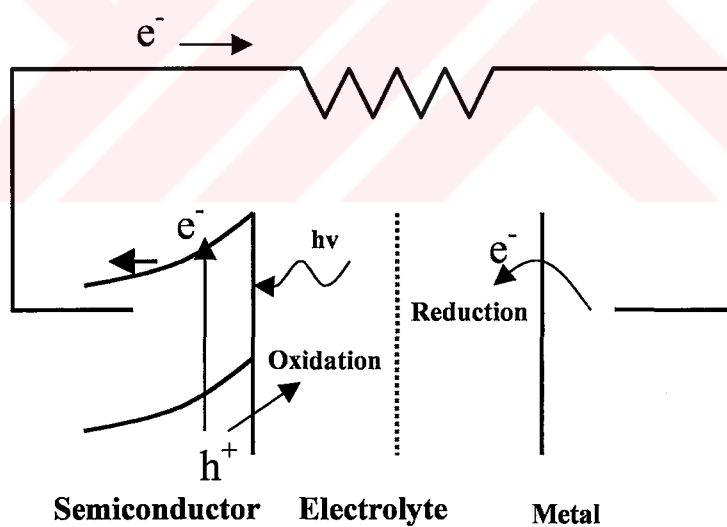
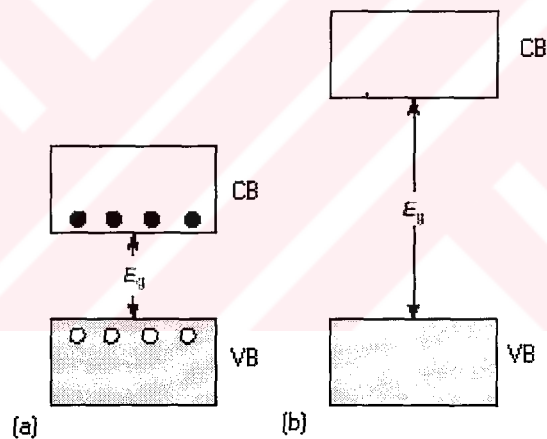


Figure 3.2. Photoelectrocatalytic process (Rajeshwar et al., 1997).

Table 3.3. Semiconductors and their properties

Semiconductor	Conductivity type(s)	Band gap energy (eV)	λ_{bg} (nm)
ZnO	n	3.35	390
TiO ₂	n	3.00	410
CdS	n	2.42	520
GaP	n, p	2.26	540
CdSe	n	1.70	730
GaAs	n, p	1.42	890
CdTe	n, p	1.50	890
InP	n, p	1.35	950
Si	n, p	1.11	1130

**Figure 3.3.** Relative disposition of the CB and VB. (a) semiconductor (b) insulator (Rajeshwar et al., 1997).

Fermi level: The Fermi level (E_f), the energy at which the probability of finding an electron is $\frac{1}{2}$, is the electrochemical potential of an electron in a metal or a semiconductor. Thus above E_f , the probability of occupancy is likely to be zero and the energy levels are empty while, below E_f , all electronic energy levels are occupied. Metals and semiconductors/insulators are distinguished by the location of the Fermi level. The location of E_f is in the energy band region for a metal, and it is inside the band gap for a semiconductor. In an intrinsic semiconductor ($n=p$), the Fermi level is precisely at the middle of the band gap. This implies that electron occupancy is very high in VB and very low in CB. Doping shifts the E_f with respect

to the band edges. For n-type semiconductors, shift of E_f is toward the valance band and for p-type toward the conduction band (Figure 3.4). Upon increasing doping level, E_f shifts closer and closer to the band edges and after one point, a very high level doping makes semiconductor becomes a metal (Finklea, 1983; Kim, 1993).

The Fermi function is expressed in equation 3.20,

$$F = 1 / [1 + \exp [(E - E_f) / kT]] \quad (3.20)$$

where f is the Fermi function, k is the Boltzman constant, and T is the temperature (K).

Another distinction between metals and semiconductors is that two different electronic carriers, holes and electrons, are possible in the semiconductor. Fermi energy can be used to describe the concentration of holes (p) in the valance band as well as the concentration of electrons (n) in the conduction band.

$$n = N_c \exp [-(E_c - E_f) / kT] \quad (3.21)$$

$$p = N_v \exp [-(E_f - E_v) / kT] \quad (3.22)$$

where N_v is the effective density of energy levels at energy E_v , N_c is the effective density of energy levels at energy E_c , k is the Boltzman constant, T is the temperature (K), n is the density of electrons in the conduction band, and p is the density of holes in the valance band. When considering $p=n$, from equation 4 and 5, equation 6 is obtained.

$$np = N_c N_v \exp [(E_v - E_c) / kT]$$

$$n^2 = N_0 \exp [-E_{bg} / kT] \quad (3.23)$$

where $N_0 = N_v N_c$. From this equation it can be seen that np is small in large bandgap semiconductors for a given temperatures. N_c and N_v are generally 10^{19} cm^{-3} so that N_0 is about 10^{38} . Lastly, one of the important properties of the Fermi level is that it is affected by the externally applied potential (Kim, 1993; Rajeshwar, 1997)

Chemical potential in solution: A solution containing a redox couple has its own chemical potential, which can be identified by the Nernst potential.

$$E_{\text{rdx}} = E_{\text{rdx}}^{\circ} + (RT/nF) \ln [C_{\text{ox}}/C_{\text{red}}] \quad (3.24)$$

where E_{rdx}° is the standard potential, E_{rdx} is the Nernst potential, R is the ideal gas constant, T is the temperature (K), n is the amount of electrons which are transferred in the redox reaction, F is the Faraday constant, C_{red} is the concentration of the reduced form, and C_{ox} is the concentration of the oxidized form. Electrochemists have generally used the standard hydrogen electrode (SHE) scale to adopt the electron energy in vacuum as a reference. SHE appears to lie at -4.5 eV with respect to the vacuum level. Figure 3.5 displays the mapping of the semiconductors band-edge position relative either to the vacuum reference or a standard reference electrode. The redox potential (E_{rdx}), defined with reference to standard hydrogen electrode (SHE), can be related with the Fermi level ($E_{\text{f rdx}}$), expressed versus the vacuum references (Kim, 1993; Rajeshwar, 1997).

$$E_{\text{f rdx}} = -4.5 \text{ eV} - e_0 E_{\text{rdx}} \quad (3.25)$$

where E_{rdx} is the Fermi energy of solution, e_0 is the electron charge and V_{rdx} is the Nernst potential of the solution.

Band bending and surface charge layer: When the semiconductor makes a junction with a solution containing a redox couple, there is charge transfer at the interface to define an equilibrium state, $E_{\text{f}} = E_{\text{rdx}}$. If the semiconductor is n-type, the electron density of semiconductor is larger than that of the solution. Thus, the Fermi level of the semiconductor moves down while the Fermi level of the solution moves up (D'Oliveira et al., 1990). The process stops when the Fermi energy of both the semiconductor and the solution becomes equal as shown in figure 3.6. If the pH of the solution is not altered, the band edges of the conduction and valance band are fixed, and band bending occurs near the surface of the semiconductor, called a space charge layer. The space charge layer is around 2-1000 nm (Peral and Mills, 1993).

As seen in figure 3.6, for n-type semiconductor, the band bending is downward, for p-type semiconductors, the band bending is upward (Rajeshwar, 1997). As a result, several layers make up this gradient (Figure 3.7). The Helmholtz layer is the closest layer, and it contains solvent molecules and sometimes specifically adsorbed ions or molecules. The Helmholtz layer width is typically 0.4-0.6 nm. Also a built in voltage,

V_{sc} , develops within semiconductor due to the band bending and under restrictive condition.

$$V_{sc} = -(qN_D/2\epsilon_s)W^2 \quad (3.26)$$

where q is the electronic charge, ϵ_s is the static dielectric constant of semiconductor, N_D is the semiconductor parameters (between 10^{16} and 10^{18} cm^{-3}), and W is the depletion layer width that is in the 10-1000 nm range (Kim, 1993; Rajeshwar, 1997).

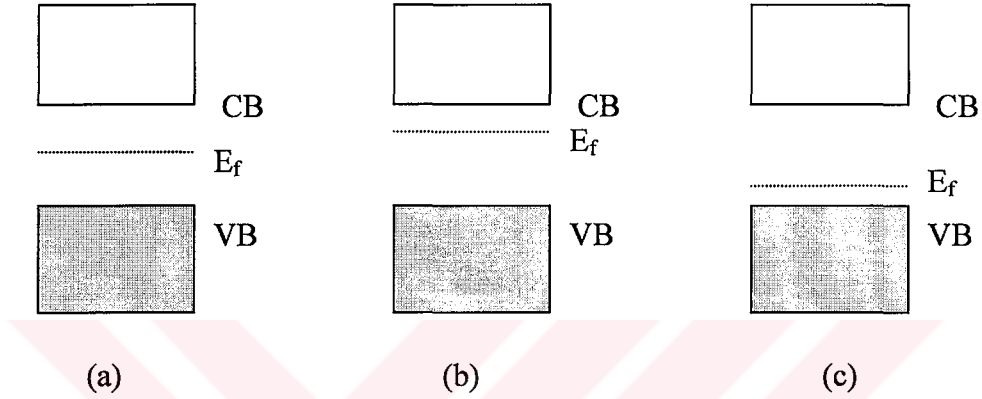


Figure 3.4. The location of Fermi Levels of semiconductors (a) an intrinsic (b) a n-type (c) p-type (Rajeshwar et al., 1997).

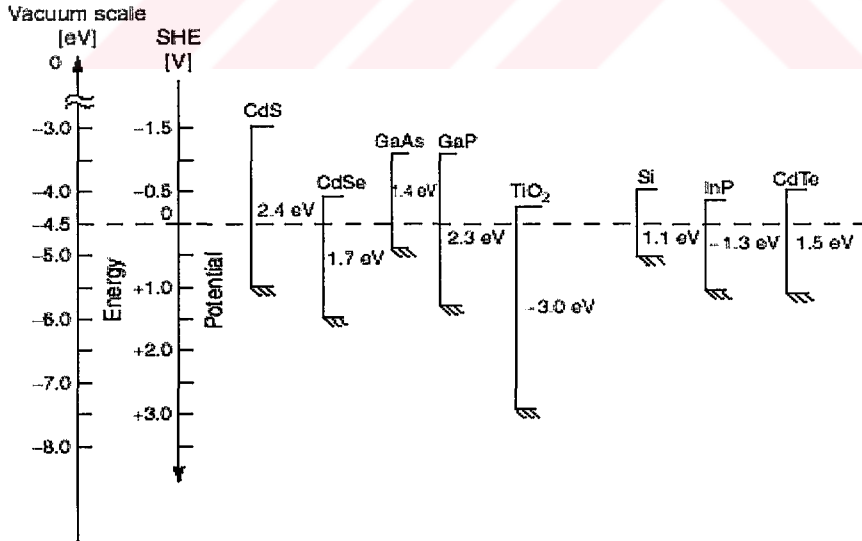
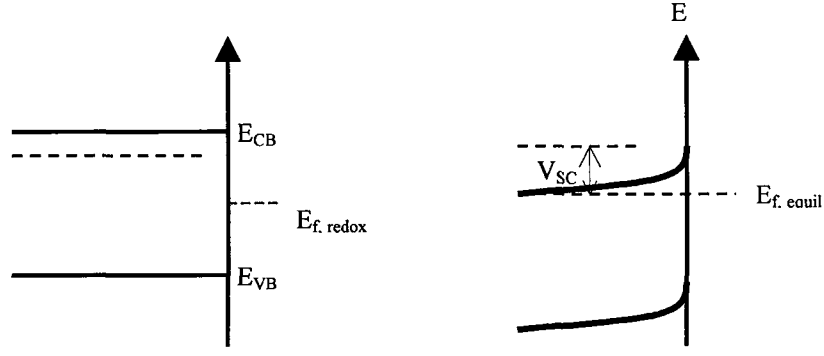
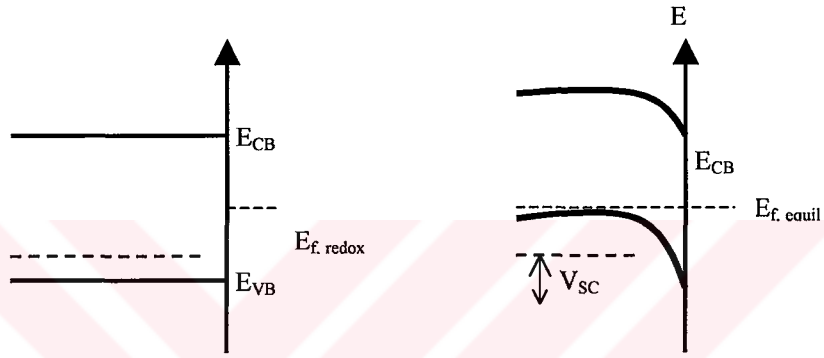


Figure 3.5. Relative disposition of various semiconductor band edge positions shown both on the vacuum scale and with respect to the SHE reference, pH 1 (Rajeshwar et al., 1997).



(a)



(b)

Figure 3.6. Energy levels in a semiconductor and a redox electrolyte. (a) for a n-type semiconductor (b) for a p-type semiconductor (Rajeshwar et al., 1997).

Flat band potential (V_{fb}): The amount of potential required to establish a state where no band bending occurs in the space charge layer is called as the flat band potential (V_{fb}) (D'oliveira, 1990). Flat band potential can be expressed by equation 9 and 10.

$$V_{cs} = V_{fb} - (E_{cb} - E_f)/q \quad (3.27)$$

$$V_{vs} = V_{cs} + E_{bg}/q \quad (3.28)$$

where V_{cs} is the potential of the edge of conduction band at the surface of the semiconductor, V_{vs} is the potential of the edge of valance band at the surface, V_{fb} is the flat band potential, E_{cb} is the energy of the edge of conduction band at the bulk of the semiconductor, E_f is the Fermi level of the semiconductor, E_{bg} is the band gap energy, and q is the electronic charge.

The flat band potential is related to the type of electrolyte and the pH of the solution because the potential drop across the Helmholtz layer is affected by the electrolyte. Both $V_{c,s}$ and $V_{v,s}$ are related to the Helmholtz layer, and are therefore affected by changes in the solution side of the interface. If only H^+ and OH^- determine surface charge, flat band potential is described by:

$$V_{fb} = V_{fb}(pzzp) - (2.3 RT/F) [pH - pH(pzzp)] \quad (3.29)$$

where pzzp is the point of zero zeta potential, $V_{fb}(pzzp)$ is the flatband potential at the point of zero zeta potential, and $pH(pzzp)$ is the pH at pzzp (Kim, 1993).

Surface state: Surface states are energy levels on the surface of the semiconductor, usually located between conduction and valance bands. Surface states occur because of defects in the crystal structure or due to adsorbed electroactive species. Surface states are described as locations for the recombination of electron-hole pairs which can cause a decrease in the activity of photocatalysts. Also, surface states can cause unexpected reactions to occur. One way to reduce recombination via surface states may be by separating the electrons and holes before they recombine at the surface states by applying a biasing potential. The electron-hole pair recombination can occur directly at the edges of the conduction band and valance band, and also indirectly at the bulk or at the surface state of a semiconductor. Fundamentally, surface states are not easily removed from the system.

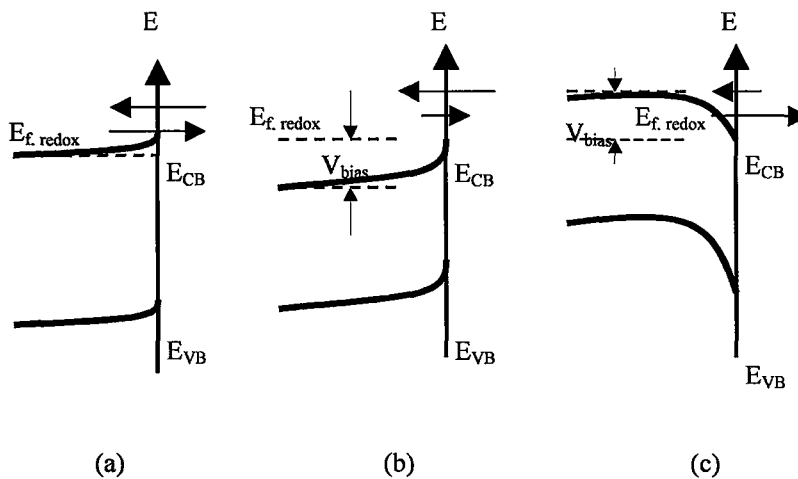


Figure 3.7. Three situations for n-type semiconductor-electrolyte interface; (a) at equilibrium, (b) under positive potential, (c) under negative potential (Rajeshwar et al., 1997).

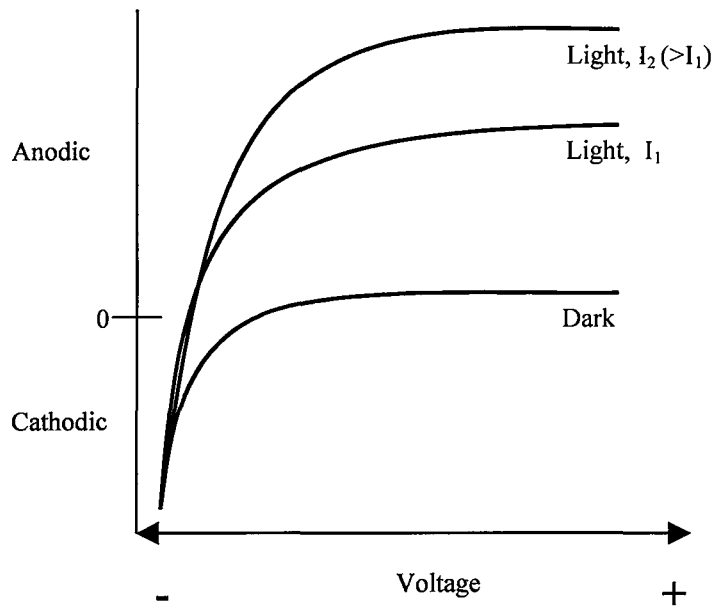


Figure 3.8. Current-potential curves for a n-type semiconductor in the dark and under band gap illumination with two level of photon fluxes (Rajeshwar et al., 1997).

Applied potential and photocurrent: As shown in figure 3.7, when n-type semiconductor is conducted with a redox electrolyte, a state of dynamic equilibrium occurs, and at this situation, there is no net current flow across the interface. If $n_s = n_{s0}$, then net current is zero as long as the semiconductor-electrolyte interface is not changed by an external potential.

The surface electron concentration is expressed with the following equation related with the bulk concentration of majority carrier (n) in the semiconductor.

$$n_{s0} = n \cdot \exp(-e_0 V_{sc} / kT) \quad (3.30)$$

Upon the application of an negative external potential, a reduction current occurs across the interface, it is such that $n_s > n_{s0}$, thus the oxidized species are converted to the reduced species. On the other hand, when a positive potential is applied, then $n_{s0} > n_s$ and the current direction is reversed, and anodic current occurs across interface, and the photocurrent is proportional to the photon as illustrated in Figure 3.8 (Rajeshwar, 1997).

3.2. Natural Organic Matter

The majority of water-soluble natural organic matter (NOM) which is a complex mixture of organic macromolecules resulting from microbial degradation processes of plants in soils and waters (Thurman, 1986; Nissinen et al., 2001) is divided into humic and nonhumic fractions (Owen et al., 1995). Humic fraction, consisting of humic and fulvic acids, is more hydrophobic and complex. The nonhumic fraction is less hydrophobic and relatively simple compounds, which are carbohydrates, carboxylic acids, amino acids and hydrocarbons. Thurman (1981 and 1986) classified dissolved organic carbon (DOC) histogram for average river water with DOC level of 5 mgL⁻¹. The largest group fraction of DOC was hydrophobic acids as humic and fulvic acids by 40% and 10% respectively. The second largest group by 30% was hydrophobic acids. The remaining 20% of the DOC contained carbohydrates (10%), carboxylic acids (7%), amino acids (3%), and hydrocarbons. These ranges may change source to source (Song, 1996).

3.2.1. Humic substances

Humic substances have been classified into three fractions, humin, humic acid and fulvic acid, (Suffet and MacCarty, 1989; Thurman and Malcolm, 1983):

- (i) *Humic acids* - the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. Humic acids are the major extractable component of soil humic substances. They are dark brown to black in color.
- (ii) *Fulvic acids* - the fraction of humic substances that is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in color.
- (iii) *Humin* - the fraction of humic substances that is not soluble in water at any pH value and in alkali. Humins are black in color.

Humic acid and fulvic acid are the most important humic substances in drinking water treatment. Humic substances consist of a heterogeneous mixture of compounds

and they have no single structural formula. Humic acids have complex aromatic macromolecules with amino acids, amino sugars, peptides, and aliphatic compounds. The model structure of humic acid and fulvic acid molecules are presented in Figure 3.9 and Figure 3.10, respectively. The low - molecular - weight fulvic acids have higher oxygen but lower carbon contents than the high - molecular - weight humic acids. Fulvic acids contain more functional groups of an acidic nature, particularly COOH. The elemental composition of humic acid is within the ranges of C, 52-62%, H, 3.0-5.5%; O, 30-33%; N, 3.5-5.0% while that of fulvic acid is within the following ranges: C, 44-49%, H, 3.5-5.0%; O, 44-49%; N, 2-4% (Weber, 2003).

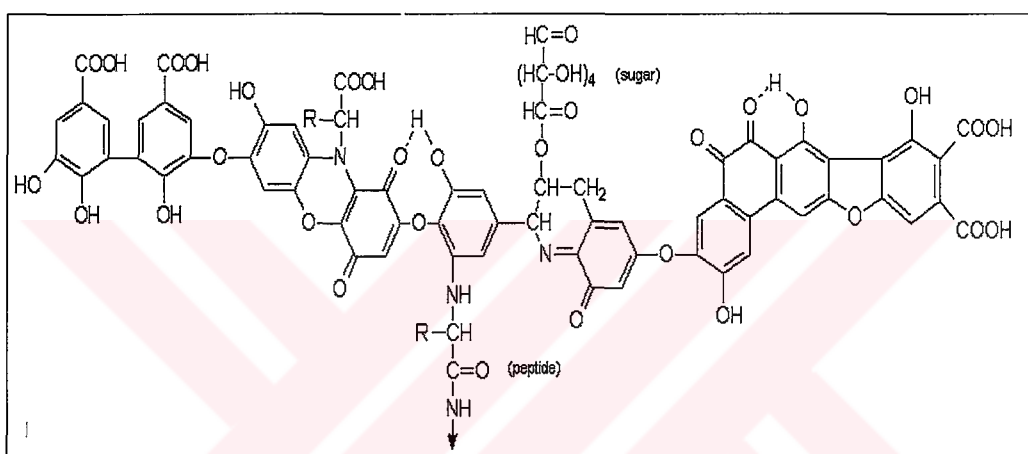


Figure 3.9. Humic acid molecular structure (Stevenson, 1982).

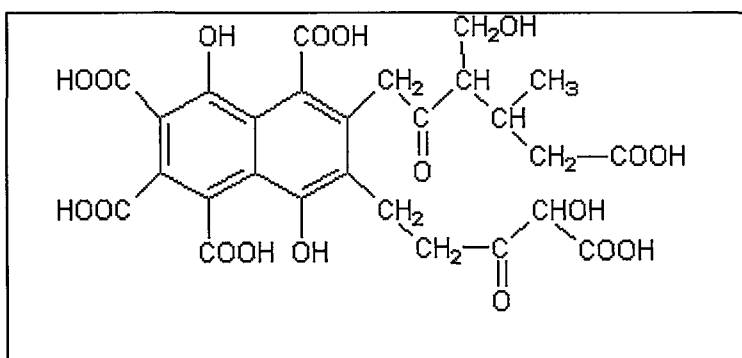


Figure 3.10. Fulvic acid molecular structure (Buffle, 1988).

On the other hand spectroscopic techniques, UV/VIS absorption, fluorescence, and nuclear magnetic resonance (NMR) can demonstrate informative differences in physicochemical properties of humic substances. Organic compounds, which are aromatic and/or contain conjugated double bonds absorb ultraviolet light at 254 nm

or 280 nm. UV absorbance at 254 nm is often used in water treatment for humic substances. Humic substances are also known to fluorescence after absorbing the incipient UV-VIS radiation (Larson and Weber, 1994). The fluorescence data for fresh water, presented in Table 3.4, indicate that the fluorescence of many freshwater humic substances is similar (Song, 1996).

Table 3.4. Fluorescence of freshwater dissolved organic matter (Larson and Weber, 1994)

Water source	λ_{max} , nm excitation	λ_{max} , nm emission
Lakes and rivers (USA)	360-370	450-460
River (USA)	375	465
Lake (Netherland)	365	470
Various waters (UK)	340-350	410-460

3.2.2 Treatment of humic substances

Humic substances represent major problem in drinking water due to the complex nature of their heterogeneous molecules that give a yellow-brown color to the water (Hiraide, 1992), form complexes with pesticides (LeChevallier et al., 1991), cause plugging and fouling problems on membranes (Yuan and Zydney, 2000), and, most significantly, act as precursors of hazardous trihalomethanes (THM) (Rook, 1974; Singer, 1999). Therefore, any attempt to lower the level of total organic carbon (TOC) that would also accomplish the removal of HA species is beneficial for minimizing the formation of chlorinated species.

Several processes have been tried for removing NOM from water. These include: conventional drinking water treatment (Jacangelo et al., 1995), TiO_2 based photocatalytic oxidation (Bekbölet and Balcioglu, 1996; Bekbölet and Ozkosemen, 1996; Richardson et al., 1996; Bekbölet et al., 1998; Odegaard et al., 1999; Wang et al., 2000; Al-Rasheed and Carddin, 2003), ozonation and/or biofiltration (Volk et al., 1997; Hozalski et al., 1999; Melin and Odegaard, 1999), adsorption (Avena and Koopal, 1999), membrane filtration (Thorsen, 1999; Yuan et al., 2000), electrochemical treatment (Motheo and Pinheiro, 2000), and photoelectrocatalytic oxidation (Li et al., 2002).

3.3. Bromate

Bromate is one of the disinfection by-products that EPA set its concentration of $10\ \mu\text{gL}^{-1}$ in drinking water. Due to the health effect of bromate, many studies have been attempted to understand the formation, control, and removal of bromate in water.

3.3.1. Use and sources of bromate in the environment

The bromate ion (BrO_3^-) exists in a number of salts, the most common of which are potassium bromate and sodium bromate. Potassium bromate is soluble and highly stable in water at room temperature. Bromate does not volatilize, and adsorbs only slightly to soil or sediment. Because it is a strong oxidant, it reacts with organic matter, which ultimately leads to the formation of bromide ion.

Potassium bromate is used primarily as a maturing agent in flour and as a dough conditioner in bread making. In Japan, it was formerly used in fish paste products (Ishidate et al., 1984; Hayashi, 1989; Kurokawa et al., 1990). It may be used in the production of cheese and beer. Potassium bromate and sodium bromate are also components of neutralizing solutions in home permanent wave kits.

Although bromate is unlikely to be formed during water chlorination, evidence has been found in U.S. and British studies that water treatment grade sodium hypochlorite solutions may contain bromate as a contaminant. Data collected suggest that bromate concentrations range from < 2 to $51\ \text{mgL}^{-1}$ in the United States (Giddings, 2000). In the United Kingdom, ranges from 50 to $1150\ \text{mgL}^{-1}$ were noted. Other researchers have found bromate concentrations much greater than $10\ \mu\text{gL}^{-1}$ in sodium hypochlorite solutions. Since chlorination activity of the solution decreases with time, it may be necessary to use larger quantities of the sodium hypochlorite solution in order to obtain the required level of disinfection. As a result, bromate levels could be high as a result of bromate's stability during long-term storage (as occurs in smaller municipalities).

Bromate is not a natural component of water, but may be formed during the ozonation of drinking water. The bromate concentrations of 8-180 μgL^{-1} were observed in drinking water (Giddings, 2000).

3.3.2. Health effects

Many studies have demonstrated that bromate, given orally up to 5 mgkg^{-1} doses, is degraded to bromide in tissues and organs (liver, kidney, spleen, stomach, small intestine, red blood cells, saliva and plasma) by the degradation, absorption and excretion at the concentrations. The bromate doses higher than 5 mgkg^{-1} can be observed in plasma and saliva. At over doses, bromate is a highly toxic substance that has caused irreversible renal failure, deafness (Gradus et al., 1984), and death subsequent to accidental poisoning. Oral lethal doses for adults are reported to be between 5 and 50 mgkg^{-1} (Giddings, 2000).

No information is available on the induction of tumours by bromate in humans. But there are enough evidences that potassium bromate induced a doses between 1.7 mgkg^{-1} and 50 mgkg^{-1} per day increase renal cell tumours in both rats and mice (Fujii et al., 1984; DeAngelo et al., 1998). Bromate gave largely negative results in bacterial mutagenicity tests, whereas positive results were obtained for clastogenic effects and DNA damage in all *in vivo* tests to date. Bromate has therefore been classified as probably carcinogenic to humans (sufficient evidence in animals; no data in humans) (Kasai et al., 1987; Awogi et al., 1992; Chipman et al., 1997).

Cancer risks have been estimated on the basis of renal cell tumours from two bioassays: one conducted in male and female rats and a second conducted at a lower range of doses in the same laboratory on males only. Using the model-free extrapolation method, it was calculated that the unit lifetime excess cancer risk associated with the ingestion of bromate at a concentration of 1 μgL^{-1} in drinking water ranges from 1.55×10^{-6} to 2.19×10^{-6} based on renal cell tumours in rats. The estimated range of bromate concentrations in drinking water corresponding to lifetime excess cancer risks of 10^{-4} , 10^{-5} and 10^{-6} for renal cell tumours based on three data sets from studies by Kurokawa and colleagues (1986) is as follows:

Lifetime risk	Concentration in drinking water (μgL^{-1})
10^{-4}	46 – 65
10^{-5}	4.6 – 6.5
10^{-6}	0.46 – 0.65

There is some discussion about the relevance of the rat toxicity data to humans given that bromate may be genotoxic via an indirect mechanism with a threshold, thus again suggesting that data obtained from studies of rats exposed at high doses are not relevant to humans exposed at low doses. However, bromate must be considered as a non-threshold carcinogen until additional research provides sufficient evidence to prove otherwise (Fujie et al., 1984; Giddings, 2000). As a result, both the European Union and the USEPA established $10 \mu\text{gL}^{-1}$ maximum contaminant level (MCL) of bromate in drinking water (von Gunten, 2003).

3.3.3. Bromide in the water

Unlike sea waters which bromide concentrations are relatively constant and typically as high as 65 mgL^{-1} (Haag and Hoigne, 1984), fresh waters contain low bromide concentrations in varying amounts with levels ranging from 0 to $3000 \mu\text{gL}^{-1}$ (Krasner et al., 1989; Kruithof and Meijers, 1993; Legube et al., 1993, Amy et al., 1993). Bromide ions enter fresh waters as a result of sea water intrusion, geological sources and human activities such as industrial and agricultural discharges. Bromide is also added to the pool and cooling water during chlorination and ozonation (Daniel et al., 1999). Because bromine is five times more active than chlorine, it exhibits low stability and hence should decay faster. Due to these characteristics, the use of bromide ions in conjunction with chlorine has been proposed as an alternative method to routine chlorination. On the other hand, ozone is unstable in the water, thus bromide is added during ozonation of pool water to produce bromine species (von Gunten, 2003)

3.3.4. Bromate formation during ozonation

Ozone-bromide reactions are well documented in the literature (Haag and Hoigne, 1983; Yates and Stenstrom, 1993; von Gunten and Hoigne, 1994; Song, 1996; von Gunten and Oliveras, 1998). According to the data, bromate formation occurs via both direct (and/or molecular ozone) and indirect (and/or radical) oxidation pathway.

Haag and Hoigne (1983) described direct ozonation (and/or molecular ozone) pathway with a series of ozone-bromide reactions as follows:



Von Gunten and Hoigne (1994) reported that 77% of the hypobromite (BrO^-) formed by ozonation is converted to bromide (Eq. 3.32) again, and remaining 23% is converted to bromate (Eq. 3.33, 3.34).

Yates and Stenstrom (1993) and later von Gunten and Hoigne (1994) concluded that indirect oxidation (radical reactions) pathways have significant effect on the bromate formation. Their results indicate that OH radicals play a dominant role with respect to the ozone-bromide interaction as described in the following equations;



The entire model postulated by Yates and Stenstrom covers a system of 65 species and 190 reactions. They concluded that not only $\text{OH}^\bullet$ radical but also other radicals affect bromate formation.

3.3.5. Effect of variables on bromate formation

3.3.5.1. Effect of pH

Ozone-BrO⁻ reaction rate is higher than ozone-HOBr reaction rate (Eq.3.33a and 3.33b). As can be seen from Eq. 3.42, at pH values higher than 8.86 the active species is BrO⁻, and at the lower pH values HOBr is the dominant bromine species in the water. Hence bromate formation under basic conditions is higher than that of expected in acidic medium (von Gunten and Hoigne, 1998; Song, 1996; Minear and Amy, 1996).



Wasterhoff et al. (1993) also found that increasing the pH from 4.5 to 8.5 results in more rapid ozone decomposition and increased bromate formation. On the other hand, increasing pH also means more OH[•] radical generation in a fixed period and more OH[•] radicals result in more bromate formation (Yates and Stenstrom, 1993). On the other hand, aqueous bromine may react with NOM resulting in organic bromine formation (Eq. 3.43). NOM-HOBr reaction is much faster than NOM-BrO⁻ reaction. Thus, the amount of total organic bromine (TOBr) concentration increases at low pH values.

3.3.5.2. Effect of bromide concentration

A linear trend was reported between initial bromide level and bromate formation, probably due to increased BrO⁻ and/or HOBr concentrations (Minear and Amy, 1996; Krashner et al., 1993). However, it is known that bromide is a significant OH radical scavenger, thus high level of bromide may stabilize ozone decomposition (Song, 1996). Wasterhoff et al. (1993) noted that even small amounts of bromide in water could lead to bromate formation. Also Amy et al. (1993) reported that there is no minimum bromide ion concentration required for bromate formation, and 50 µg/L⁻¹ bromide concentrations with even in the presence of DOC could produce bromate concentration greater than 10 µg/L⁻¹.

3.3.5.3. Effect of NOM and ozone dose

NOM can play several roles in bromate formation. First, ozone-NOM and ozone-free radicals reaction rates are faster than ozone-bromide reaction rates (Hoigne and Bader, 1985; Reckow et al., 1986; Xiong, et al., 1992). Therefore, it reduces the molecular ozone to oxidize bromide species (von Gunten and Hoigne, 1992; Song, 1996). Second, NOM may result in ozone decomposition and free radical generation by producing hydrogen peroxide (Xion et al., 1992). The effect of hydrogen peroxide will be discussed in section 3.35.6. Third, as shown in Eq. 5.13, NOM can react hypobromous acid and form brominated organics. As a result, it can reduce bromate formation (Song, 1996).

Westerhoff et al. (1993) investigated the interaction between NOM fractions and bromate formation. They found that larger NOM fraction (30.000-1000 daltons) increases the ozone demand of water, which left less ozone for bromate formation.

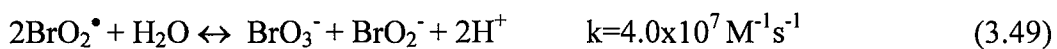
Amy et al. (1993) and Siddique et al. (1993) reported the issue of an ozone dose threshold, which is the minimum ozone dose to form bromate in the presence of NOM. They found an ozone/DOC ratio as 0.5 mgmg^{-1} . It means that ozone dose higher than the threshold results in bromate formation.

3.3.5.4. Effect of alkalinity

von Gunten and Hoigne (1992) investigated the effect of alkalinity on bromate formation and reported that bromate formation increases with increasing alkalinity concentration. It is concluded that four possible reasons may result in the enhanced bromate formation in the presence of total inorganic carbon (TIC) (Minear and Amy, 1996).

Carbonate radicals ($\text{CO}_3^\bullet$) are formed in the presence of ozone (Eq. 3.44 and 3.45) and they act as a secondary oxidant which, like OH radical, can also oxidize hypobromite ions (BrO^-)





Secondly, the carbonate radical is known to react selectively in the oxidation of organics and inorganics. Thus, OH radical oxidizes preferentially a great variety of organic and inorganic species compared to the carbonate radical.

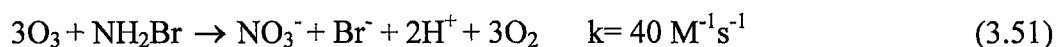
Thirdly, both HCO_3^- and CO_3^{2-} scavenge OH radicals. As a result half-life of dissolved ozone is increased. Thus, bromate formation may increase under these conditions.

Finally, despite the competition for $\text{OH}^\bullet$ by NOM, Br^- , and $\text{HCO}_3^-/\text{CO}_3^{2-}$, bromate formation achieved via a radical oxidation pathway may be still be significant.

3.3.5.5. Effect of ammonia

The effect of ammonia on the formation of bromate have been documented very well by a number of researchers (Haag et al., 1984; Hoigne et al., 1985; von Gunten and Hoigne, 1992; Glaze et al., 1993; Minear and Amy, 1996; Song, 1996).

Ammonia-ozone reaction rate is known to be very slow at pH levels lower than 9.3 (Snoeyink and Jenkins, 1980). In the presence of bromide, HOBr may react faster with ammonia and ozone may react with the formed NH_2Br (Eq. 3.50 and 3.51).



These reactions reduce the reaction of HOBr/ BrO^- with O_3 and retard bromate formation (Gunten and Hoigne; 1993), but O_3 - NH_2Br reaction rate is very low according to inter action reactions among aqueous bromine- O_3 -radicals (Eqs. 3.31-3.49). Krashner et al. (1993) investigated the effect of ammonia addition on the

bromate formation in several pilot plants, and it has been concluded that ammonia addition did not control bromate formation.

3.3.5.6. Effect of hydrogen peroxide

Experimental data have shown that hydrogen peroxide expresses both increasing and decreasing effects on the bromate formation. These variable effects are resulted from two different reaction pathways.

Firstly, H₂O₂ addition eliminates the ozone residual immediately. Bromate formation still occurs due to the OH radicals originated from ozone-hydrogen peroxide reaction (Eq. 3.53 and 3.55). Also, the promoted bromate formation in the presence of H₂O₂ may be due to the synergistic effect of ozone and OH radicals (Minear and Amy, 1996).



Secondly, H₂O₂ can act as a OH radicals scavenger, as a result, bromate formation may decrease in the presence of H₂O₂ during ozonation. Additionally, the quenching effect of H₂O₂ on hypobromous acid (Eq.3.56) may reduce bromate formation.



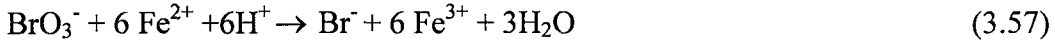
3.3.6. Bromate removal after ozonation

3.3.6.1. Fe(II) reduction

If bromate occurs after preozonation of drinking water, Fe(II) can be added at the subsequent rapid mixing process to reduce BrO₃⁻.

Chemical reduction of BrO₃⁻ to Br⁻ is feasible through the use of ferrous iron (Fe²⁺) as a reducing agent which is then converted to ferric iron (Fe³⁺). Dissolved ozone

(DO₃) and dissolved oxygen in the water can also convert Fe(II) to Fe(III) as summarized in the below reaction scheme:



However, Fe²⁺ coagulation after ozonation is an effective method to remove BrO₃⁻, but required Fe²⁺ concentration is very high even at very low bromate concentrations (Siddique et al. 1994).

3.3.6.2. Activated carbon reduction

Both powdered activated carbon (PAC) and granular activated carbon (GAC) can reduce BrO₃⁻ to Br⁻ according to the following reactions:



where *C represents the activated carbon surface and *CO₂ represents a surface oxide. In this process, the surface area and surface characteristics of activated carbons, salt, DOC and pH are the most important parameters that affect bromate reduction. Especially, salt and DOC dramatically inhibit bromate reduction. It has been reported that activated carbon process may not be economical for bromate reduction (Minear and Amy, 1996).

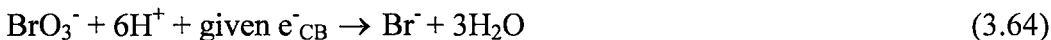
3.3.6.3. UV irradiation

Even though, it is mentioned that UV irradiation may not be a cost effective method for BrO₃⁻ removal, it can be used for BrO₃⁻ destruction as described by the following equations.



UV irradiation results in the decomposition of bromate leading bromide and oxygen as end products via complex reactions generated by photolysis.

On the other hand, photocatalytic reduction of bromate has also been studied in literature. In the photocatalytic process bromate reduction occurs via photogenerated electrons as in the following reaction;



It was concluded that photocatalysis is impractical method for the reduction of bromate due to the long reaction time required (Mills et al., 1996; Noguchi et al., 2003).

3.3.6.4. Biological reduction of bromate

Activated carbon biological method has also been reported for bromate reduction in literature. Microorganisms present in the water can colonize the GAC, and they can use biodegradable organics as an electron donor. Some studies showed that some microorganisms might be able to use bromate as an electron acceptor.

Hijnen et al. (1995) found that a group of mixed denitrifying organisms could reduce bromate to bromide in the absence of oxygen and nitrate. Using half reaction, reduction potentials were calculated for bromate, nitrate, and oxygen.



Bromate is a stronger oxidant than both oxygen and nitrate as shown by the calculated reduction potentials. Although bromate has a greater reduction potential than oxygen and nitrate, reaction kinetics must also be considered. Enzymes strongly affect the kinetics of electron acceptor utilization. It is reported that bromate reduction could be catalyzed by spinach nitrate reductase (Krisits, 1997). The concentration of oxygen affects the formation and activity of nitrate reductase. For example, 30 μM of dissolved oxygen inhibits the formation of reductase. If the oxygen concentration is too high, this enzyme may not be available for nitrate or

bromate reduction. If the condition permits nitrate reductase activity, then nitrate and bromate could be competing for use as electron acceptors. But it seems that the biological reduction of bromate is impractical for ozonated water. Because DO and nitrate (NO_3) serve as common microbial electron acceptors. DO is known to be very high in ozonated water. In the presence of oxygen, microorganisms use oxygen as an electron acceptor, thus DO oxygen should be removed before biological process for bromate reduction. On the other hand, Robertson and Kuenen (1992) found that aerobically grown *Thiosphaera pantotropha* were able to use nitrate. Furthermore, these investigators found that *Thiosphaera pantotropha* could use oxygen and nitrate simultaneously. Thus, complete removal of oxygen may not be necessary for bromate reduction (Krisits, 1997).



4. MATERIAL AND METHODS

4.1. Materials

4.1.1. Chemicals

Nitric acid, titanium(IV) isopropoxide, hydrochloric acid, humic acid sodium salt, and potassium indigotrisulfonate were supplied from Aldrich and sodium bromide (NaBr), sodium bromate (NaBrO₃) and potassium iodide (KI) were supplied from Merck company (Milwaukee-USA).

4.1.2. Thin-film photoelectrodes

Titanium (IV) isopropoxide was used as a precursor for preparing TiO₂ colloidal suspensions. Briefly, 20 mL of titanium isopropoxide was added to a nitric acid solution keeping the ratio Ti/H⁺/H₂O at 1/0.5/200. The resulting precipitate was continuously stirred until completely peptized to a stable colloidal suspension. This suspension was dialyzed against Milli-Q water to pH 3.5 by using a Micropore 3500 MW cutoff membrane (Kim and Anderson.,1994). Thin-film electrodes were cast onto titanium foil (0.5 mm, Goodfellow Cambridge Ltd) back contacts following a sequence of dipping, drying and firing at 300 °C for 3 hours (Figure 4.1). Further details are available in the literature (Xu and Anderson.,1991).

4.1.3. Titanium dioxide

Commercial TiO₂ (Degussa P-25 and Merck) was used in the catalytic ozonation experiments.

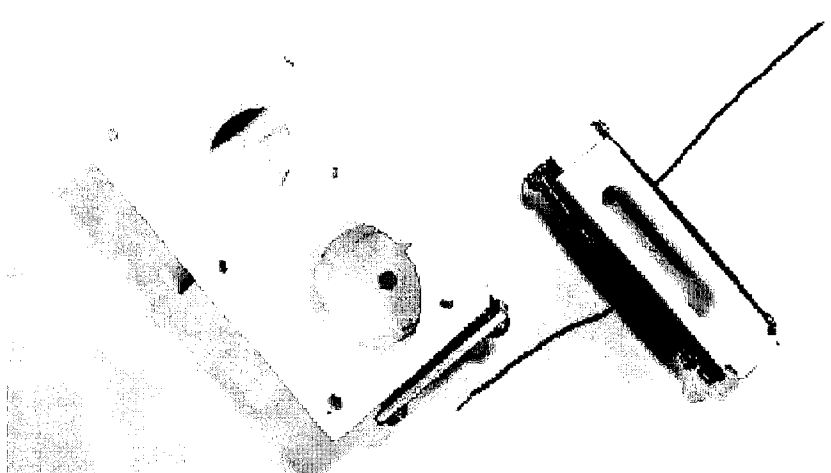
4.1.4. Humic acid solution

A 100 mgL⁻¹ stock solution of HA was prepared in Milli-Q water and filtered through 0.22 µm Millipore membrane. Aliquots were diluted with MQ water and the appropriate quantity of electrolyte added. The initial TOC level and absorbance values of a 25 mgL⁻¹ HA solution at 254 nm (UV₂₅₄) and 400 nm (Vis₄₀₀) were 8.4 mgL⁻¹, 0.67 cm⁻¹ and 0.24 cm⁻¹ respectively.

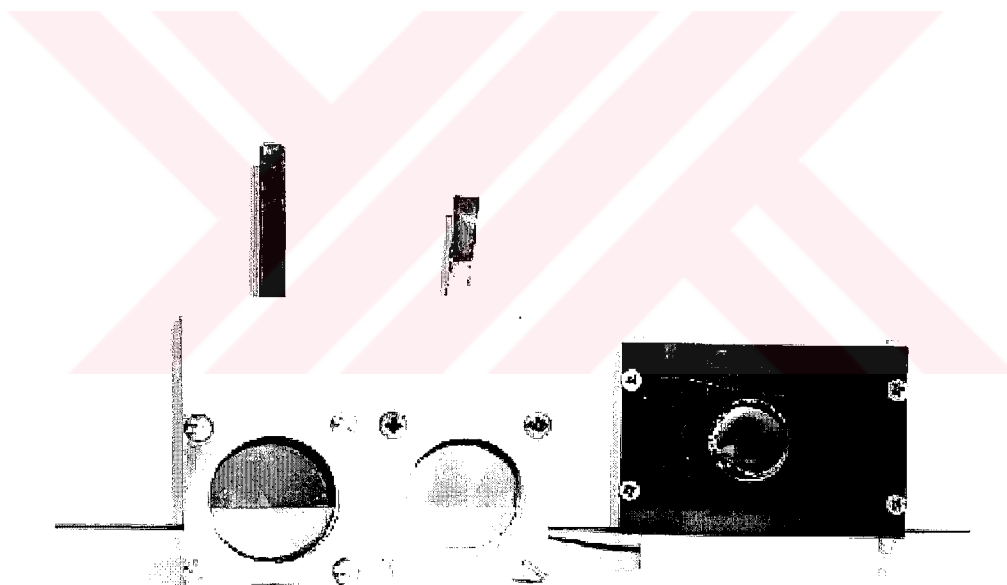
4.2. Experimental Procedures

4.2.1. PEC experiments

As seen in Figure 4.1 and 4.2, PEC experiments were conducted in a two-compartment PEC reactor having a cylindrical compartment with a diameter of 40 mm and height of 120 mm in each side (isolated by a Nafion 117 membrane). A Princeton Applied Research (PAR) potentiostat, model 6310 was used to bias the TiO₂ photoanode against perforated platinum foil used as counter electrode and a saturated calomel electrode (SCE) as a reference. All experiments were carried out utilizing 100 mL test solutions in each compartment. The photoactive area of the anode was 20 cm² (4cmx5cm) and was illuminated by a 450W Xe-Hg arc lamp Oriel, model 6262 UV light source (260-360 nm wavelength and maximum 250 mWcm⁻² UV intensity). The light intensity on electrode surface was measured with an International Light Inc. photometer; model IL 1400A. Pure oxygen was bubbled into the solution during all experiments. The pH of the solution was measured with a double-junction combination electrode (Orion Model 81-72BN) connected to a Fisher Scientific Accumet 50 pH meter. All experiments were performed at room temperature (around 20 ± 3 °C). Dissolved oxygen (DO) was measured by DO meter (Great Lakes Instruments, Model 867). The dissolved oxygen concentration was around 31 mgL⁻¹ in aqueous solution in the PEC reactor when oxygen was supplied.



(a)



(b)

Figure 4.1. Pictures of the reactor system performed in the PEC and PC studies (a) reactor (b) reactor with electrodes.

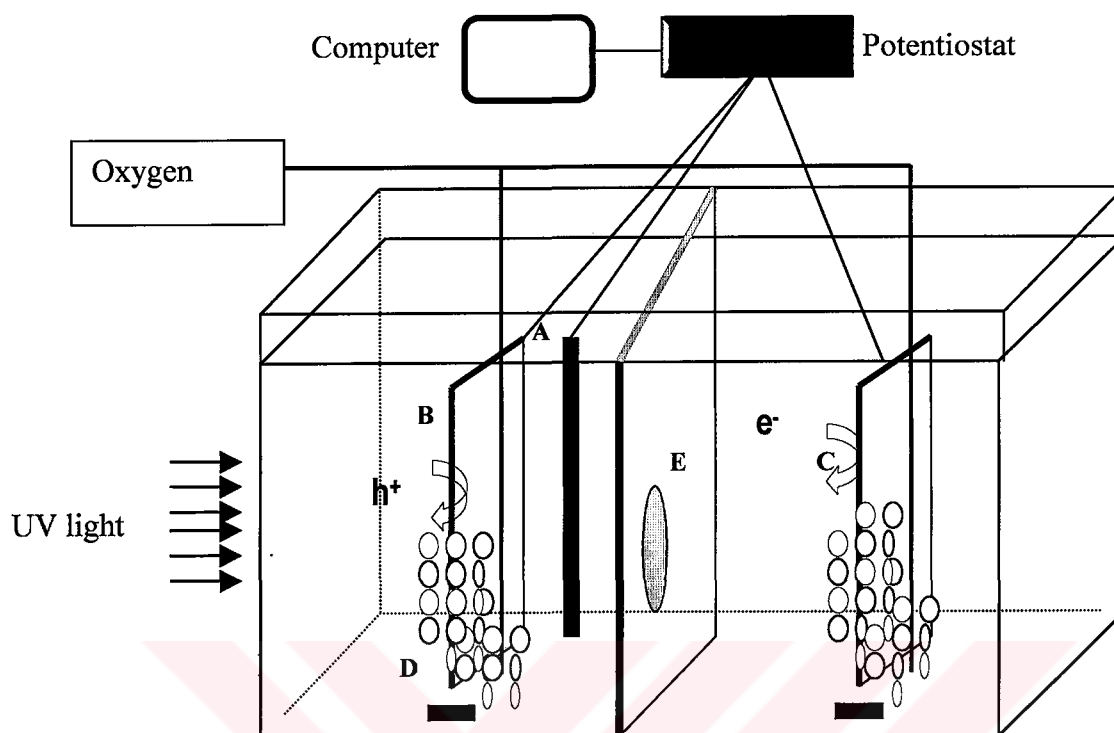


Figure 4.2. Diagram for the reactor system for the photoelectrocatalytic reactions: A, reference electrode (Saturated calomel electrode); B, photoanode TiO_2 coated electrode; C, cathode electrode; D, stirring bar; E, Nafion 117 membrane.

4.2.2. PC experiments

PC experiments were carried out using TiO_2 electrode in 100 mL HA and bromide test solutions under illumination in the photoanode cell without any bias connections to compare PEC and PEC process with respect to humic acid degradation, bromine generation and bromate formation. Neither of bromine generation nor bromate formation was observed while PC humic degradation.

4.2.3. Photolysis

100 mL test solutions in the anode cell were illuminated under the same irradiation conditions without electrodes and bias to determine the effect of photolysis on the humic acid degradation. No photolysis of HA was observed in the experiments during 3-hr.

4.2.4. Electrochemical experiments

The electrochemical experiments were performed biasing the TiO₂ photoanode with 1 V potential against perforated platinum foil used as counter electrode and a saturated calomel electrode (SCE) as a reference but without UV illumination. 100 mL test solution was used in each compartment and samples were taken from anode compartment for analytical measurements. None of the electrochemical HA degradation, bromine generation and bromate formation could be determined during the specified reaction periods (3-hour for HA degradation and 30 minutes for bromine and bromate formation blank experiments).

4.2.5. Ozonation experiments

Ozone was generated from air by ozone generator (PCI model, GL-1). A closed cylindrical pyrex glass reactor with a diameter of 40 mm and height of 1100 mm was used in the ozonation and catalytic ozonation experiments. A tubular cylindrical porous diffuser was replaced at the bottom of the reactor to transfer input ozone gas into aqueous solution. Teflon tubing line was used for the connection between ozone generator and reactor. The appropriate ozone concentrations were adjusted by changing the electrical current of the ozone generator. All experiments were performed at room temperature (25 °C) using 1 L aqueous solution. Two bubblers containing of 250 ml 2% KI solution was used to trap the ozone in off gas (Figure 4.3). Then, a sodium thiosulphate titration method was performed to measure the trapped ozone concentration in the KI solutions. Indigo method was employed to determine aqueous dissolved ozone concentrations. The transferred ozone (TO₃) was calculated as follows;

$$TO_3 = \text{Total used ozone} - (\text{Ozone in off gas} + \text{dissolved ozone in solution})$$

4.2.6. Catalytic ozonation experiments

Commercial TiO₂ of Degussa P-25 and Merck were used as a catalyst in the catalytic ozonation experiments. Appropriate concentration of TiO₂ was added into bromide content aqueous solution then ozone was employed into the solution as a similar with ozone experiments.

4.3. Analytic Measurements

4.3.1. Spectrophotometric measurements

Absorbencies were measured at 254 nm (UV_{254}) and 400 nm (Vis_{400}) in a 10 mm pathway quartz cell using a Hewlett Packard spectrophotometer, model HP 8452A in order to follow the degradation of HA.

The concentration of active bromine was determined by the standard colorimetric method based on the indicator N, N-diethyl-p-phenylenediamine (DPD), at an absorbance of 512 nm using an HP 8452A Hewlett Packard spectrophotometer and a 10 mm cell.

4.3.2. Organic carbon analysis

A total organic carbon analyzer (Shimadzu Instruments, Model TOC 500) was used to measure dissolved organic carbon. The inorganic carbon ($H_2CO_3^*$, HCO_3^- , and CO_3^{2-}) was removed by acidifying the sample to pH values between 2 and 3 with 1.0 N hydrochloric acid (HCl) followed by sparging with CO_2 free air. Thus, the measured dissolved carbon is equal to dissolved organic carbon (Song, 1996). The dissolved organic carbon was converted to carbon dioxide in a combustion tube at 680 °C in the presence of a platinum oxidation catalyst. A non-dispersive infrared gas analyzer detected the CO_2 .

4.3.3. Bromate and bromide analysis

A Dionex ion chromatograph (DX 300) with an IonPac™ AS9-SC anion column and an AG9-SC guard column with 500 ml loop was employed to determine bromate and bromide concentrations. A bicarbonate eluent (0.9 mM $NaHCO_3$) was used for both bromate and bromide analysis. Since the eluent enabled good separation between bromate and chlorate and provided $3 \mu g L^{-1}$ detection limit for bromate there was no need to remove chloride by silver filters.

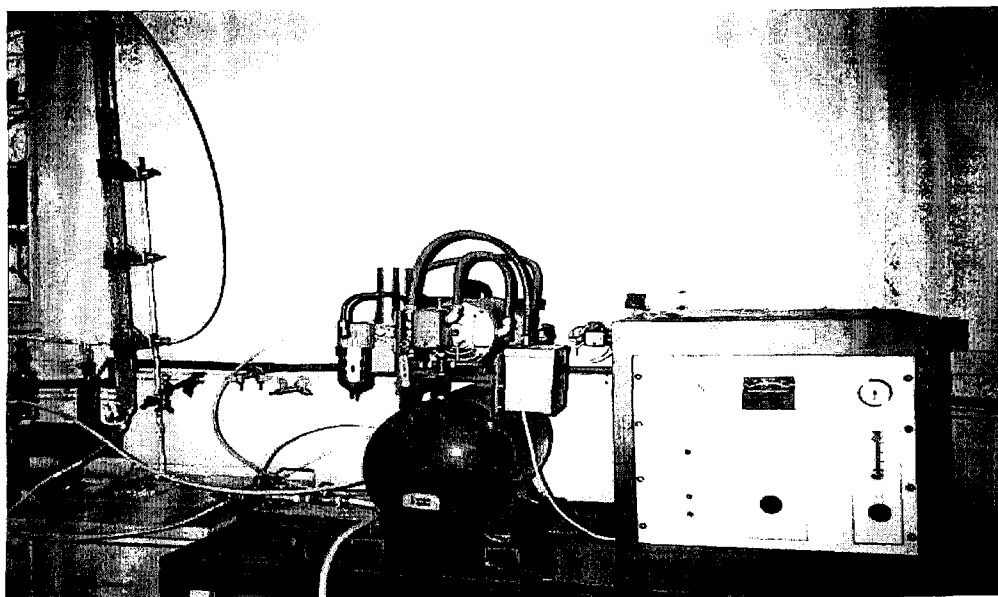


Figure 4.3. Ozone generator.

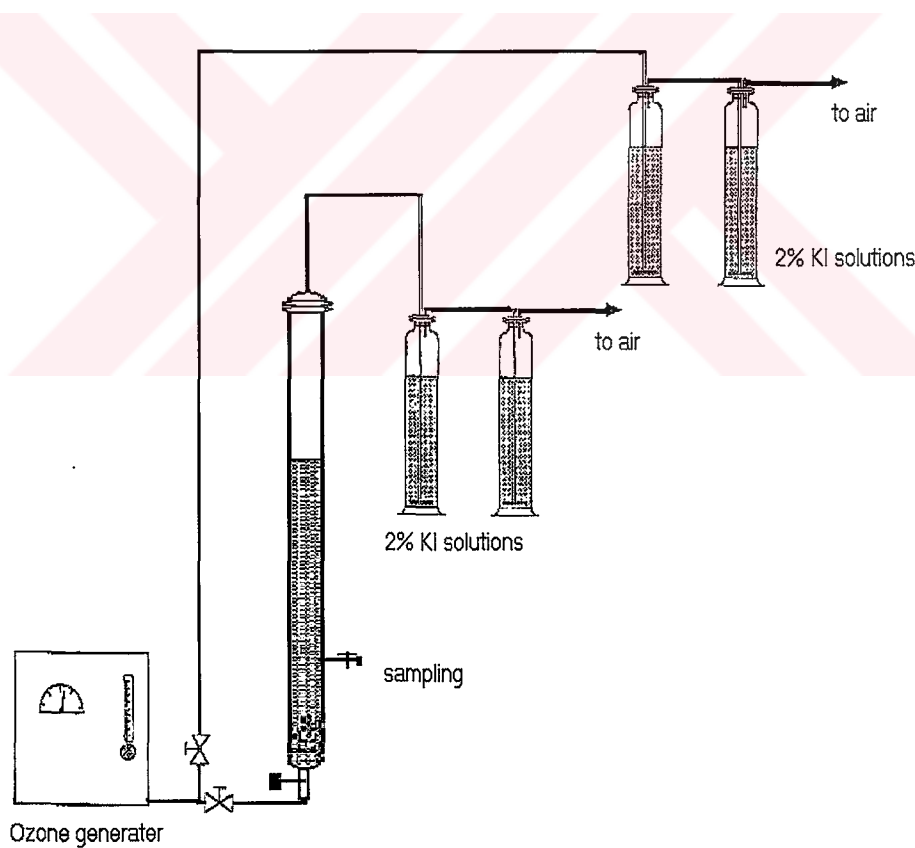


Figure 4.4. Experimental set-ups for the (catalytic) ozonation experiments.

5. RESULTS AND DISCUSSION

5.1. PEC Humic Acid Degradation

PC and PEC methods were performed for the treatment of HA in a model solution. The effects of treatment and solution variables on both methods were also investigated and results were comparatively presented.

5.1.1. Preliminary experiments

5.1.1.1. Adsorption of HA

Preliminary experiments were designed to ensure that there was no disappearance of HA due to specific adsorption on the surface of the reactor and the TiO₂ electrode. Both TOC and UV₂₅₄ levels were the same during the 3-hr period of the experiment. This does not imply that HA is not adsorbed by these surfaces, but rather that there is not sufficient surface area to produce any change in the HA concentration over this time period.

5.1.1.2. Evaporation of HA

No spontaneous evaporation of HA from the sample solution was detected while oxygen was bubbled through the solution for 3-hr.

5.1.1.3. Photolysis of HA

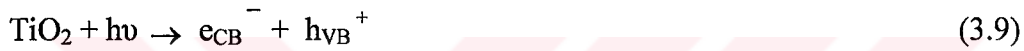
While HA does absorb some light in the spectral range of 300-400 nm no significant photolysis of HA (<5%) was noticed under the conditions employed in our experiments.

5.1.1.4. Electrolysis of HA

Experiments were performed using the same conditions with the same biasing potentials without UV illumination in order to determine electrochemical performance in this process. Under the applied potential conditions no substantial electrochemical current was detected indicating HA degradation, Vis_{400} and or TOC removal during the typical 3-hr period of these reactions.

5.1.2. Changes in pH

When TiO_2 is illuminated with the energy higher than the band gap energy ($E > E_{bg}$), the primary oxidation and reduction reactions occur on the surface as expressed by the following reactions:



The photo-generated species take part in oxidation and reduction reactions occurring on the surface of the catalyst. Biasing of immobilized TiO_2 in the PEC system inhibits the recombination of electrons (e_{CB}^-) and holes ($h\nu_B^+$). As a result, the photocatalytic performance of TiO_2 increases upon increases in external biasing potential up to 1 V vs. SCE. However, further increases in potential do not improve the photocatalytic oxidation performance of TiO_2 . Also, the photoanode and cathode are separated in this PEC reactor and photo-generated electrons are withdrawn to the cathode cell while holes remain at the surface of photoanode. As a result of separating the electrons and holes, it was expected that pH might decrease in the photoanode and increase in the cathode compartments.

To test this hypothesis, a sample solution containing 25 mgL⁻¹ HA in 1.25x10⁻² M NaCl was employed to determine how pH changes over time during a typical experiment. The pH trends in the solutions of both compartments of the reactor as a function of the time are shown in Figure 5.1. After 40 min, pH was at the steady state condition: about 3 in the anode and 11 in the cathode compartment. The aggregation of HA was not observed at pH 3 in the photoanode.

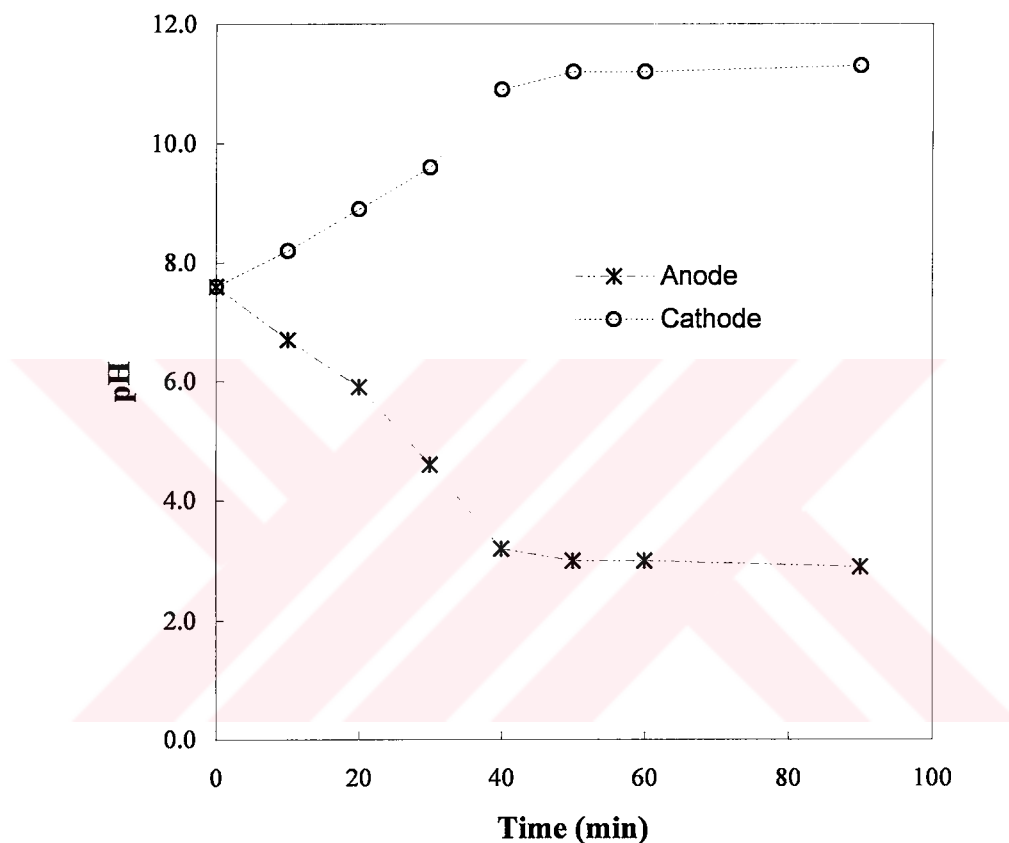


Figure 5.1 Trends in pH in photoanode and cathode over the time of PEC treatment of 25 mgL⁻¹ HA in 1.25x10⁻² M NaCl solution using a titanium dioxide thin-film electrode biased at E=1 V vs. SCE.

5.1.3. HA degradation

A humic acid test solution (25 mgL⁻¹ humic acid, 1.25x10⁻³ M NaCl at pH 3) in the photoanode cell was degraded by PEC method using a biased TiO₂ photo-anode with 1 V vs SCE external potential under illumination. Humic acid degradation was followed by measuring TOC loss and absorbance at 254 nm (UV₂₅₄) over the time. PC method was also carried out under the same conditions. Results show that PEC process is much more effective than PC process. UV₂₅₄ removal was about %50 and

TOC removal was about 60% higher than the photocatalytic degradation at pH 7. Over 50% PEC degradation of UV₂₅₄ was gained in 45 minutes while TOC removal was ≤ 8%. An exponential decay was observed and, for prolonged irradiation, 80% TOC removal was achieved at steady-state conditions in a 120 min time period. Approximately 20% of the remaining organic compounds were found to be very refractory and degradation was insignificant after 120 min (Figure 5.2.).

5.1.4. PEC humic acid removal kinetics

A zero order kinetic reaction, described by Eq. 5.3, has been extensively used in the literature to fit the degradation kinetics of various organic compounds in water (Wu et al., 1998).

$$-dC/dt = k_0 \quad (5.3)$$

By using Eq. 5.3 the half life, $t_{1/2}$ can be calculated as follows;

$$t_{1/2} = C/2k_0 \quad (5.4)$$

C: Concentration of the solute, UV₂₅₄, cm⁻¹ or TOC, mgL⁻¹

k_0 : Zero order degradation constant, cm⁻¹ min⁻¹ or mgL⁻¹ min⁻¹

$t_{1/2}$: The half life for zero order kinetic model, min.

Also, UV₂₅₄ degradation in TiO₂ suspensions under UV illumination follows a first order kinetic model (Bekbolet and Balcioglu, 1996).

$$-dC/dt = k_1[C] \quad (5.5)$$

Integration of Eq 5.5 gives the half life equation (9)

$$t_{1/2} = 0.693/ k_1 \quad (5.6)$$

Using k_1 and C, Eq 5.7 gives first order rate (R)

$$R = C k_1 \quad (5.7)$$

where;

k_1 : Pseudo first order degradation constant, min^{-1}

C: Concentration of the solute, UV_{254} , cm^{-1} or TOC, mgL^{-1}

R: Pseudo first order degradation rate $\text{mgL}^{-1}\text{min}^{-1}$

$t_{1/2}$: the half life for a first order kinetic model, min.

To study the PEC humic acid degradation kinetics, a humic acid test solution (25 mgL^{-1} humic acid, TOC= 8.4 mgL^{-1} , 1.25×10^{-3} M NaCl at pH 3) in the photoanode cell was degraded using a biased TiO_2 photoanode with 1 V vs SCE external potential under illumination. Humic acid degradation was followed by measuring TOC loss and absorbance at 254 nm (UV_{254}) over time. Zero and first order reaction kinetics rate expressions were applied to UV_{254} and TOC degradations and it was found that UV_{254} removal followed zero order kinetics giving a zero order kinetic constant, $k_0 = 7.3 \times 10^{-3} \text{ cm}^{-1}\text{min}^{-1}$. On the other hand, when compared to the degradation rate of UV_{254} , a lower rate of removal of TOC ($\leq 8\%$) was obtained in 45 min time period (Figure 5.2.). After lag period of 45 min, TOC removal followed first order kinetic model giving a first order rate constant of $2.4 \times 10^{-2} \text{ min}^{-1}$ (Appendix A).

5.1.5. Effect of HA concentration

The PEC treatment method was applied to humic acid solutions with 5 mgL^{-1} , 10 mgL^{-1} and 25 mgL^{-1} HA concentrations with 1.25×10^{-3} M NaCl at pH 3. The degradation of humic acid was followed by measuring both UV_{254} and TOC parameters.

The degradation profiles exhibited a steady decrease with respect to time, reaching 90% removal in 15 min, 25 min, and 80 min for 5 mgL^{-1} , 10 mgL^{-1} , and 25 mgL^{-1} HA concentrations, respectively.

The linear decreasing trend observed for UV_{254} removal was evaluated by a zero-order reaction kinetic model (Table 5.1 and Appendix B). Zero order rates were found as $7.3 \times 10^{-3} \text{ mgL}^{-1}\text{min}^{-1}$, $8.2 \times 10^{-3} \text{ mgL}^{-1}\text{min}^{-1}$ and $7.3 \times 10^{-3} \text{ mgL}^{-1}\text{min}^{-1}$ for solutions of 5 mgL^{-1} , 10 mgL^{-1} and 25 mgL^{-1} respectively. According to the zero order rates,

obtained for HA concentrations of 5 mgL⁻¹ and 25 mgL⁻¹, approximately a 12% increase was observed for HA concentration of 10 mgL⁻¹.

The TOC removal profile exhibited an exponential decay trend for the 10 mgL⁻¹ HA solution with $k_1=2.3 \times 10^{-2} \text{ min}^{-1}$. However, for the 25 mgL⁻¹ solution a lag period of 45 minutes was observed that was followed by an exponential decay (Appendix B). The first order rate constant $k_1=2.4 \times 10^{-2} \text{ min}^{-1}$, resulting in a first order degradation rate of 0.20 mgL⁻¹min⁻¹, which is 60% higher than $7.6 \times 10^{-2} \text{ mgL}^{-1}\text{min}^{-1}$ achieved in the case of the 10 mgL⁻¹ solution of HA.

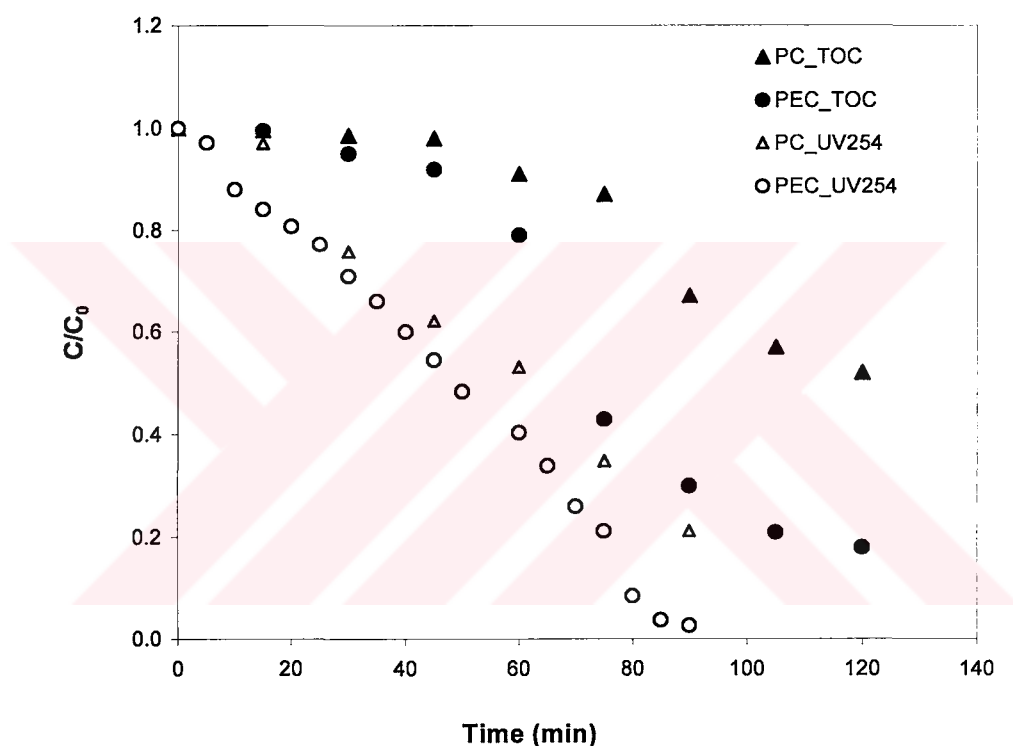


Figure 5.2. PEC and PC removal of 25 mgL⁻¹ HA in 1.25×10^{-2} M NaCl solution using a titanium dioxide thin-film electrode.

5.1.6. Effect of chloride

The presence of chloride in the range $0-1.25 \times 10^{-2}$ M affected the UV₂₅₄ removal rate less than 5% (Appendix C). When chloride concentration increased from 1.25×10^{-2} M to 5.0×10^{-2} M, the observed zero order rate decreased by approximately 10%.

Figure 5.3 and Appendix C display the effect of chloride ions on the PEC TOC removal. The PEC TOC removal rate increased by 10% in the presence of 1.25×10^{-2} M Cl⁻ and the half life decreased from 39 min to 35 min. On the other hand, when

5.0×10^{-2} M was used, the first order removal rate of TOC decreased by 25% and $t_{1/2}$ increased from 39 min to 53 min. It is thought that charge carriers are necessary for electrochemical treatment process and thus small chloride concentrations (up to 1.25×10^{-2} M) accelerate PEC TOC removal rates. On the other hand, since chloride ions are negatively charged and can be adsorbed on the positively charged TiO_2 photoanode electrode surface, higher chloride concentrations could decrease organic substrate adsorption onto the photoanode surface as has it been shown to affect conventional PC degradation (Abdullah et al., 1990; Bekbölet et al., 1998).

5.1.7. Effect of sulfate

Sulfate (SO_4^{2-}) anion is the another common ion found in drinking and wastewater. Sulfate ions can be adsorbed on the positively charged photoanode surface in the photoelectrocatalytic process. Under illumination they react with photogenerated holes and give electron yielding sulfate radicals. The influence of sulfate on the removal of Vis_{400} and UV_{254} degradation was investigated through experiments conducted with 25 mgL^{-1} of HA in Na_2SO_4 at initial of $\text{pH}=6.5$. As can be seen in Figure 5.4, almost the same Vis_{400} and UV_{254} degradation efficiencies were gained by adding sulfate to reaction medium. The observed 8% increase in TOC removal with SO_4^{2-} as the electrolyte is attributed to the effect of the oxidation of sulfate anions to persulfate, a well-known strong oxidant (Patermarakis and Fountoukidis, 1990) (Table 5.2).

Table 5.1. UV_{254} zero order and TOC first order kinetic parameters for the PEC degradation of different HA concentrations in 1.25×10^{-2} M NaCl solution ($\text{pH}=3$, $E=1.0$ V vs SCE)

HA (mgL^{-1})	UV ₂₅₄		TOC		
	k_0 ($\text{cm}^{-1}\text{min}^{-1}$)	$t_{1/2}$ (min)	k_1 (min^{-1})	R ($\text{mgL}^{-1}\text{min}^{-1}$)	$t_{1/2}$ (min)
5	7.3×10^{-3}	8	n.a.	n.a.	n.a.
10	8.2×10^{-3}	13	2.3×10^{-2}	7.6×10^{-2}	26
25	7.3×10^{-3}	45	2.4×10^{-2}	0.2	29

n.a. not available, correlation coefficients, $r > 0.90$ for all data

Table 5.2. Comparison of influences of SO_4^{2-} and Cl^- anions on the PEC performance (pH =6, E=+1 V vs SCE, t= 2 h)

Electrolyte	HA removal (%)		
	UV ₂₅₄	Vis ₄₀₀	TOC
No electrolyte	95	97	72
1.0×10^{-2} M Na_2SO_4	98	98	81
1.0×10^{-2} M NaCl	93	92	73

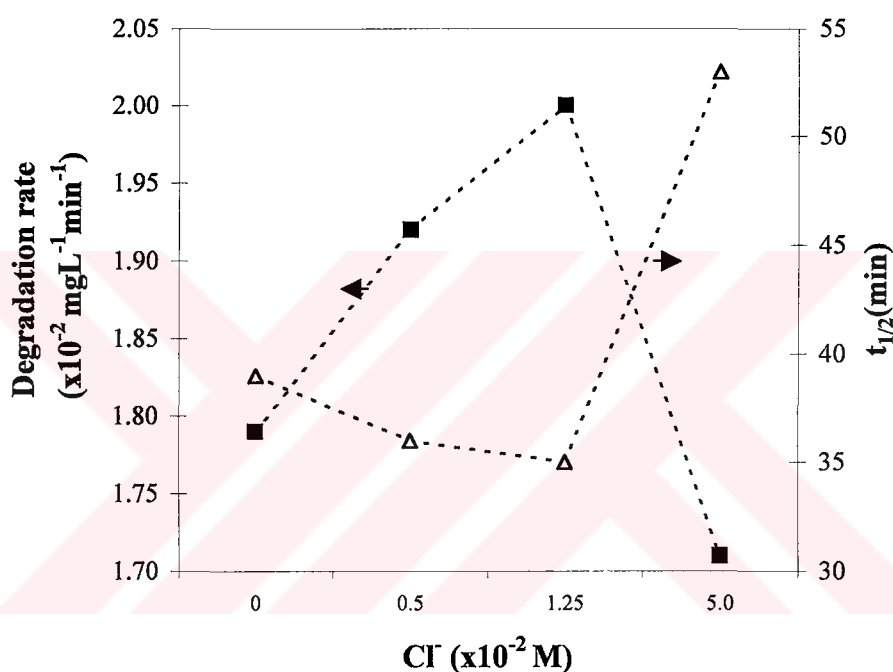


Figure 5.3 Effect of chloride on the PEC TOC degradation kinetics of 25 mgL^{-1} HA solution (pH=3 and E =1 V vs SCE).

5.1.8. Effect of pH

The adsorption of organics on the TiO_2 surface is a necessary prerequisite for the oxidation of these substances due to the surface oriented nature of the photocatalytic process. Previous studies have shown that adsorption of organics onto the TiO_2 surface depends both on the nature of the surface and the conditions of the solution. The TiO_2 surface can acquire negatively or positively charged sites according to the pH of the aqueous medium. The pH value at which the number of the positively and

negatively charged surface sites are equal is defined as the point of zero charge value (pH_{pzc}). The polarity of the TiO_2 surface has been expressed by equations 5.8 and 5.9:



From Eqs. 5.8 and 5.9 pH_{pzc} of TiO_2 can be calculated using the acidity constants (K_{a1} and K_{a2}) as $\text{pH}_{\text{pzc}} = (\text{pK}_{\text{a1}} + \text{pK}_{\text{a2}})/2$. Under natural pH conditions, and due to deprotonation of the carboxylic groups present on the humic acid molecules, ion exchange might occur between the anionic groups of humic acid and OH_2^+ and OH^- groups on the TiO_2 surface. When $\text{pH} < \text{pH}_{\text{pzc}}$ the surface of TiO_2 is positively charged and this condition attracts negatively charged humic acid moieties. As a result, higher oxidation efficiencies of humic acid are expected at lower pH values. When pH is higher than the pH_{pzc} of TiO_2 , the surface of TiO_2 is negatively charged causing electrostatic repulsion between negative humic acid molecules and the TiO_2 surface (Tunesi and Anderson, 1991; Bekbölet et al., 1998).

To compare PC and PEC processes at different pH values of 3.0, 7.5 and 10.5, a test solution of humic acid (25 mgL^{-1} humic acid, $1.25 \times 10^{-2} \text{ M NaCl}$) was submitted to both PC (without external potential) and PEC degradation (biasing the photoanode 1 V vs SCE potential). Upon applying a zero order reaction kinetic model to fit the data, it was shown that PEC method was more efficient under all pH conditions than PC method in terms of the removal of UV_{254} (Appendix D). Although the PC removal rate decreased by 74% under alkaline conditions with respect to the rate achieved under acidic conditions, no distinct change was recorded between the removal rate increases under neutral ($\text{pH} = 7.5$) and alkaline pH ($\text{pH} = 10.5$) conditions for the PEC treatment methods (Table 5.3). The fact that the highest removal rates were attained under acidic pH, is explained by favorable conditions of electrostatic interaction between HA and the surface of TiO_2 .

On the other hand, PC TOC removal rates were strongly affected by the pH of the reaction medium (Table 5.4 and Appendix D). Under acidic conditions, 50% removal was obtained after 120 minutes of irradiation time. Under neutral conditions 20% removal and at a pH of 10.5 only 5% removal rates could be achieved in the PC method. The PEC process is thus more effective than PC process under all applied pH

conditions for TOC removal. Following an initial lag period of 45 min, the first order reaction rate constant was found to be 0.20 min^{-1} at pH: 3.0. Under neutral conditions, reaction rate decreased 50%. A drastic decrease of 85% was achieved under alkaline conditions at pH 10.5 (Appendix D). The corresponding half-life values were 29 min, 58 min and 194 min for acidic, neutral, and alkaline conditions respectively. Under acidic conditions two times (Table 5.4) and under neutral and alkaline conditions four times much higher TOC degradation rates were achieved in the PEC process over the more conventional PC process. It was also found that remaining refractory level of TOC was 67% lower in the PEC method as compared to the PC method (Figure 5.2 and 5.4).

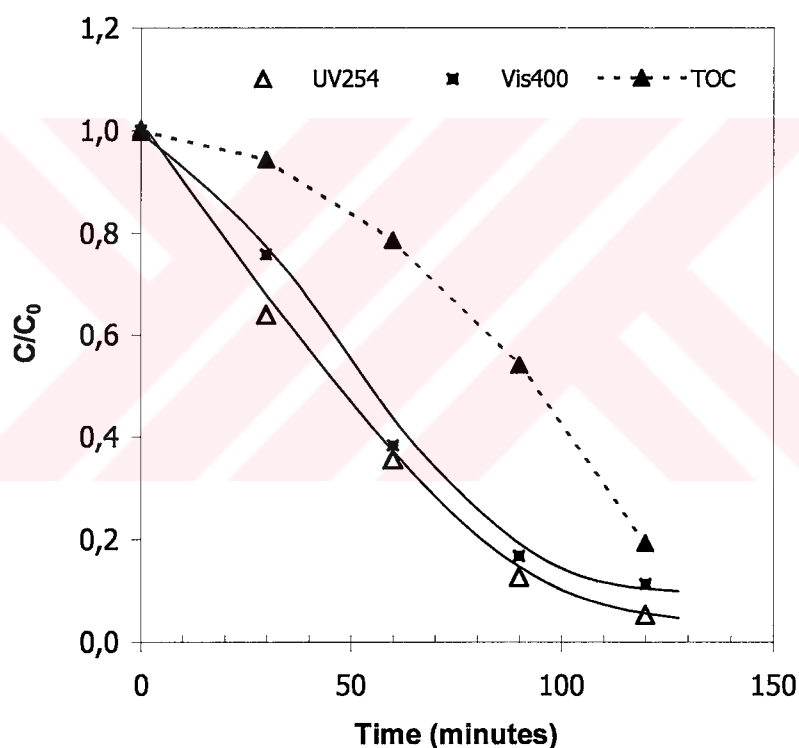


Figure 5.4. PEC degradation of HA in $1.0 \times 10^{-2} \text{ M Na}_2\text{SO}_4$ ($E=+1 \text{ V}$ vs SCE, initial pH=6.5).

Table 5.3. Zero order degradation rate kinetics of 25 mgL⁻¹ HA in 1.25x10⁻² M NaCl solution in the PC and PEC processes under different pH values (E =1 V vs SCE).

pH	PC		PEC	
	k_0 (cm ⁻¹ min ⁻¹)	$t_{1/2}$ (min)	k_0 (cm ⁻¹ min ⁻¹)	$t_{1/2}$ (min)
3.0	5.1x10 ⁻³	64	7.3x10 ⁻³	45
7.5	1.9x10 ⁻³	171	6.8x10 ⁻³	48
10.5	1.6x10 ⁻³	210	5.6x10 ⁻³	59

Correlation coefficients, $r > 0.95$ for all data

Table 5.4. First order degradation rate kinetics of HA under different pH values.

pH	PC			PEC		
	k_1 (min ⁻¹)	R (mgL ⁻¹ min ⁻¹)	$t_{1/2}$ (min)	k_1 (min ⁻¹)	R (mgL ⁻¹ min ⁻¹)	$T_{1/2}$ (min)
3.0	1.0x10 ⁻²	8.7x10 ⁻²	67	2.4x10 ⁻²	2.0x10 ⁻¹	29
7.5	2.9x10 ⁻³	2.5x10 ⁻²	236	1.2x10 ⁻²	1.0x10 ⁻¹	58
10.5	8.3x10 ⁻⁴	7.0x10 ⁻³	830	3.6x10 ⁻³	3.0x10 ⁻²	194

Correlation coefficients, $r > 0.92$ for all data

5.1.9. Effect of external potential

Experiments were conducted in a 25 mgL⁻¹ HA solution to find an optimum potential for this process. Potentials ranging between 0 and +2.0 V vs SCE and UV₂₅₄ and Vis₄₀₀ removals as well as TOC removal were monitored over a 2 h period. Results are presented in Figure 5.5. These results clearly demonstrated that the photoelectrocatalytic process was far better than the conventional photocatalysis, showing that the applied external potential improve the oxidation of organic contaminants in this system. The degradation of HA (as represented by TOC removal) increased as a function of the applied potential up to 1 V vs SCE. Further increases in the applied potential expressed no effect on the degradation. This can be explained by the fact that in a photoelectrocatalytic system the rate of conversion does not depend directly on the applied potential or on current density but rather depends on the electrocatalysis properties such as: adsorption and desorption of reactants and products, and specific features of the semiconductor such as electron-hole recombination rate, diffusion length of the minority carriers and intensity of the

electric field in the space charge region. The function of the applied potential is to prevent as much as possible the charge recombination so as to improve the efficiency of the photocatalytic oxidation of the contaminant.

Additionally, photoelectrocatalytic UV_{254} and Vis_{400} degradation were higher than in photocatalytic degradation but, in this case, 0.0V of applied potential was enough to achieve maximum photoelectrocatalytic UV_{254} degradation, as shown by Figure 5.5. We explain this finding by considering the location of the flatband potential of TiO_2 which is -0.38 V vs SCE, as has been determined from onset potential measurements. All of the applied potentials employed in this study are positive with respect to this flat-band potential. Therefore, there is always a potential gradient over the titania film, resulting in an electric field, which keeps the photogenerated charges apart. These results suggest that adsorption of the HA is enhanced and the generation and separation of electron/hole pairs are achieved even at potentials as low as 0.0 V vs SCE. As a result, the rate of recombination decreases, so as to increase the photocurrent as a function of the applied potential. Accordingly, more of the active oxidizing radical species are thereby formed, which subsequently promotes a more rapid decomposition of organic species. increase of 10% was observed in TOC removal with SO_4^{2-} as the electrolyte (Table 1). This increase may be attributed to the effect of the oxidation of sulfate anions to persulfate, a well-known strong oxidant.

5.1.10. Photocurrent in the PEC treatment

Demand for an electrolyte is a disadvantage of the electrochemical processes. But the photoelectrocatalytic process is slightly different from electrochemical process. Negative charged sulfate and chloride anions can be adsorbed on the positively charged photoanode surface in the photoelectrocatalytic process. Under illumination they react with photogenerated holes and give electron yielding sulfate and chloride radicals. These reactions also decrease the recombination rate of the electron-hole pair (Finklea, 1988; Zaroni et al., 2002).

As can be seen in Figure 5.6, however the photocurrent density increased to 1.8 $mAcm^{-2}$ in the absence of the electrolyte, to 8.0 $mAcm^{-2}$ in the presence of 1.0×10^{-2} M of sulfate and to 10.0 $mAcm^{-2}$ in the presence of 1.0×10^{-2} M chloride, reaching a steady state condition after 2 hours. But almost the same UV_{254} and Vis_{400} removals were gained by adding the electrolytes. 7-8% more TOC degradation observed in the

presence of 1.0×10^{-2} M of sulfate was attributed to the effect of persulfate formed on the photoanode rather than the effect of the photocurrent.

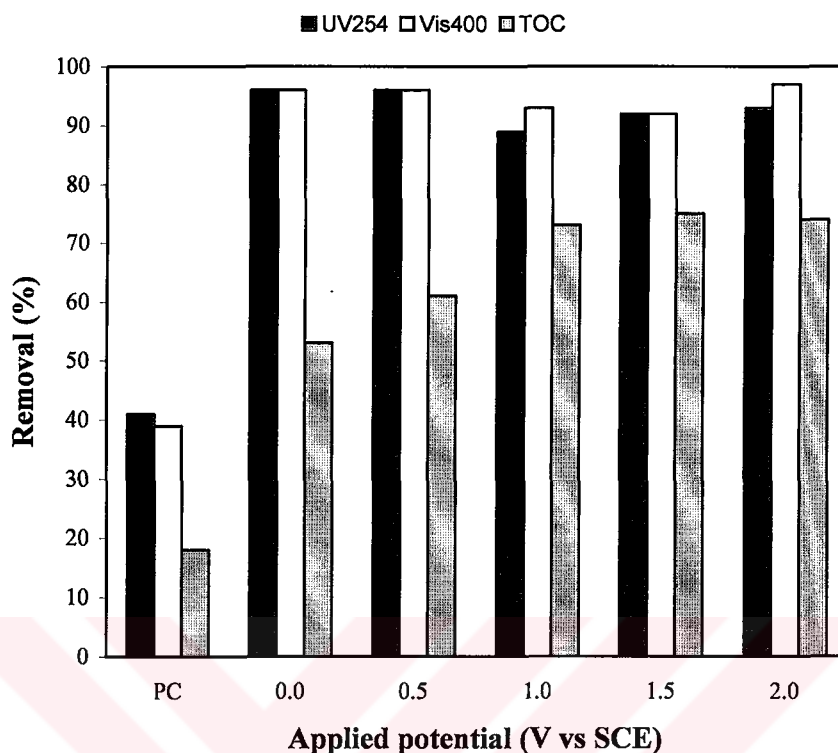


Figure 5.5. Effect of applied potential on the PEC HA removal (HA=25 mgL⁻¹; initial pH=7, t=2 hr).

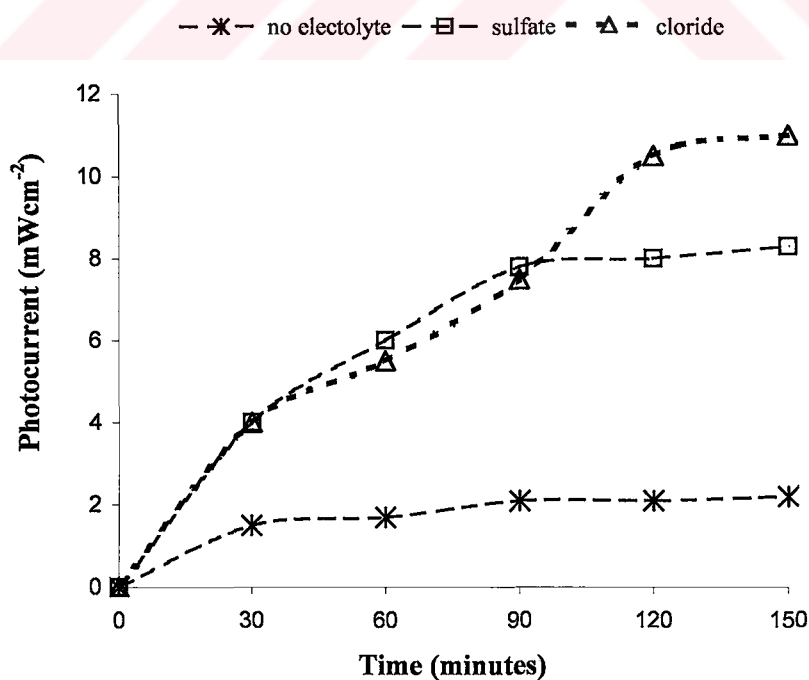


Figure 5.6. Photocurrent change during PEC degradation of HA (HA=25 mgL⁻¹; E=+1 V vs SCE, pH=3).

5.2. PEC Treatment of River Water

5.2.1. Characterization of river water

The water sample was taken from the Moose River/Wisconsin-USA. The common inorganic ion composition of the river water was presented in terms of chloride, nitrate, phosphate and sulfate ions. The dissolved organic matter content was expressed as UV-Vis absorption characteristics measured at 254 nm and 400 nm and given as UV_{254} and Vis_{400} respectively. Carbon content was considerably high as 48 mgL^{-1} , and high humic matter content (Table 5.5.). Eight-fold dilution was employed in all of the experiments performed.

5.2.2. PEC/PC degradation

As can be seen in Figure 5.7 and 5.8, the treatment performance of the PEC method was much more effective than that of PC method alone. Almost 90% UV_{254} and 97% Vis_{400} removal were achieved over same time period while TOC removal was very low in the first 2 hour period and increased sharply after prolonged reaction periods. TOC removal of 58% was obtained in the photoanode compartment under illumination with the UV intensity of 6 mWcm^{-2} in 6 hour reaction time (Table 5.6).

Table 5.5. Characterization of Moose River water

Parameters	
Chloride (mgL^{-1})	0.3
Nitrate (mgL^{-1})	0.6
Phosphate (mgL^{-1})	0.4
Sulfate (mgL^{-1})	1.2
PH	6.68
UV_{254} (cm^{-1})	2.00
Vis_{400} (cm^{-1})	0.24
TOC (mgL^{-1})	48

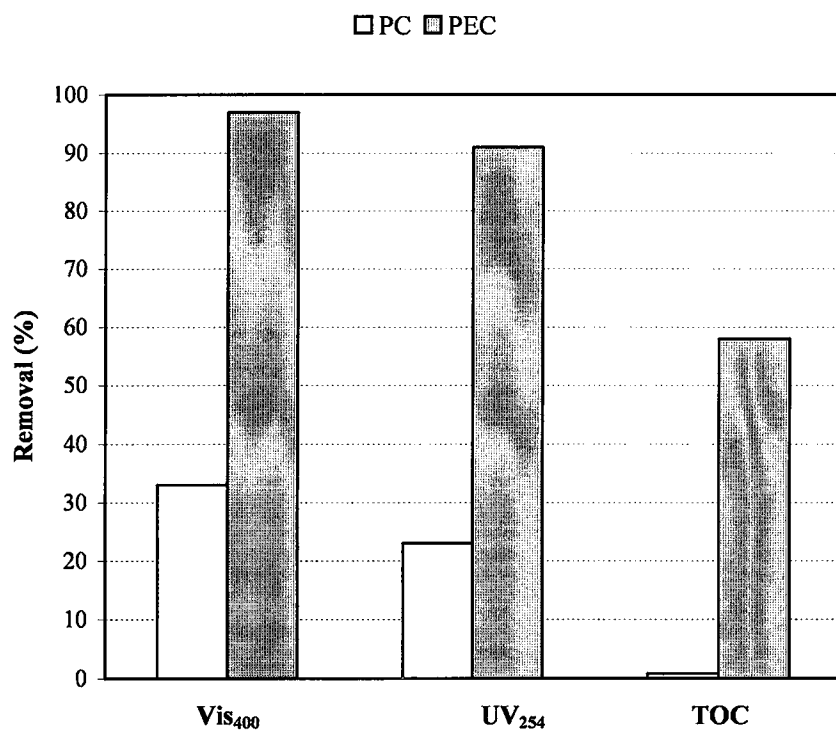


Figure 5.7. PC and PEC treatment of Moose River water

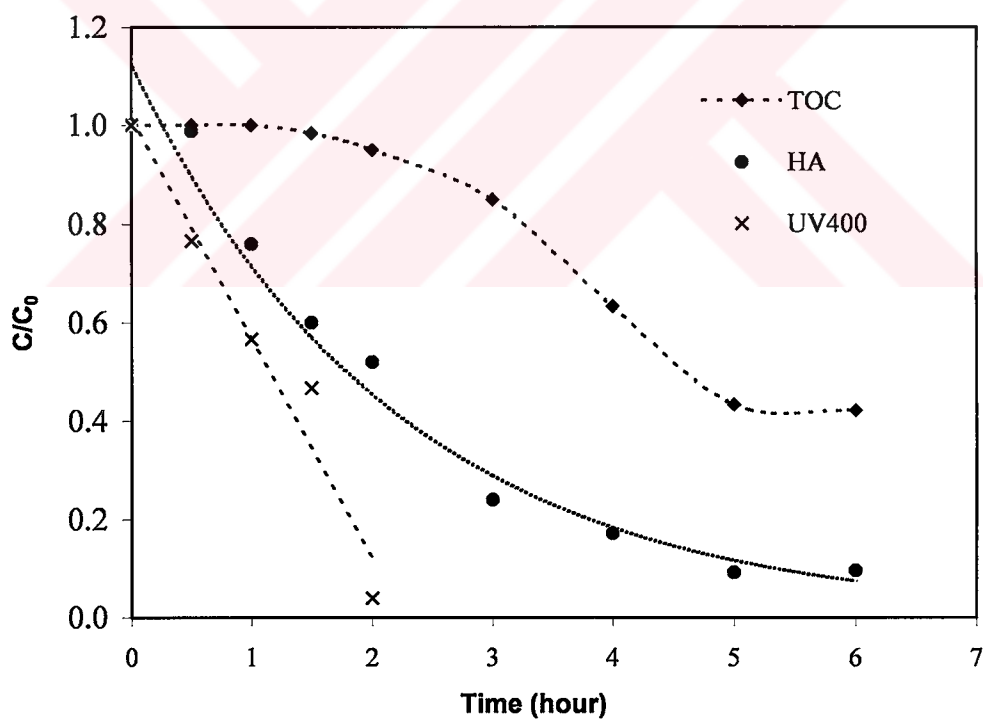


Figure 5.8. Kinetics of PEC degradation of UV₂₅₄, Vis₄₀₀ and TOC (UV intensity=6 mWcm⁻², E= 1 V vs SCE, pH=6.0).

5.2.3. Effect of UV intensity

The photocurrent in the PEC system is known to be a function of UV intensity thus, enhancement in the photocurrent can be observed at higher UV intensity values. According to the data, increasing UV intensity required shorter reaction time periods to reach higher removal efficiencies. TOC degradation of 58-81% was attained under steady state conditions where 300 min to 30 min was achieved in relation to UV intensity values of 6 mWcm⁻² to 100 mWcm⁻², respectively.

The remaining organics fraction observed in the PEC process decreased with increasing UV intensity (Table 5.6). Results indicate that refractory organics also form on the biased TiO₂ photoanode surface. The longer reaction time results in the higher level of remaining organics. The presence of the increased amount of the remaining organic level in the PEC was attributed to the longer reaction time required at low UV intensity values to reach steady the state condition.

Table 5.6. Effect of UV intensity on the performance of the PEC process (E= 1 V vs SCE, pH=6.0)

UV intensity (mWcm ⁻²)	Time (minutes)	Photocurrent (mAcm ⁻²)	TOC removal (%)	UV ₂₅₄ removal (%)	Vis ₄₀₀ Removal (%)
6	300	0.4	58	91	97
25	215	0.9	64	90	96
50	120	1.4	72	94	99
75	45	3.1	77	97	99
100	30	5.8	81	95	99

5.2.4. Effect of oxygen

Not only hydroxyl radical but also oxygen plays a critical role in photocatalytic oxidation of organics to CO₂. To understand the effect of oxygen on the humic acid mineralization in both treatment processes, nitrogen was bubbled through the solution until all oxygen was removed. As can be seen from Figure 5.9, 52% decrease was

attained in TOC removal, while 9% decrease was detected in PEC process. Results are attributed to the oxygen formation on the surface of photoanode in the PEC process.

5.2.5. Effect of external potential

In order to establish the maximum effect of an applied potential, experiments were performed using external potential between -0.5 and 1 V vs SCE. Almost 90% UV_{254} and 97% Vis_{400} removal were obtained for all of the studied conditions. This can be explained by the fact that in a PEC system, the destruction of HA does not depend directly on the applied potential or on current density but depends on the electrocatalytic properties such as: adsorption, desorption of reactants and products. On the other hand, the degradation rate of TOC increased with increasing potential (Figure 5.10). The improvement under positive potential was explained by the decreased recombination rate of holes and electrons by applied potential as reported by previous studies (Kim and Anderson, 1994; Candal et al., 1999) while that under negative potential was attributed to hydrogen peroxide formation in the cathodic reactions (Vinodgopal et al., 1996).

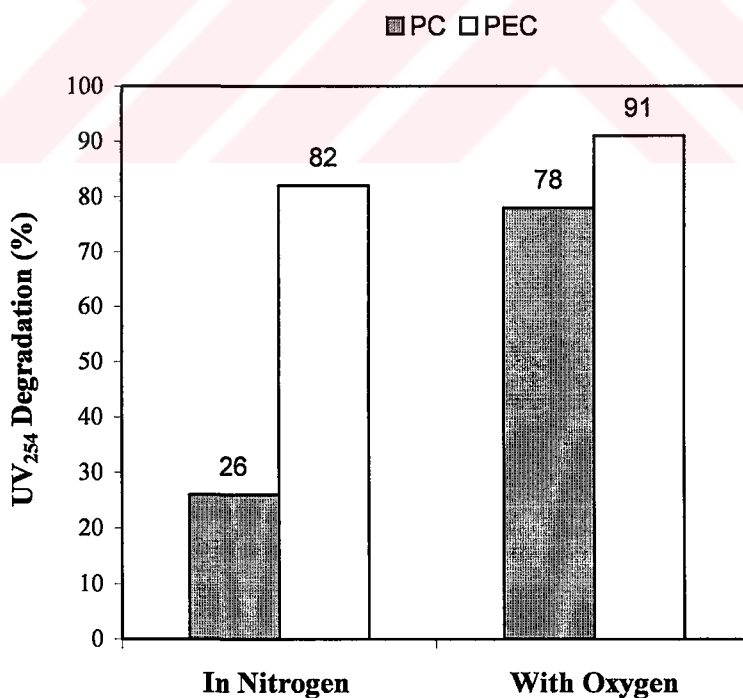


Figure 5.9. Effect of oxygen on the degradation of UV_{254} (UV intensity= 6 mWcm^{-2} , $E=1$ V vs. SCE, $\text{pH}=6.0$, $t=6$ hr).

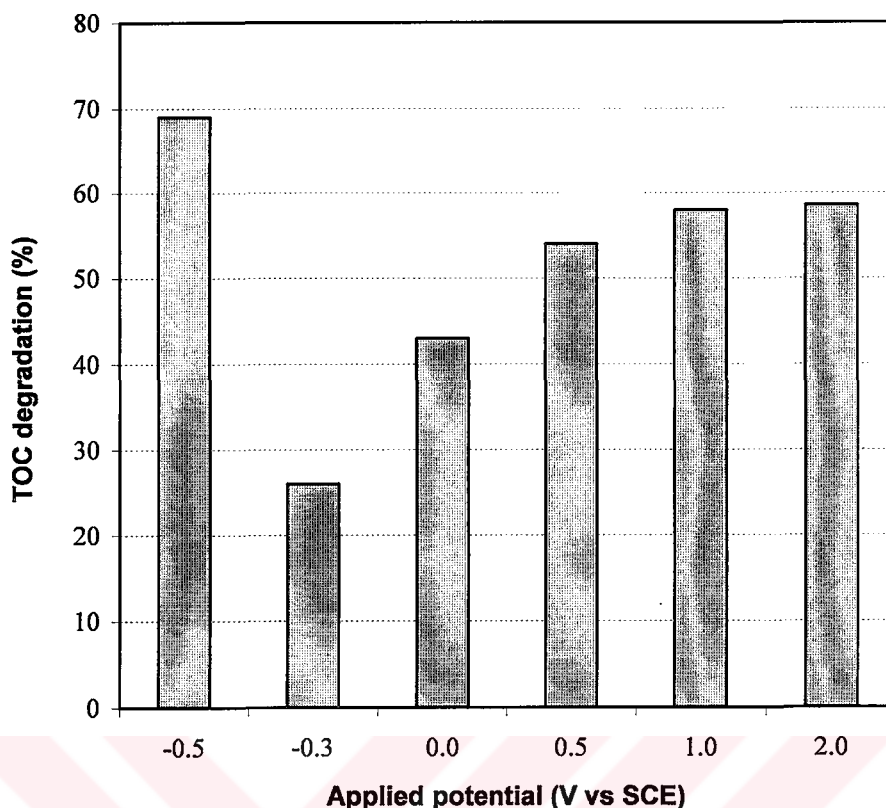


Figure 5.10. Effect of applied potential on the TOC degradation (UV intensity= 6 mWcm^{-2} , pH=6.0 and $t=6 \text{ hr}$).

5.3. Behavior of Bromide in the PEC Process

5.3.1. Blank experiments

Preliminary experiments were performed to ensure that there were no electrochemical or photocatalytic bromine generation and bromate formation in the process.

Photocatalysis: Photocatalytic (PC) experiment was carried out using TiO_2 electrode in 100 mL bromide test solution containing $1.0 \times 10^{-2} \text{ M NaBr}$ under illumination in the photoanode cell without any bias connections. Neither bromine generation nor bromate formation was observed in 45 minutes period.

Electrolysis: The electrochemical experiments were performed biasing the TiO_2 photoanode with 1 V vs SCE potential against perforated platinum foil used as counter electrode and a saturated calomel electrode (SCE) as a reference but in the absence of UV illumination. 100 mL test solution containing $1.0 \times 10^{-2} \text{ M NaBr}$ was used in each

compartment. Samples were taken from anode compartment for analytical measurements. None of bromine generation or bromate formation was determined in 45 minutes electrolysis period.

5.3.2. pH trends in the cells

Photogenerated electrons at surface of the semiconducting anode are driven toward the cathode by the action of the applied potential leaving behind a number of positive holes. Photogenerated electrons and holes take part in water splitting reactions and H^+ is produced on the photoanode and OH^- on the cathode as expressed with Eqs. 5.1-5.2.

The biasing of semiconductors with a external potential in PEC system decreases the recombination rate of holes and electrons. 1 V vs SCE potential is the optimum potential to achieve maximum photocurrent in the system. Hence, 1 V vs SCE external potential was used for all experiments performed. Figure 5.11 shows the trend in pH in a typically two-compartment reactor using a titanium dioxide thin-film electrode as photoanode and a platinum electrode as cathode under initial pH condition of 9.3.

An aqueous solution containing only 1.0×10^{-2} M NaBr was electrolyzed under illumination using 1.0 V SCE of biasing potential in a time-controlled experiment. Changes in the composition of the solutions were observed during the time. After 45 min, the pH reached a steady-state condition. That is about 3 in the anode and 11 in the cathode compartment. The changes in pH and pOH at the anode and cathode compartments respectively were found to be equal (1.0×10^{-3} M) after 45 minutes time period (Figure 5.11).

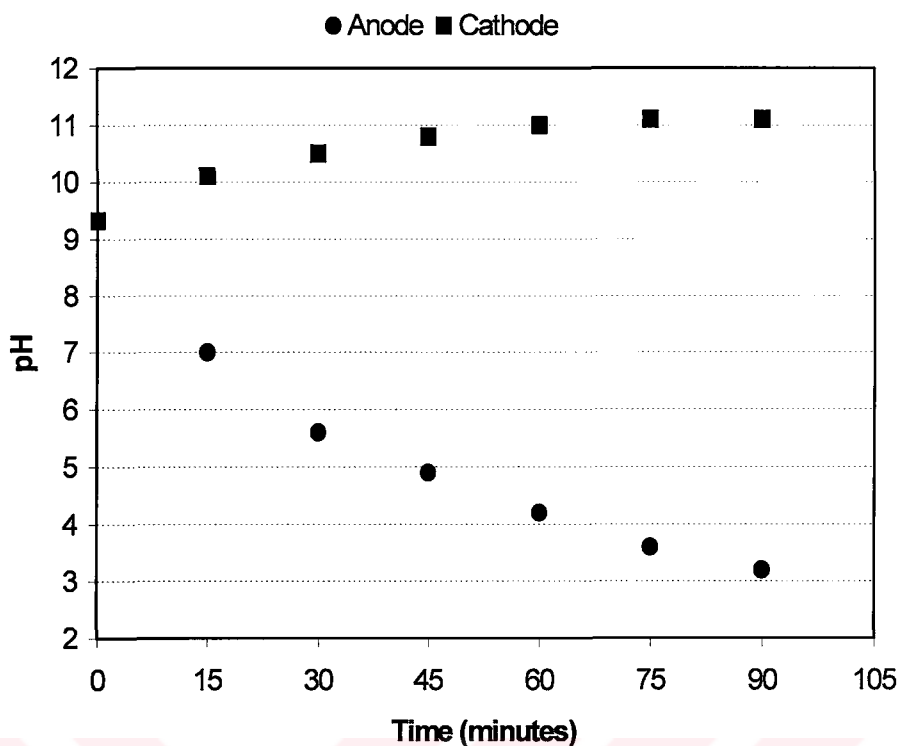


Figure 5.11. Trends of pH in the cathode and anode compartments (1.0×10^{-2} M NaBr solution at initial pH=9.33 and $E=1$ V vs. SCE).

5.3.3. Bromine generation

Bromide is a negatively charged ion and can be adsorbed on the positively charged photoanode where it may be subsequently oxidized by photogenerated holes yielding the oxidized product, bromine (Eq. 5.12). This Br_2 spontaneously reacts with water yielding aqueous bromine species (Br_2 , HOBr, and BrO^-) as described with Eqs. 5.13-5.14. Br_2 at $\text{pH} < 5.0$, HOBr at pH values between 5.0 and 8.7 and OBr^- at $\text{pH} > 8.7$ are the dominant aqueous bromine species in water (Fujihara et al., 1998).



Photolysis of bromine may also occur during the photoelectrocatalytic process. Bromide ions (Br^-), bromide radicals ($\text{Br}^\cdot$) and hydroxyl radicals may be formed

during the photolysis of HOBr and BrO⁻ (Buxton et al., 1988; Leitner and Dore, 1992; Nowell and Hoigne, 1992).



A solution containing 1.25×10^{-2} M NaBr at pH 3 was oxidized to determine the rate of bromine generation. The concentration of active bromine generated as a function of the time is shown in Figure 5.12. A constant concentration of 212 mgL⁻¹ of active bromine was obtained after 30 min of treatment. Although the bromine evolution depends on the photocurrent, the bromine photolysis side reaction seems to play a role in this process limiting the maximum concentration of bromine in solution in the same way as been noted in chlorine photolysis (Buxton et al., 1988; Leitner and Dore, 1992; Nowell and Hoigne, 1992). Accordingly, we conducted all subsequent investigations using 30 min as the reaction time.

It is also important to note that bromine is not generated using either the photocatalytic (i.e. only UV light) or the electrocatalytic (i.e. only applied potential) treatment under the experimental conditions reported in this study. Only by combining an external positive biasing potential with UV illumination can one successfully generate active bromine under the conditions employed in our studies.

5.3.4. Effect of pH

The adsorption of bromide on the TiO₂ surface is a necessary prerequisite for the oxidation of bromide to bromine species. Previous studies have shown that adsorption of species onto the TiO₂ surface depends both on the nature of the surface and the conditions of the solution. When $\text{pH} < \text{pH}_{\text{pzc}}$ the surface of TiO₂ is positively charged and this condition attracts negatively charged bromide ions. When pH is higher than the pH_{pzc} of TiO₂, the surface of TiO₂ is negatively charged causing electrostatic repulsion between negative surface of TiO₂ and bromide ions (Bekbölet, 1998; Zaroni et al., 2002).

PEC experiments were carried out to investigate the influence of pH on the aqueous bromine production and bromate formation. As displayed in Figure 5.13, even though

the pH_{pzc} of TiO_2 was found to be at pH 5.9 (Xu and Anderson, 1991), almost constant aqueous bromine production was achieved (around 300 mgL^{-1}) in the range of pH=4 and pH=6, but decreased sharply with increasing pH and there was no significant bromine formation at pH=11 in the solution. This result may cover the following points such that;

1. Since, positively applied potential improves the adsorption of negatively charged bromide and OH ions, almost constant bromine concentration was observed at pH=7.5. The influence of pH_{pzc} of TiO_2 becomes effective at higher pH values, resulting in decreased adsorption and thereby reduced oxidation of bromide to bromine.
2. On the other hand, photolysis of bromine (HOBr/OBr^-) occurs under UV illumination. Nowell and Hoigne (1992) have reported that the photolysis of OCl^- is higher than HOCl , which leads to a high rate of chlorine photolysis at pH>7. In an almost identical fashion, pK_a value of HOBr/OBr^- dissociation is 8.5 it means that OBr^- is the predominant bromine species in water at higher pH values (Tunesi and Anderson, 1991; Nowell and Hoigne, 1992). Consequently, the strong effect of pH on bromine formation at high pH values can be attributed in part to the photolysis of bromine in a process analogous to that of chlorine photolysis.
3. Lastly ozone- OBr^- reaction is faster than ozone- HOBr reaction (von Gunten and Hoigne, 1992; Özekin et al., 1998). Thus the decrease in bromine concentration in the photoanode at basic pH values may also be attributed to oxidation of OBr^- by ozone generated on the photoanode surface.

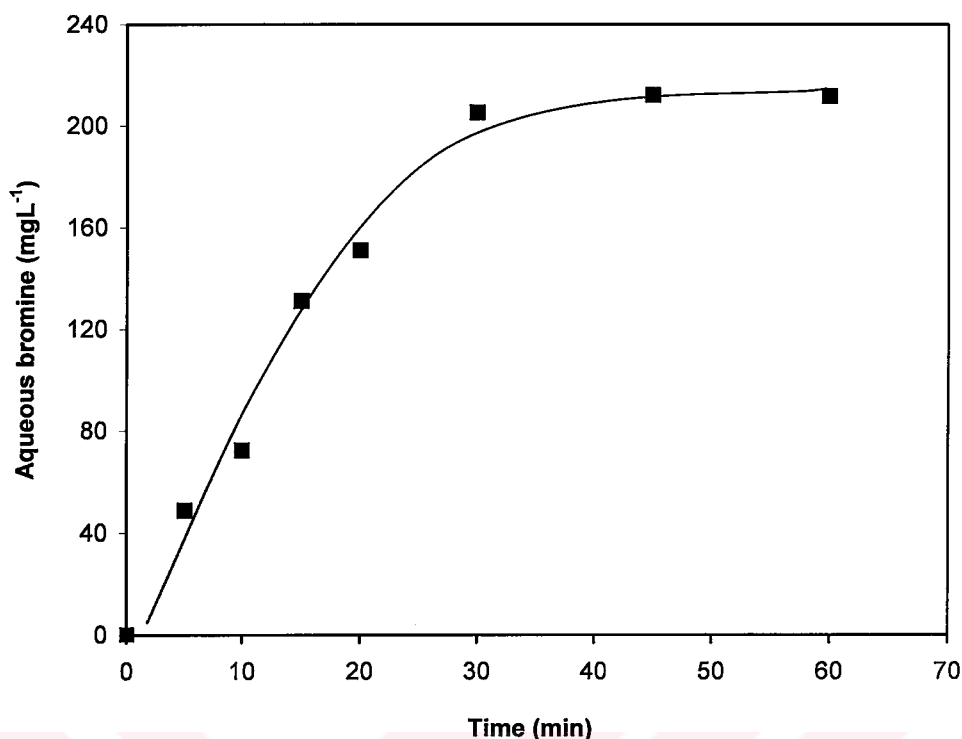


Figure 5.12. Aqueous bromine formation over TiO_2 thin-film electrode as a function of the time in 1.25×10^{-2} M NaBr solution (pH=3, $E = +1.0$ V vs SCE).

5.3.5. Effect of applied potential

The dependence of aqueous bromine production on the applied potential was investigated by employing the proposed method to oxidize 1.25×10^{-2} M bromide solutions with the potentials ranging from -0.4 V vs SCE to 2 V vs SCE (Figure 5.14). Aqueous bromine generation is not observed when the applied potential is -0.4 V vs SCE. This potential lies to the left of the flat band potential of TiO_2 ($E = -0.34$ V vs SCE and pH=3), which means that at this condition there is no current flow on the electrode because the electric field in the semiconducting material is null. However, at potentials positive to the flatband potential, aqueous bromine increased with the increasing in the applied potential until reaching a steady state condition at 1 V vs SCE. As can be seen in Figure 5.14, aqueous bromine can be produced even in potential as low as 0.0 V vs SCE.

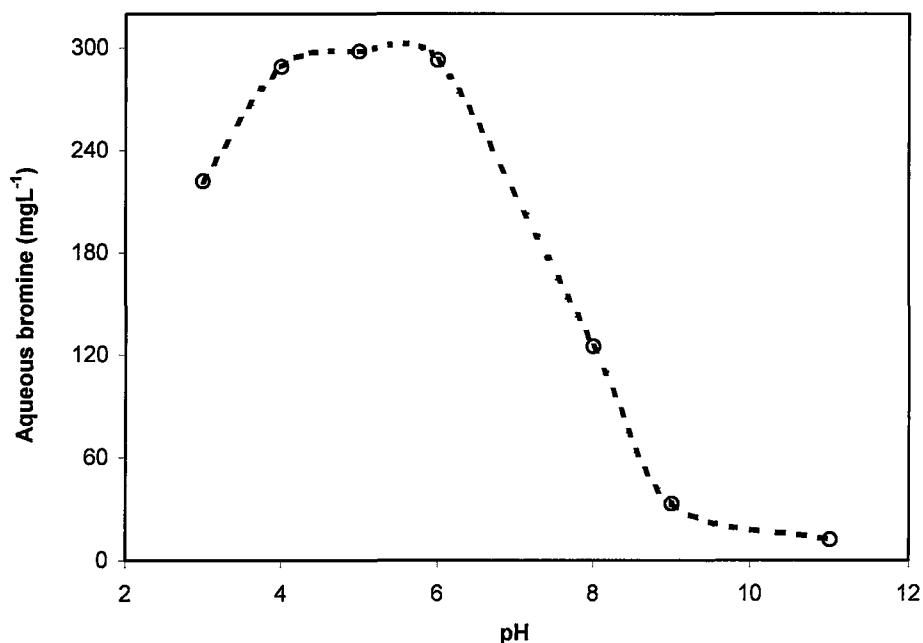


Figure 5.13. Aqueous bromine formation as a function of the pH in 1.25×10^{-2} M NaBr aqueous solution using a TiO_2 photoanode and a Pt cathode ($E = +1$ V vs. SCE and $t = 30$ minutes).

5.3.6. Effect of bromide concentration

The influence of initial concentration of NaBr on the photoelectrocatalytic bromine generation using a TiO_2 photoanode was investigated using different concentrations of NaBr at pH=3.0, under UV illumination and 1.0 V vs SCE of applied potential. The reaction took place over a 30 minute time frame. As shown in Figure 5.15, bromine production increased with an increase in bromide concentration up to a 10^{-2} M NaBr concentration. Further increases in bromide concentration did not promote any additional change in the rate of bromine generation, thereby showing that the rate of oxidation of bromide ion also depends on other factors such as the rate of charge transfer on the electrode surface.

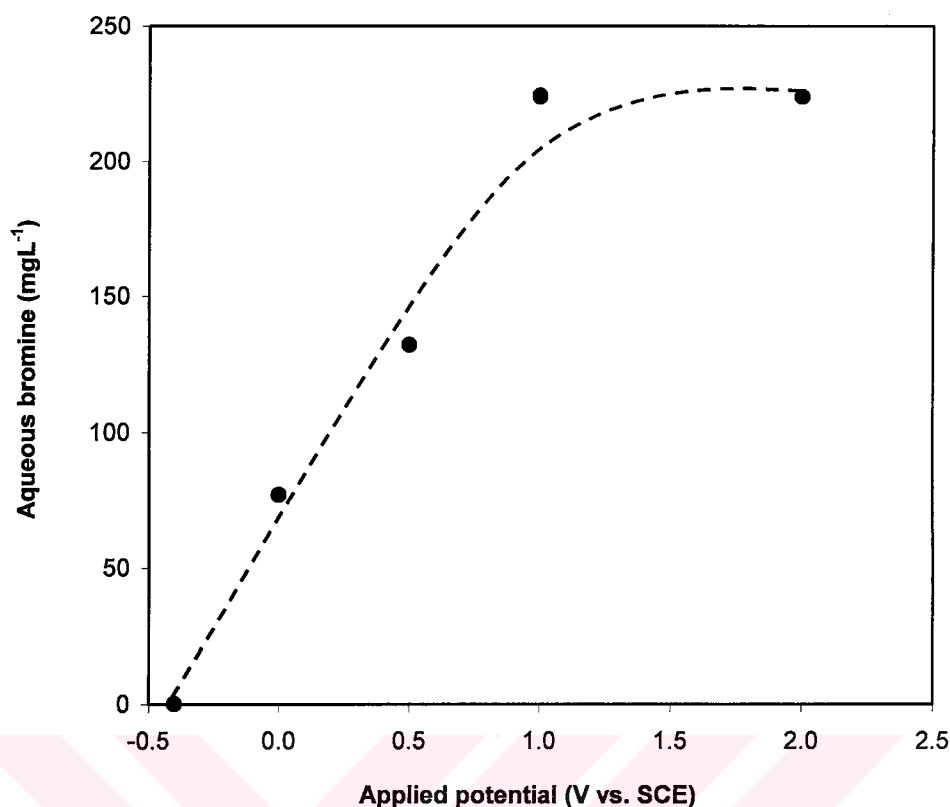


Figure 5.14. The effect of applied potential on aqueous bromine formation over a TiO_2 thin-film electrode ($\text{pH}=3.0$ and $t=30$ minutes).

5.3.7. Effect of UV intensity

As generation of hole or photocurrent in the PEC process is a function of UV intensity, increasing UV intensity resulted in a steady increase in the photocurrent and also bromine generation. Upon application of UV intensity conditions of $I_0 = 5.7 \text{ mWcm}^{-2}$ and 100 mWcm^{-2} , 25 mgL^{-1} and 234 mgL^{-1} bromine generation were achieved respectively (Figure 5.16).

5.3.8. Photocurrent in the process

As presented in the second chapter, upon the application of a negative external potential a reduction current occurs across the interface in the electrochemical process, thus the oxidized species are converted to the reduced species. On the other hand when a positive potential is applied the current direction is reversed and anodic current occurs across interface.

In the photocatalytic process, the current, called photocurrent is created by photon energy. If a semiconductor is illuminated by photon energy greater than the band gap energy of semiconductor ($E_{hv} > E_{bg}$) an electron can be excited from the valence band to the conduction band leaving holes in the valence band. Thus greater photon energy resulted in higher photocurrent and bromine generation in the PEC process.

In the PEC process very small external potential was applied to decrease the recombination of holes and electrons. In the absence of light no photocurrent was observed in the process under the potential conditions between 0.0-2.0 V vs SCE. Upon illumination of photocathode, photocurrent occurred and reached a steady-state condition in a minute. As can be seen in Figure 5.17, photocurrent increased with applied external potential but after 1.0 V vs SCE potential there was no increase in the photocurrent staying almost same. Oxidation and reduction reactions in the PEC process are the functions of photogenerated electrons and holes, thus bromine generation increased with the higher photocurrent.

On the other hand, negatively charged electrolyte is the another important factor to increase photocurrent via giving electron by reacting with holes. Thus, upon increasing the concentration of sodium bromide up to 1.5×10^{-4} M increased the photocurrent resulting higher bromine generation (Figure 5.15 and 5.18).

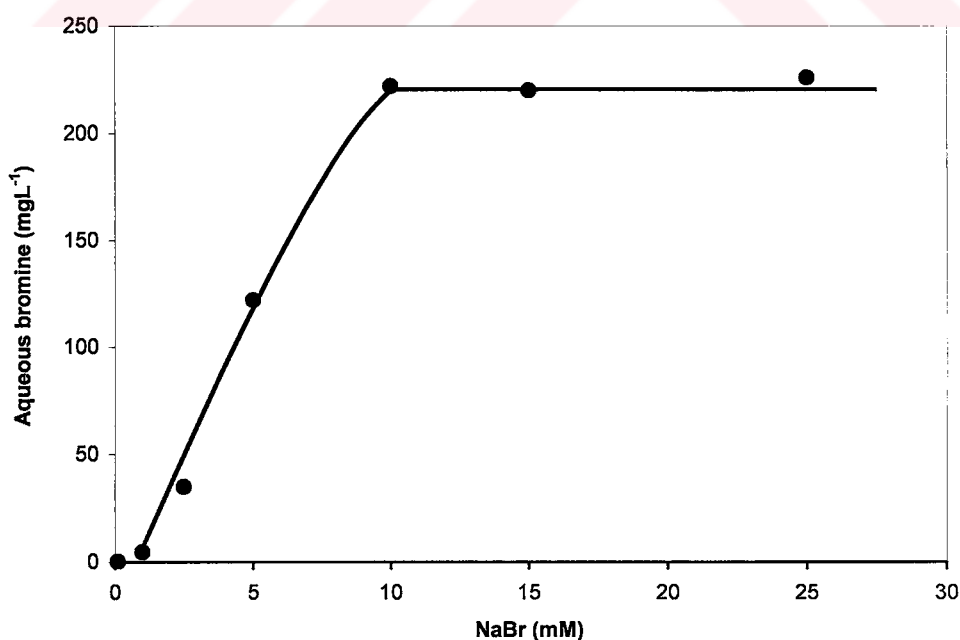


Figure 5.15. The effect of bromide concentration on aqueous bromine formation over a TiO_2 thin-film electrode ($E=+1$ V vs. SCE, $\text{pH}=3.0$ and $t=30$ minutes).

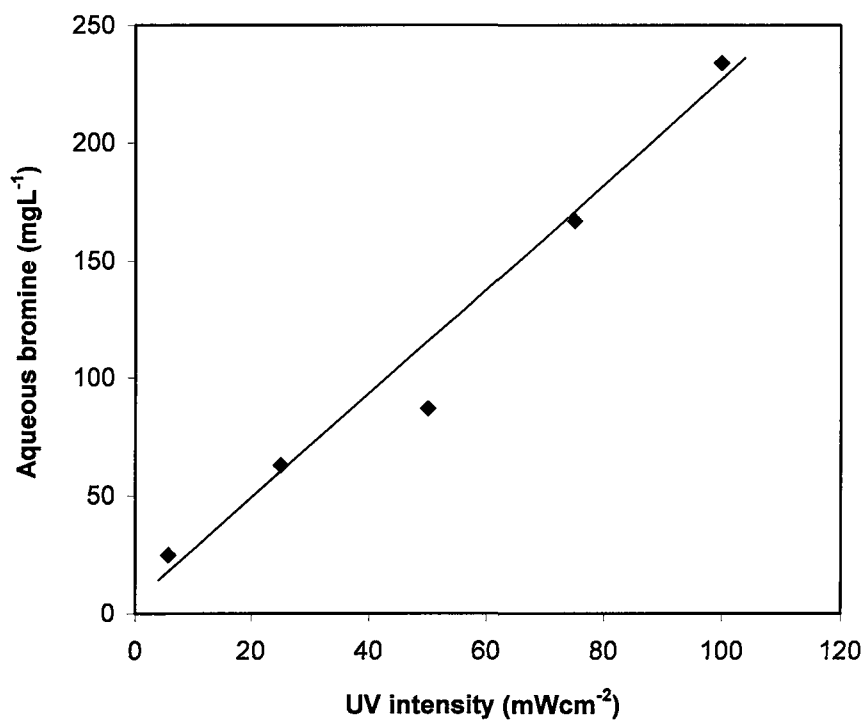


Figure 5.16. Effect of UV intensity on the bromine generation ($E=1.0$ V vs SCE).

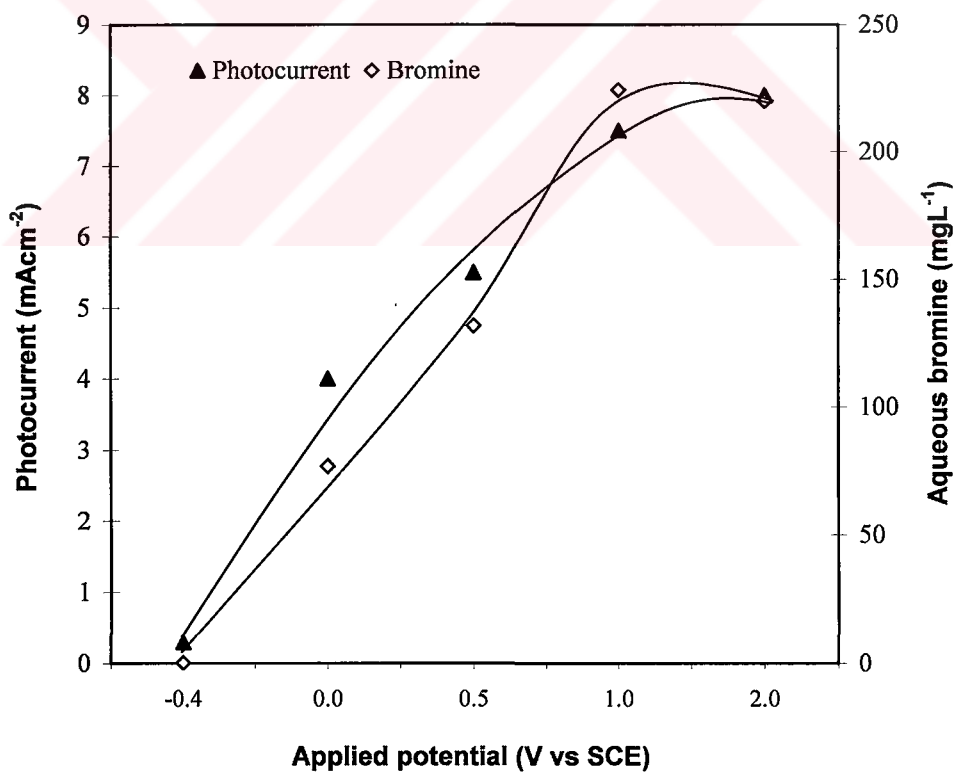


Figure 5.17. Photocurrent and bromine generation according to the applied potential

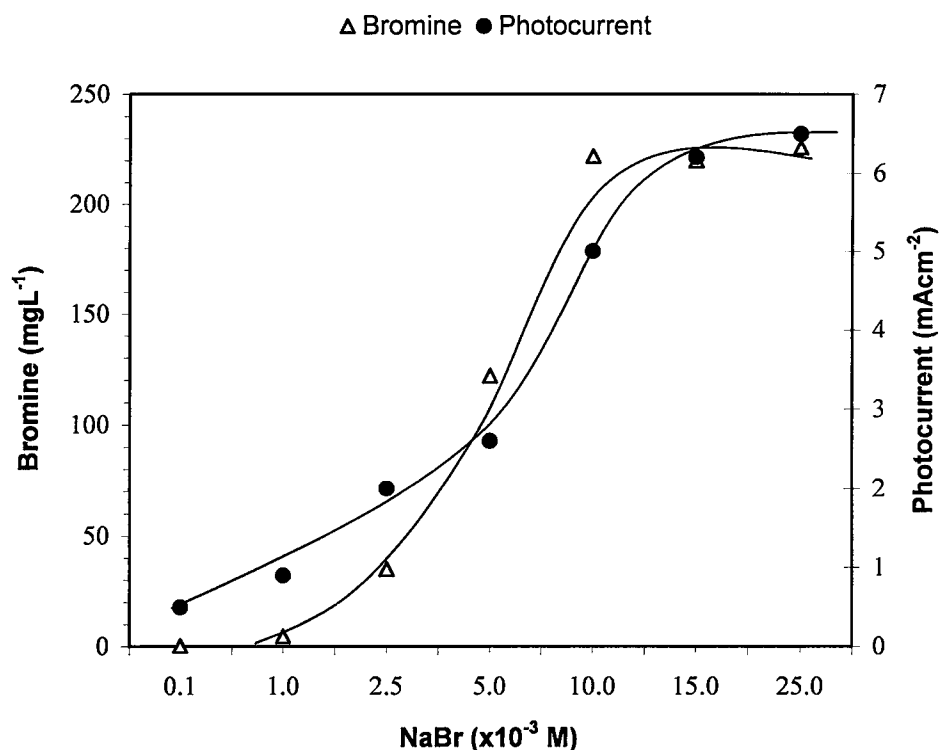


Figure 5.18. Photocurrent and bromine generation according to the bromide concentration

5.4. Bromate Formations/Effects of Variables

5.4.1. Bromate formation

To investigate photoanodic bromate formation in the PEC system besides bromine, the amount of bromate was also monitored as a function of time during the experiments which were performed at the conditions of applied potential of +1.0 V to bias the photoanode, 5.7 mW cm^{-2} UV intensity and $1.0 \times 10^{-2} \text{ M}$ NaBr solution at pH 6. Bromate formation was observed after 15 minutes and increased linearly with time, while aqueous bromine production reached a steady-state level in 45 minutes. No steady state condition for bromate formation could be attained during the reaction period of 120 minutes (Figure 5.19). Bromate formation was attributed to the ozone generation (Eq. 5.17, 5.18) and ozone-OH radical-bromide interactions via generated ozone (Eq. 5.19, 5.29) that may take place on the photoanode as explained below;

Beyond water splitting and bromide reactions, the adsorbed hydroxide ion (OH_{ads}) may yield anodic oxygen species on the photoanode then they may play a role for the

formation of ozone (O₃) in the photoanode cell, as illustrated by following pathway (Silve et al., 2003);



Ozone-bromide reactions are well documented in the literature (Haag and Hoigne, 1984; Amy et al., 1993; von Gunten, 2003). According to the presented data bromate formation occurs via both direct (and/or molecular ozone) and indirect (and/or radical) oxidation pathways. Haag and Hoigne (1984) described direct ozonation (and/or molecular ozone) pathway as follows;



It is stated that very complex indirect pathways have significant effect on the bromate formation. The results of present studies indicate that OH[•] radicals play a dominant role for bromate formation as described by the following reactions;



On the other hand, bromate may also be formed by anodic oxidation of hypobromite (OBr^-) and/or hypobromous acid (HOBr), generated in the PEC process as similar with chlorate formation in the electrochemical process as given follows (Czarnetzki and Janssen, 1991).

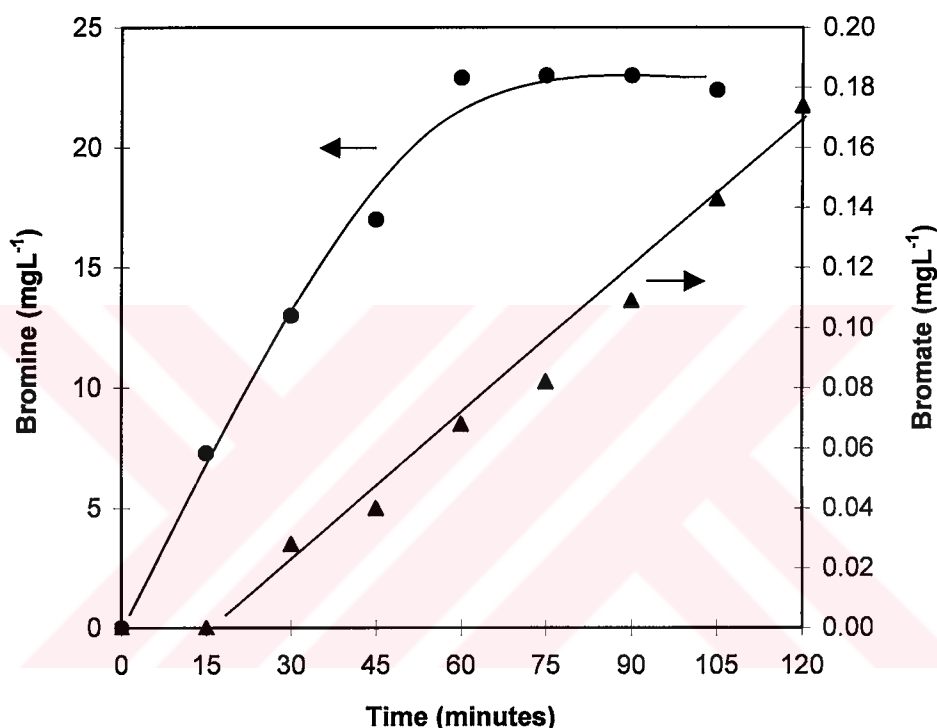
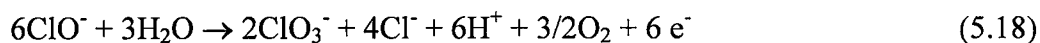
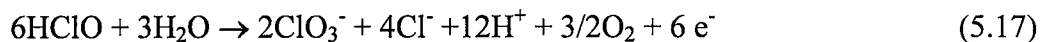


Figure 5.19. Bromine and bromate formation in PEC process (pH=6, E=1 V vs SCE, TiO_2 coated photoanode, Pt. Cathode).

5.4.2. Influence of pH on bromate formation

pH not only changes the surface charge of TiO_2 , it also affects the species distribution profile of HOBr . As a result, HOBr can only be present alone at pH values up to 6.0 and OBr^- can only present at pH value higher than 9.0. However HOBr reacts with ozone resulting in bromate formation, however the reaction rate of HOBr^- ozone is very low with respect to that of OBr^- -ozone. In order to investigate the influence of pH on bromate formation, PEC experiments were carried out at different constant pH

values. No bromate formation was observed at pH values less than 6.0. This may be explained by the photolysis of bromate as follows (Farkas and Klain, 1948).



Bromate formation was observed at pH 6.0 and increased rapidly with increasing pH up to pH 8.5. The rapid increase in bromate formation is attributed to high OBr^- and $\text{OH}^\cdot$ radical concentrations under pH conditions of ≥ 6.0 . Due to the low bromine generation, bromate formation slightly decreased after pH values higher than 8.5 (Figure 5.20).

Bromate formation was not observed under low pH conditions. Also, no bromate formation was determined under basic pH values up to 15 minutes reaction time period. On the other hand, reduction reactions yield OH^- and oxidation reactions gives H^+ ions. Hence, the separation of hole and electron reactions results in decreased pH conditions at the photoanode. Thus, replicate experiments were also performed at different initial pH values without adjusting pH during experiments. It was observed that there was no bromate formation at initial pH values < 9.0 (Table 5.7).

5.4.3. Effect of oxygen

To investigate the effect of oxygen on the bromate formation, PEC experiment was carried out under the experimental condition of 1.0×10^{-2} M NaBr at pH=6.0, 1 V vs SCE applied potential and 5.7 mWcm^{-2} UV intensity. Oxygen was bubbled through the solution in 60 minutes and bromate formation was monitored over time. As can be seen from Figure 5.21, bromate formation increased by the utilization of oxygen in the process. Second experiment was performed under the same experiment conditions in the presence of nitrogen. 86% decrease in bromate formation was observed by using nitrogen. As expected, results showed that oxygen plays an important role for the bromate formation in the PEC process.

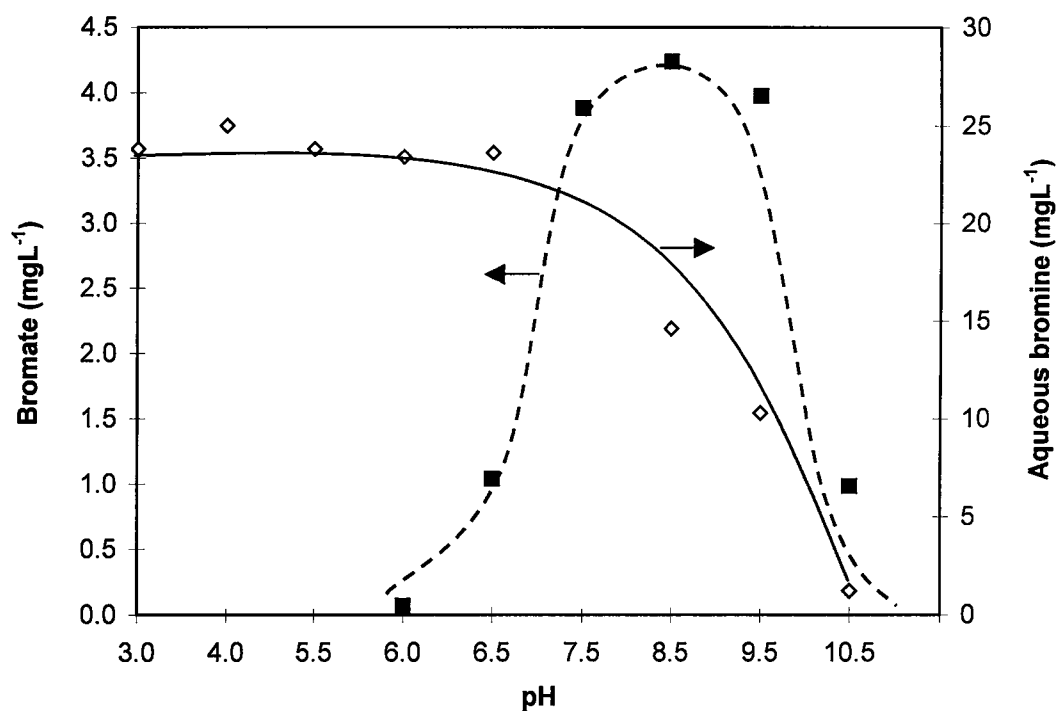


Figure 5.20. Effect of pH on the bromate formation in PEC process (TiO₂ coated photoanode, Pt. cathode, 1.0x10⁻² M NaBr, UV intensity=5.7 mW.cm⁻², E=1 V vs SCE, t = 45 minutes).

Table 5.7. Bromate formation under controlled and initial pH values

pH	Bromate (mgL ⁻¹) (Under controlled pH)	Bromate (mgL ⁻¹) (At initial pH)
5.0	n.d.	n.d.
5.5	n.d.	n.d.
6.0	0.068	n.d.
6.5	1.04	n.d.
7.5	3.88	0.005
8.5	4.24	0.018
9.5	4.00	0.186
10.0	3.08	2.20
10.5	0.98	2.45

n.d.; not detected

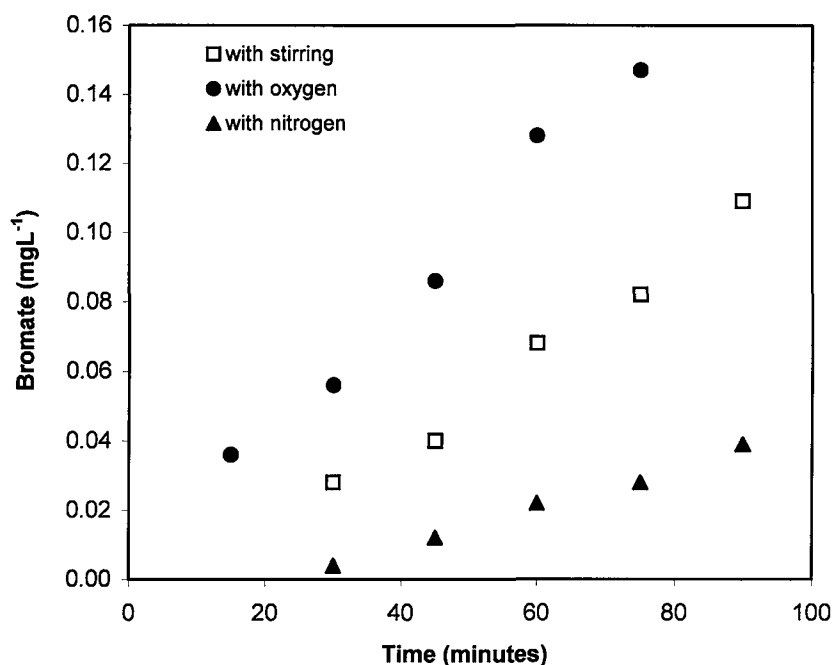


Figure 5.21. Effect of oxygen on the bromate formation ($E=1$ V vs SCE; $\text{pH}=6.0$, $t=60$ minutes and $\text{UV intensity}=5.7 \text{ mW.cm}^{-2}$).

5.5. Catalytic Ozonation

Comparative studies were carried out applying ozonation and catalytic ozonation processes to investigate the effect of catalytic ozonation on the formation of bromate in bromide containing MQ-water test solution.

5.5.1. Ozone decomposition

In order to determine the transfer of ozone in ozonation and catalytic ozonation system, the test solution containing the bromide concentration of $700 \mu\text{gL}^{-1}$ was prepared with milli-Q water and its pH was adjusted to 8.0. An ozone experiment was carried out passing the ozone dose of $10.5 \text{ mgL}^{-1}\text{min}^{-1}$ into the test solution and the transferred ozone was monitored as a function of time. Catalytic ozonation was performed loading $1.0 \text{ gL}^{-1} \text{ TiO}_2$ under the same condition with ozonation experiment.

As can be seen in Figure 5.22, the transferred ozone in catalytic process was insignificantly higher than that in merely ozone process in 15 minutes and it was almost the same in both processes after 15 minutes. Thus, both applied and transferred ozone were used to compare two processes in further studies.

5.5.2. Bromate formation

Preliminary experiment was performed to determine possible adsorption of bromide and bromate on TiO_2 surface at $\text{pH}=8.0$. For that purpose, 1 grL^{-1} TiO_2 was loaded in the test solution containing $50 \text{ }\mu\text{gL}^{-1}$ bromate and $700 \text{ }\mu\text{gL}^{-1}$ bromide and air passed from solution in 30 minutes, then the solution was filtered through $0.45 \text{ }\mu\text{m}$ Millipore membrane. Results showed that the decrease in both bromide and bromate in catalytic ozonation by adsorption was insignificant ($<5\%$). For comparison of merely ozone and catalytic ozone processes, pH condition of 8 was used in most of experiments to avoid the adsorption of bromide and bromate on the catalyst surface.

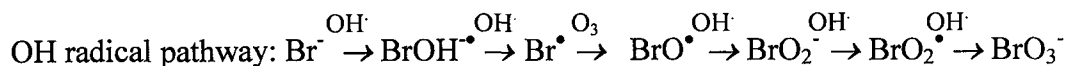
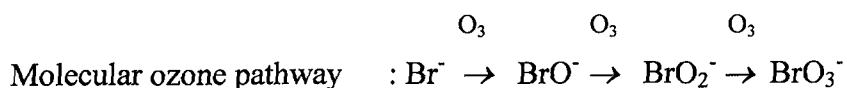
To compare ozonation and catalytic process with respect to the bromate formation, ozone dose of $10.5 \text{ mgL}^{-1}\text{min}^{-1}$ was passed from the test solution ($700 \text{ }\mu\text{gL}^{-1}$ bromide at $\text{pH}=8.0$) and bromate formation was determined over time. As presented in Figure 5.23 bromate formation in the catalytic process loaded with 1.0 gL^{-1} TiO_2 was 50-90% lower than that in the ozone process. Significant decreased was observed in 15 minutes and $236 \text{ }\mu\text{gL}^{-1}$ in ozonation process decreased to $36 \text{ }\mu\text{gL}^{-1}$ with the presence of 1 gL^{-1} TiO_2 . The increase in bromate formation in 15 minutes was very low in catalytic ozonation process, but it increased sharply after 15 minutes while, in ozonation process, the bromate formation increased steadily during 30 minutes of run time.

The complex chemistry of aqueous ozone is explained in detail in literature (Alder and Hill, 1950; Kilpatrick et al., 1956; Rankas et al., 1964; Gurol and Singer, 1982). Primary steps involve the decomposition of the ozone via a chain reaction mechanism resulting in the production of reactive hydroxyl free radical species. The reaction of hydroxyl ion with ozone produces one superoxide anion radical ($\text{O}_2^{\bullet-}$) and one hydroxyl radical ($\text{HO}_2^{\bullet}$). Addition of organic solutes can result in either:

1. The direct consumption of the ozone before the chain reaction begins,
2. Production of the ozonide anion radicals ($\text{O}_3^{\bullet-}$) by electron transfer.

Upon protonation within the aqueous system, the ozonide anion decomposes into hydroxyl radical, which is a non-selective oxidizing agent, and plays an important role for the formation of bromate in bromide-containing water. The following

reactions scheme briefly explains ozone-hydroxyl-bromide interaction and bromate formation.



The chemical reaction involved during catalytic ozonation is still unidentified. However, a previous study (Paillard et al., 1991) has demonstrated that a hydroxyl radical oxidation pathway does not necessarily occur in catalytic ozonation. Afterward, Bulanin et al. (1994) reported that ozone adsorption onto oxide surfaces results in the production of surface bound $\text{O}^\bullet$ radicals. In aqueous solution, $\text{O}^\bullet$ radicals react with bromide and brominated by-products as in the following reactions.



The formations of $\text{BrOH}^\bullet$, $\text{Br}^\bullet$, $\text{BrO}^\bullet$, BrO_2^- and $\text{BrO}_2^\bullet$ via OH radical pathway play critical role in bromate formation. However there are still many questions about chemical reactions in catalytic ozonation, it is known that bromide reaction rate with $\text{O}^\bullet$ radical ($k = 2.2 \times 10^8 \text{ L mol}^{-1} \text{s}^{-1}$) is about 100 fold slower than that with OH radical ($k=1.1 \times 10^{10} \text{ L mol}^{-1} \text{s}^{-1}$). This may be one of the reasons for lower bromate formation in the catalytic process.

5.5.3. Effect of ozone dose

In order to determine the effect of ozone dosage on the bromate formation in catalytic ozonation, four different ozone doses $18.0 \text{ mgL}^{-1}\text{min}^{-1}$, $10.5 \text{ mgL}^{-1}\text{min}^{-1}$, $6.5 \text{ mgL}^{-1}\text{min}^{-1}$ and $3.2 \text{ mgL}^{-1}\text{min}^{-1}$ were applied into the semi-batch reactor containing $1.0 \text{ grL}^{-1} \text{ TiO}_2$ and $700 \text{ }\mu\text{gL}^{-1}$ bromide solution at pH 8.5.

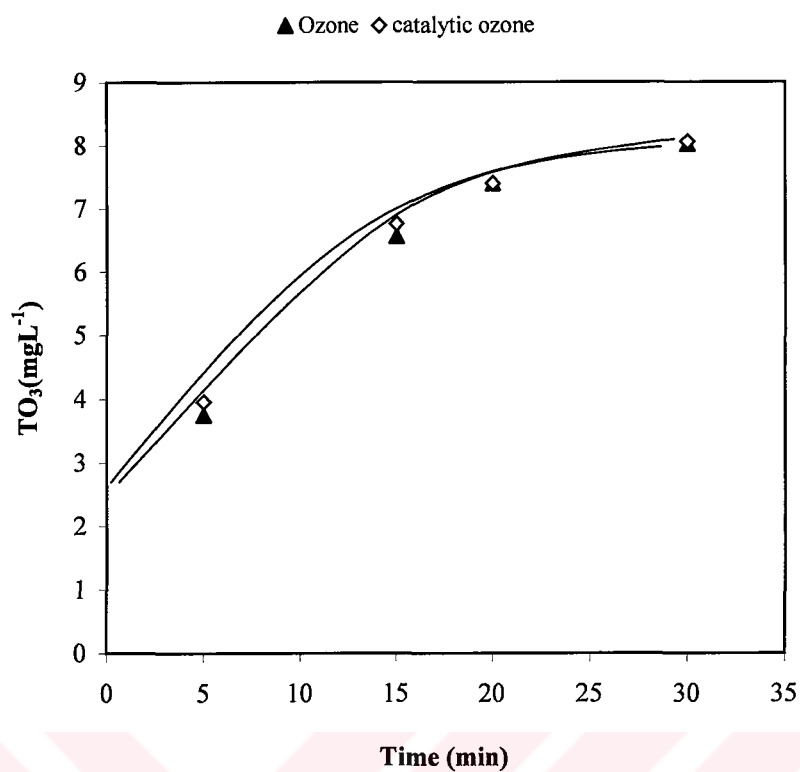


Figure 5.22. Transferred ozone in ozonation and catalytic ozonation processes in $700 \mu\text{gL}^{-1} \text{Br}^-$ solution at $\text{pH}=8.5$.

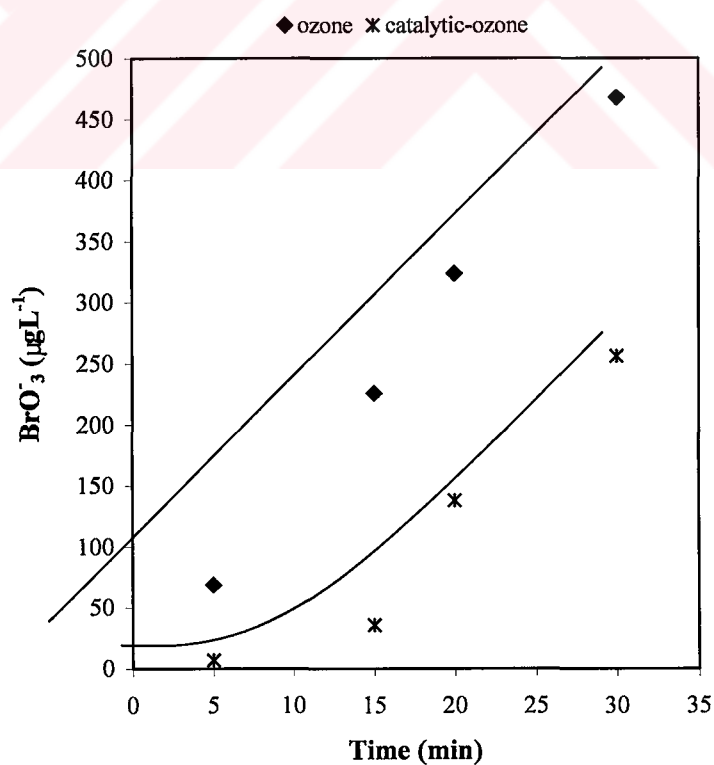
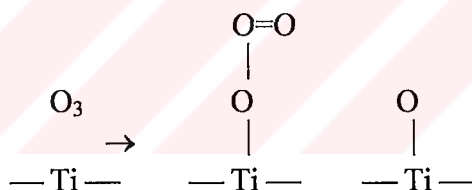


Figure 5.23. Bromate formation in ozonation and catalytic ozonation processes in $700 \mu\text{gL}^{-1} \text{Br}^-$ solution at $\text{pH}=8.0$.

Figure 5.24 shows the effect of three different ozone doses on the bromate formation in catalytic process. The formation of bromate as a function of time was linear at high ozone dose ($18 \text{ mgL}^{-1}\text{min}^{-1}$), but it exhibited a nonlinear trend at lower ozone concentrations. It decreased with decreasing ozone dose and no bromate formation was observed in 60 minutes in catalytic ozonation system under applied ozone dose of $3.2 \text{ mgL}^{-1}\text{min}^{-1}$. High ozone concentration introduced into semi-batch system provides significantly higher transferred ozone concentrations (Minear and Amy, 1996). Thus, bromate formation via ozone pathway increases with the transferred or applied ozone dose. The obtained results indicates that, at high ozone doses, ozone pathway is dominant for the formation of bromate, and thus, other possible pathways which possibly control bromate formation in catalytic process, are insignificant to reduce bromate formation

On the other hand, Bulanin et al. (1995) performed an experimental study for the adsorption of ozone on TiO_2 surface. They reported that ozone adsorption on the stronger Lewis sites should lead to a further distortion of the molecule until it becomes unstable into a surface oxygen atom, which remains attached to the titanium ion:



It may indicate that the ratio of applied ozone (AO_3)/ total surface area (TSA) of catalyst or transferred ozone (TO_3)/TSA increases ozone conversion to $\text{O}^\bullet$, $\text{O}_3^\bullet$, $\text{O}_2^\bullet$ est. As a result, the lower ozone doses applied in semi-batch reactor resulted in the lower bromate formation in the catalytic ozonation system.

5.5.4. Effect of TiO_2 loading

In order to find optimum TiO_2 loading for the bromate control, different amount of TiO_2 concentrations were used in a semi-batch reactor. A constant ozone dose of $18 \text{ mgL}^{-1}\text{min}^{-1}$ and reaction time of 20 minutes were applied continuously to the solution containing $700 \text{ }\mu\text{gL}^{-1}$ bromide at pH 8.0.

Figure 5.25 demonstrates the effect of various TiO_2 loading on the bromate formation. In the absence of TiO_2 about $324 \mu\text{gL}^{-1}$, bromate formation was observed. Increasing TiO_2 loading decreased bromate formation to $138 \mu\text{gL}^{-1}$. Bromate formation decreased with increasing TiO_2 loading and over 90% decrease in bromate formation was obtained at the optimum TiO_2 loading (2.5 mgL^{-1}).

5.5.6. Effect of the type of TiO_2

Two different TiO_2 specimens, Degussa P25 and Merck were used to compare their effect on the formation of bromate in catalytic ozonation process. The same amount (1.0 mgL^{-1}) of Degussa P25 and Merck type TiO_2 were used under identical experimental conditions (Br^- $700 \mu\text{gL}^{-1}$, pH 8.0, applied ozone concentration $10.5 \text{ mgL}^{-1}\text{min}^{-1}$) and bromate formation was monitored over time. As can be seen in Figure 5.26, Degussa P25 resulted in significantly lower bromate formation than Merck type TiO_2 . Results were attributed the higher surface area of Degussa P25.

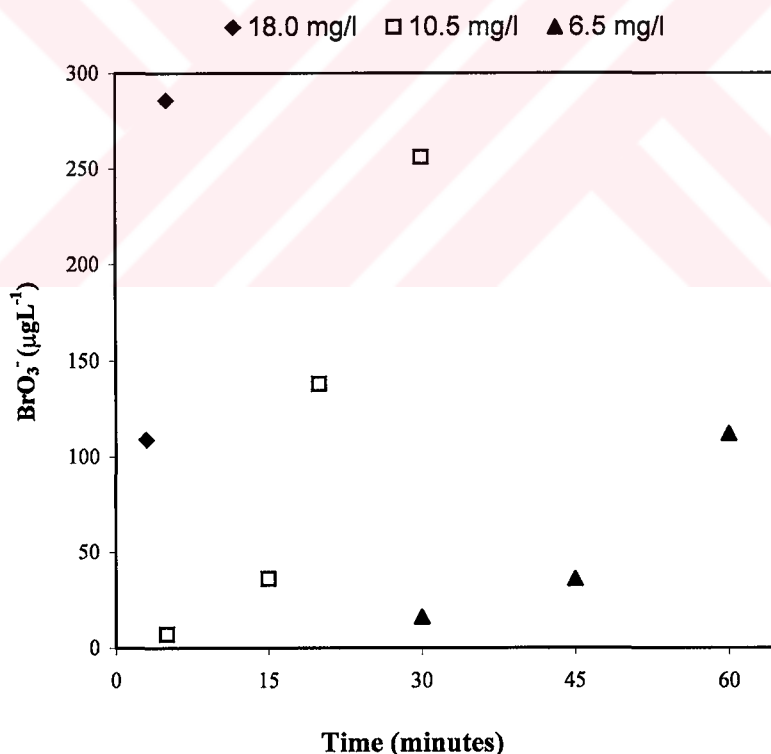


Figure 5.24. Effect of ozone dose on the formation of bromate in catalytic ozonation (TiO_2 : 1.0 gL^{-1} , Br^- : $700 \mu\text{gL}^{-1}$, pH= 8.0).

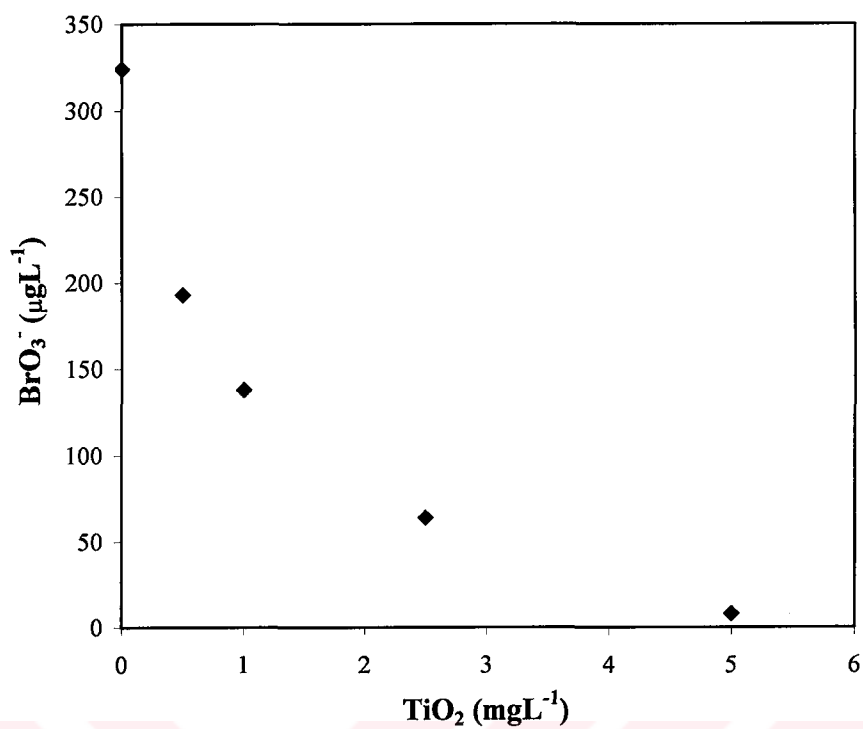


Figure 5.25. Effect of TiO₂ loading on the bromate formation

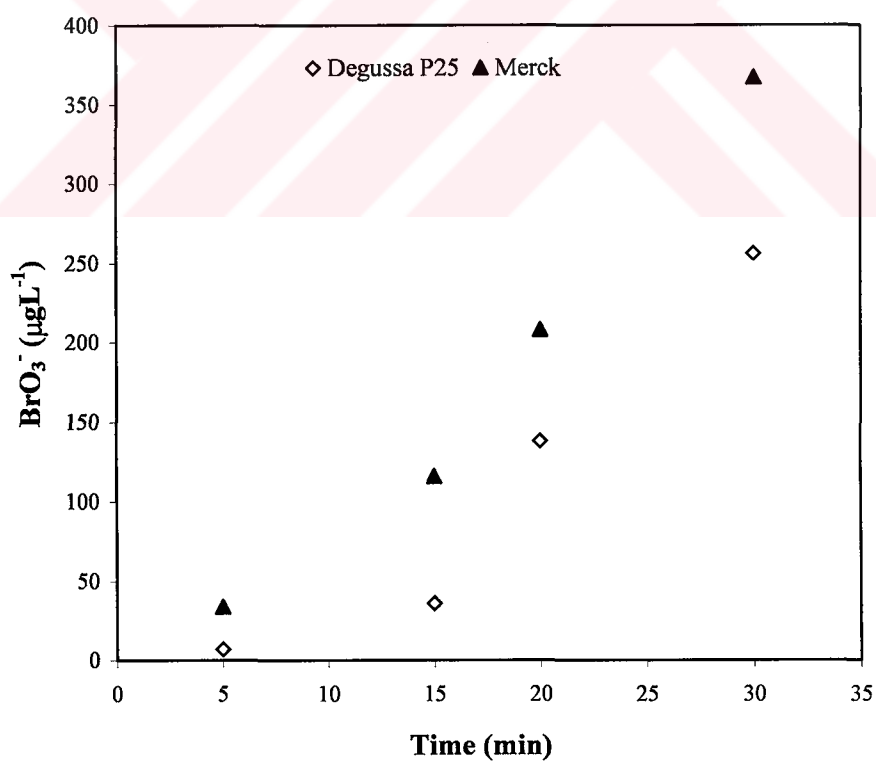


Figure 5.26. Comparison of Degussa and Merck type TiO₂ with respect to bromate formation.

5.6. Application of Catalytic Ozonation

5.6.1. Characterization of drinking water

Water samples were taken from the Büyükçekmece lake (BÇL)/İstanbul, which has high total organic carbon (TOC) and bromide content.

Table 5.7. Characterization of BÇL water

Parametre	
TOC (mgL ⁻¹)	5.5
pH	8.3
UV ₂₅₄ (abs)	0.012
Br ⁻ , (µg ⁻¹)	205.8
Cl ⁻ , mgL ⁻¹	57
Alkalinity, mg CaCO ₃ L ⁻¹	175
Ammonia, mgL ⁻¹	<0.05
Temperature, °C	20

5.6.2. Ozone demand of BÇL water

In order to determine ozone demand of BÇL water, the ozone dose of 22 mgL⁻¹min⁻¹ was applied into the semi-batch reactor containing BÇL water. Experiments were carried out at different pH values of 6.1, 7.5 and 8.4. As can be seen in Figure 5.27, the transferred ozone amounts (TO₃) increased with increasing pH values. The transferred ozone amounts were found to be 7.56 mgL⁻¹, 8.85 mgL⁻¹ and 11.42 mgL⁻¹ under pH conditions of 6.1, 7.5 and 8.5 respectively in 3 minutes reaction time period. Ozone transfer rates were almost the same in few minutes at the beginning (about 2.5 mgL⁻¹min⁻¹ at pH, 2.9 mgL⁻¹min⁻¹ and 3.9 mgL⁻¹min⁻¹ for pH values of 6.1, 7.5 and 8.4 respectively), and then decreased over time (Figure 5.28).

A complementary experiment was also carried out using BÇL water at pH 8.4 to determine TO₃ in the catalytic ozonation system in the presence of 1.0 mgL⁻¹ TiO₂. Comparatively, TO₃ was slightly higher than merely ozone in three minutes but the amounts of TO₃ were found to be equal in both systems in longer time period (Figure 5.29).

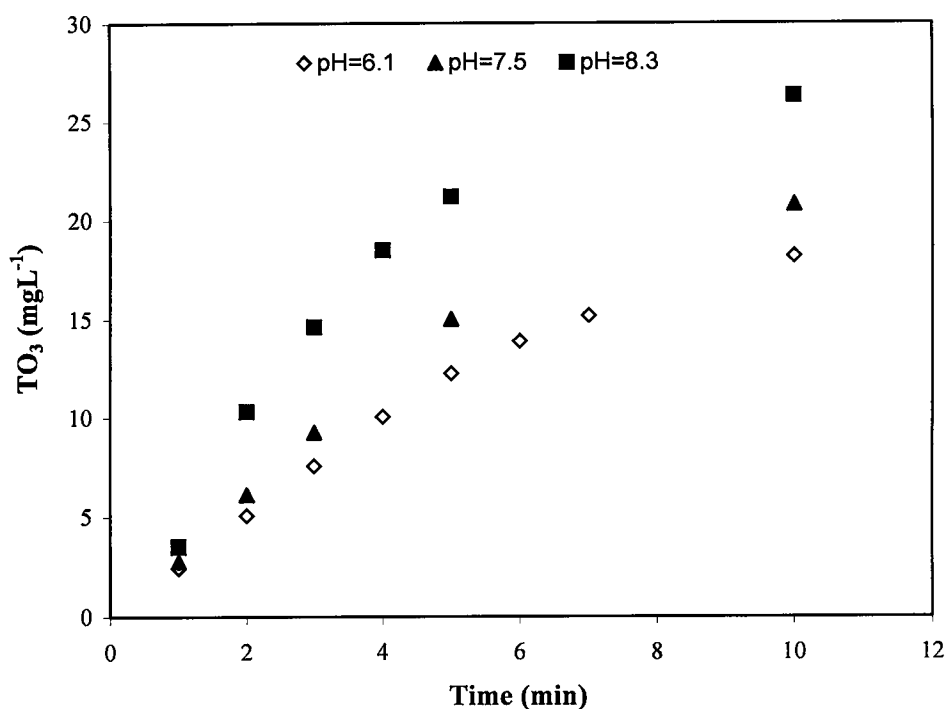


Figure 5.27. Transferred ozone at different pH values

5.6.3. Bromate Formation

In order to compare ozone and catalytic ozone systems, two experiments were conducted under $22 \text{ mgL}^{-1}\text{min}^{-1}$ ozone dose for bromate formation pathways in BCL water. As can be seen in Figure 5.30, first bromate formation was observed around 4.3 mgL^{-1} TO_3 concentrations and increased over time, reaching to $58 \text{ }\mu\text{gL}^{-1}$ at TO_3 concentration of 12.2 mgL^{-1} . On the other hand, bromate formation was around $7\text{-}12 \text{ }\mu\text{gL}^{-1}$ up to 10.5 mgL^{-1} TO_3 concentrations after the transferred ozone value of 10.5 mgL^{-1} bromate increased rapidly.

Bromide ion reacts with both molecular ozone and hydroxyl radical and can influence ozone decomposition rates and the amount of bromate formation. Thus increasing bromide, hydroxyl radicals and ozone concentrations result in an increase in bromate formation. As mentioned in 5.5.2 section, it has been demonstrated that a hydroxyl radical oxidation pathway does not occur in catalytic ozonation (Paillard et al., 1991). Instead, ozone adsorption on the catalyst surface produces surface bound $\text{O}^{\bullet-}$ radicals (Bulanin et al., 1994) and its reaction with bromide ion is slower than hydroxyl-bromide reaction. Results indicate that different ozone-bromide-radicals interaction may occur in the catalytic process.

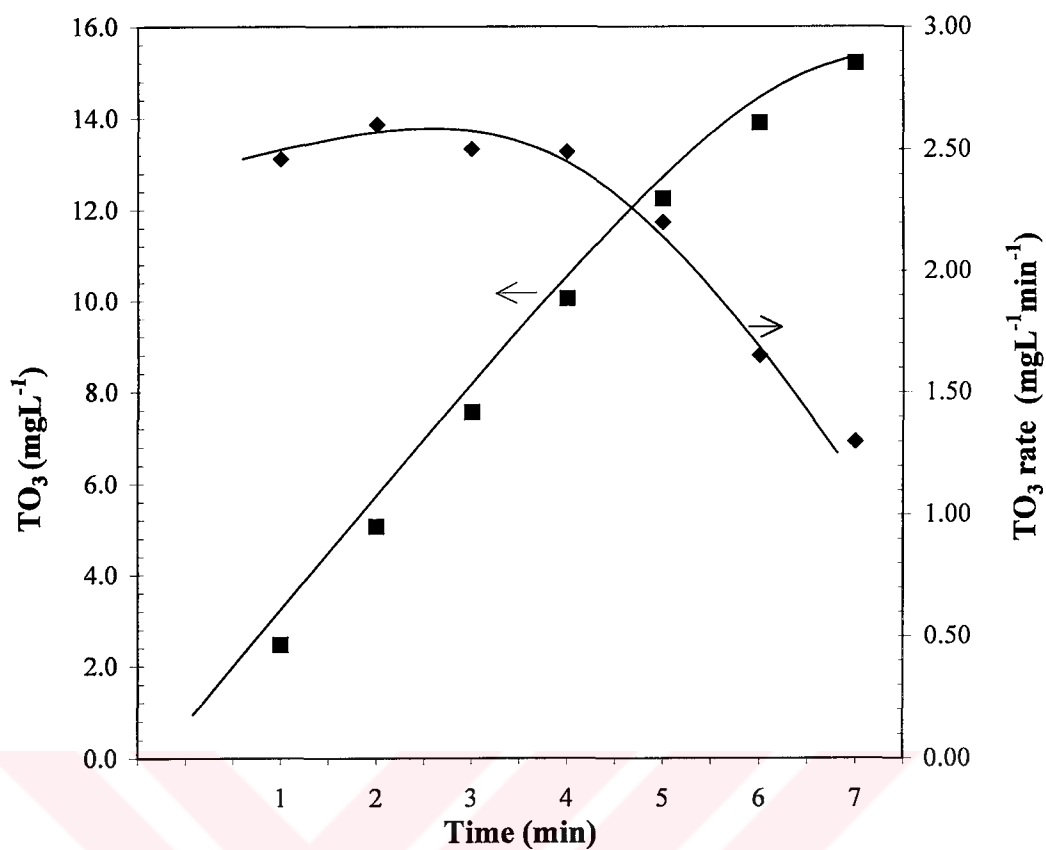


Figure 5.28. TO₃ in BCL water and its rate in ozonation system.

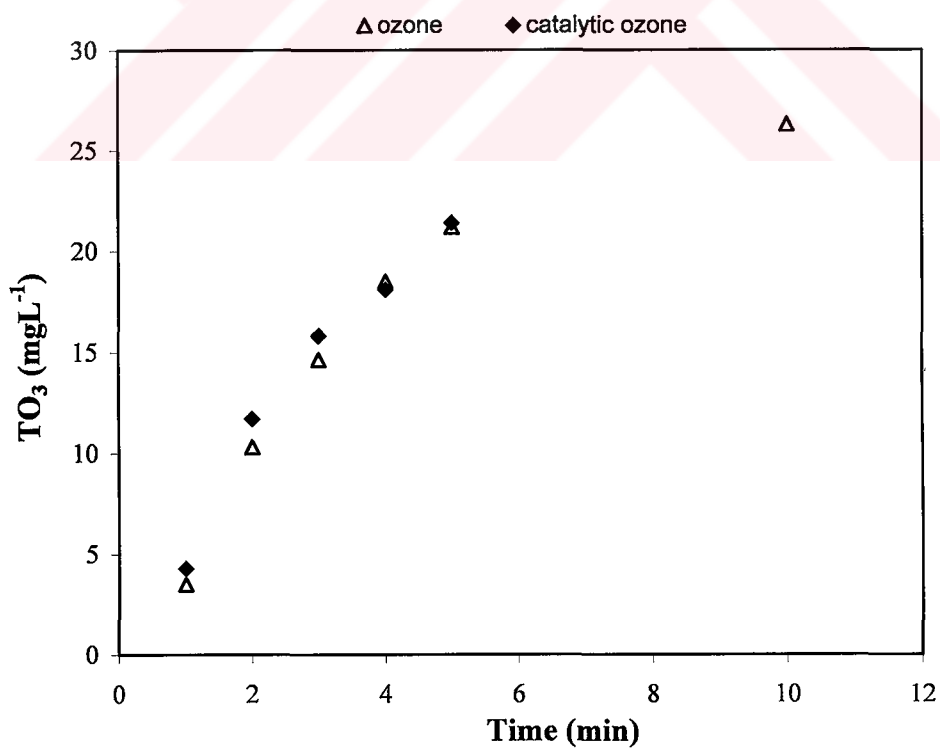


Figure 5.29. The comparison of TO₃ in ozone and catalytic ozone systems

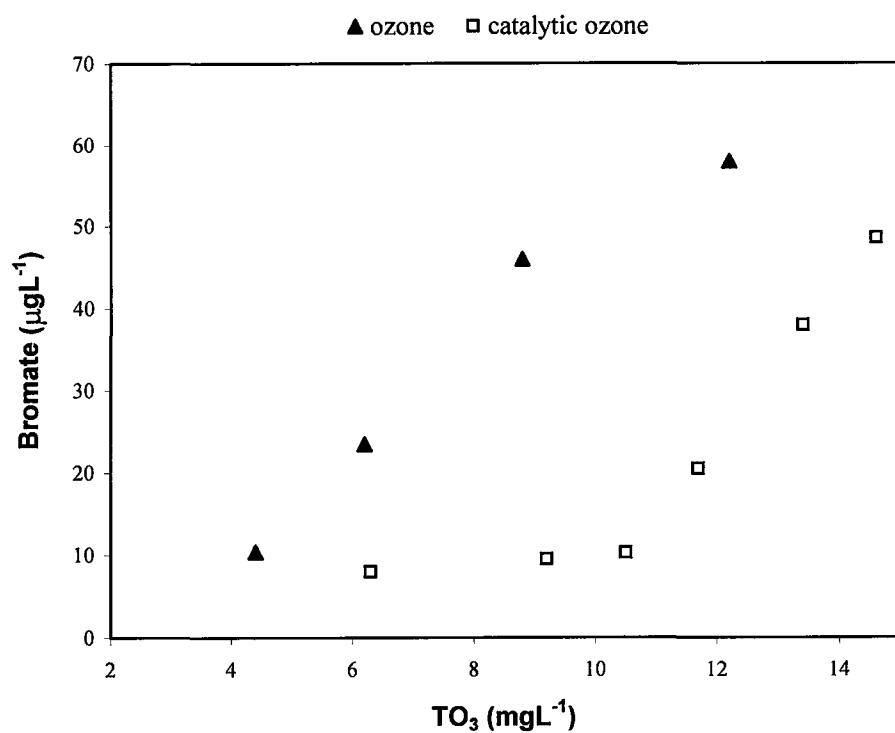


Figure 5.30. TO₃ in ozonation and catalytic ozonation systems and bromate formation in BÇL water.

6. CONCLUSIONS

In this study, two new treatment systems, photoelectrocatalytic and catalytic ozonation, were performed to compare PC/PEC and ozone/ catalytic ozonation processes. For these purposes, humic acid degradation and bromide oxidation were comparatively studied in the PC and PEC processes. Ozonation and catalytic ozonation processes were also carried out for the comparison of two systems with respect to the bromate formation. Thus, the conclusions of the study have been given in two main categories, PEC treatment and catalytic ozonation.

PEC treatment:

Humic acid degradation: The use of a titanium dioxide thin-film electrode constructed of TiO₂ nanoparticles made by sol-gel chemistry and deposited on a titanium foil has been demonstrated to be a simple and efficient method of treating water containing humic substances. By using a conductive substrate, the photoelectrode can be biased by a positive potential which improves the adsorption of the HA organic molecules and contributes to the separation of the photogenerated electron/hole pairs. As a result, the degradation of HA and the removal of TOC are far better than the conventional photocatalytic water treatment process. Additionally, this method has the advantage over a photocatalytic slurry reactor in that the catalyst is immobilized as a ceramic film and does not need to be filtered after treatment. The following conclusions were also reached:

- 95% degradation of UV₂₅₄ and 80% of TOC removal were achieved by photoelectrocatalytic treatment at humic acid concentration of 25 mgL⁻¹ which is the photoelectrode was biased at +1 V (SCE);
- Experiments were conducted using 25 mgL⁻¹ of HA to find optimum applied potential level for this process. Potentials were ranged between 0 and +2.0 V (vs. SCE). Results showed that the applied external potential improved the oxidation of organic contaminants in this system. The degradation of TOC

increased as a function of the applied potential up to 1 V vs SCE. Further increases in the applied potential had no effect on the degradation. UV₂₅₄ and Vis₄₀₀ removals did not change with increasing external potential, and over %95 of both UV₂₅₄ and Vis₄₀₀ removal was removed in the PEC system.

- The photoelectrocatalytic treatment was observed to improve the HA degradation as well as TOC removal under acidic, neutral and alkaline pH values due to the decreasing pH in the photoanode via separation of holes and electrons in the PEC system, Therefore, the separation of anodic and cathodic reactions seems to be of a great advantage to create a pH-independent photocatalytic process;
- As opposed to the electrocatalytic treatment, the photoelectrocatalytic degradation of HA is not affected significantly by the concentration of the electrolyte. This finding reveals that adsorption of organic pollutants on the photoelectrode surface may be improved by applying a positive potential which in turn improves PC degradation of HA.
- The influence of sulfate on the removal of Vis₄₀₀ and UV₂₅₄ degradation was investigated through experiments conducted with 25 mgL⁻¹ of HA in 1.0x10⁻² M Na₂SO₄ at initial pH 6.5. Almost the same Vis₄₀₀ and UV₂₅₄ degradation were gained by adding the sulfate. When compared to the PEC TOC removal in the presence of 1.0x10⁻² M, a remarkable increase of 7%, was observed in the PEC TOC removal with SO₄²⁻ as the electrolyte.
- In the electrochemical process, oxidation or degradation efficiency is a function of the electrochemical current, and anion concentration. In the applied PEC system, the photocurrent density increased to 1.8 mAcm⁻² in the absence of the electrolyte, to 8.0 mAcm⁻² in the presence of 1.0x10⁻² M of sulfate and to 10.0 mAcm⁻² in the presence of 1.0x10⁻² M chloride. Almost the same UV₂₅₄ and Vis₄₀₀ removals were gained by adding the electrolytes and 7-8% higher TOC degradation achieved in the presence of 1.0x10⁻² M sulfate was attributed to the effect of persulfate formed on the photoanode rather than photocurrent. Thus, it is concluded that photocurrent does not

directly affect organic removal in the PEC process. Intermediate products such as persulfate and anion radicals may increase organic removal.

PEC treatment of Moose River water: PEC method was also applied for the treatment of a river water (Moose River Wisconsin/USA). The following conclusive remarks can be stated for the Moose River water:

- Regardless of UV intensity, 90% UV_{254} degradation and 97% UV_{400} removal were achieved in the PEC process. The stronger the UV intensity is, the higher the TOC removal is in PEC process. TOC removal of 58-81% was attained in river water.
- The efficiency of PEC method was higher than that of PC method with respect to UV_{254} , UV_{400} and TOC degradation of the river water.
- -0.5 and $+1V$ vs SCE potentials were determined to establish the maximum effect of an applied potential on TOC removal while $0.0 V$ vs SCE was enough to establish maximum UV_{254} and UV_{400} degradation.
- Not only photogenerated hydroxyl radical but also oxygen is necessary for the photocatalytic oxidation. In the PEC system oxygen may be generated on the photoanode. To investigate the effect of oxygen, both photocatalytic and PEC process were carried out using nitrogen instead of oxygen. The efficiency of photocatalytic process was reduced by 52% while the PEC treatment performance decreased by just 9% in the absence of oxygen.

Bromide in the PEC process: Photoanodic bromide oxidation and bromate formation were investigated in the PEC process. From the results of the present work, the following conclusions can be drawn:

- Bromine evolution is almost the same at pH values between 4 and 6. Bromine generation is very poor under conditions where the solution has $pH > 7$ due to photolysis effects and the competition of hydroxide anions for the photogenerated holes. As noted above, due to the formation of H^+ on the anode, pH decreased to 3 in the anode compartment after 30-40 minutes of operation.

- These results show that active bromine formation begins around the flatband potential of TiO_2 (-0.34 V vs SCE at pH 3.0) and increases with the applied potential until it reaches a steady-state condition at $+1.0$ V. Beyond this potential, bromine evolution was almost invariable. Concentrations up to 300 mgL^{-1} of active bromine were generated in the photoelectrocatalytic process on our TiO_2 photoanode. No bromine evolution was detected using photocatalytic or electrocatalytic methods under the same conditions.
- An increase in bromide concentration resulted in an increase in bromine generation reaching a steady state condition at $1.0 \times 10^{-2} \text{ M NaBr}$.
- The photocurrent, and thus hydroxyl radical concentration increases with increasing UV intensity. To investigate the effect of UV intensity on the bromine generation, varying UV intensities were used in the PEC system. It is concluded that high UV intensity favored bromine evolution. The bromine concentrations of 300 mgL^{-1} and 25 mgL^{-1} were obtained at steady-state condition under high (100 mWcm^{-2}) and low (5.7 mWcm^{-2}) UV intensity respectively.
- Bromate formation was observed at pH 6.0 and increased with increasing pH, but due to the low bromine concentrations under basic conditions, bromate formation decreased slightly after pH 8.5. On the contrary, no steady-state condition for bromate formation was achieved since a steady increase was observed following a lag phase of 15 minutes.
- Previous studies (Vinodgopal et al., 1996; Butterfield et al., 1996; Pelegrini et al., 1999; Harper et al., 2001; Li et al., 2002) suggested that this photoelectrocatalytic process may be a more effective and economic treatment and disinfection method than the standard photocatalytic process. It is concluded from this study that photoelectrocatalytic process is slightly different and more complex, hence, further studies may be needed to completely verify this supposition.

Catalytic ozonation:

The aim of the research in this section was to compare the bromate formation in TiO_2 based catalytic ozone and ozone processes occurring in a semi batch reactor. The following is the summary of the major conclusions of findings of this research.

- Even though ozone consumption in the catalytic process was slightly higher than that in ozonation process, bromate formation was significantly lower in the catalytic process under same experimental conditions. Also, bromate formation in catalytic ozonation system exhibited an exponential decay while it increased linearly over time in ozonation process.
- Bromate formation in the presence of TiO_2 appeared to be linearly related to ozone dose and amount of TiO_2 . Bromate formation decreased with increasing TiO_2 loading and increased with increasing ozone dose. Optimum ozone dose/ TiO_2 loading for the %90 reduction of $324 \mu\text{gL}^{-1}$ bromate concentration that formed ozonation process at 20 minutes time period was found to be $7.2 \text{ mgL}^{-1} \text{ gL}^{-1}$.
- Two different TiO_2 specimens, Degussa P25 and Merck were used to compare their effect on the formation of bromate in catalytic ozonation process. Significantly low bromate formation in the presence of Degussa P25 was observed indicating that bromate formation appears to be related to the surface area of catalyst.
- Both catalytic ozonation and ozonation were performed for the treatment of Büyükçekmece lake water. The transferred ozone rate of $3.9 \text{ mgL}^{-1} \text{ min}^{-1}$ was determined at the original pH values under $25 \text{ mgL}^{-1} \text{ min}^{-1}$ ozone dose for Büyükçekmece lake water. TO_3/TOC ratio of 1.25 mgmg^{-1} was determined in catalytic ozonation system for the appearance of bromate concentration higher than EPA standard ($10 \mu\text{gL}^{-1}$) while it was found to be 0.76 mgmg^{-1} in the ozonation process. Bromate formation restricts the usage of ozone in the bromide containing waters. Thus it is concluded that catalytic ozonation may provide a great advantage to use much more ozone (1.7 fold) for the

deactivation of pathogen microorganisms controlling bromate formation during ozonation of the bromide-containing water.



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APPENDICES

Appendix A. Calculation of the first order kinetics for TOC removal

Appendix B. HA degradation in the PEC system at different HA concentrations

Appendix C. Effect of chloride on the PEC efficiency

Appendix D. Effect of pH on the PEC HA degradation



Appendix A. Calculation of the first order kinetics for TOC removal

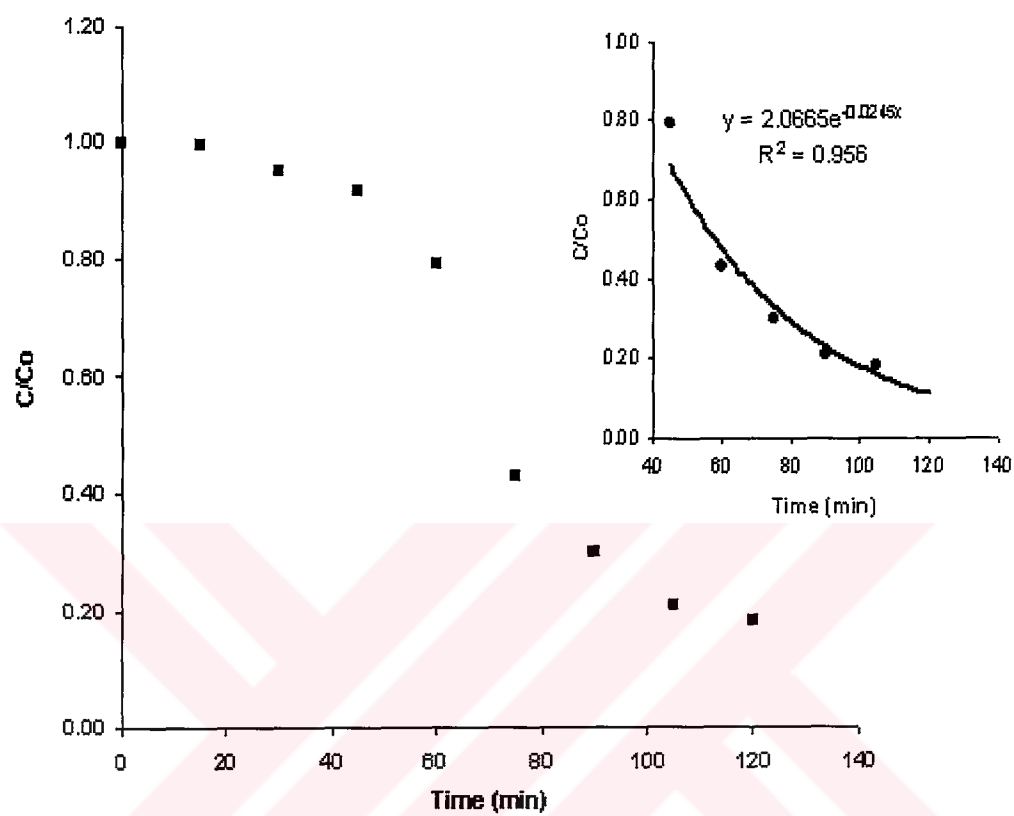


Figure A.1. Calculation of the first order kinetics for TOC removal.

Appendix B. HA degradation in the PEC system at different HA concentrations

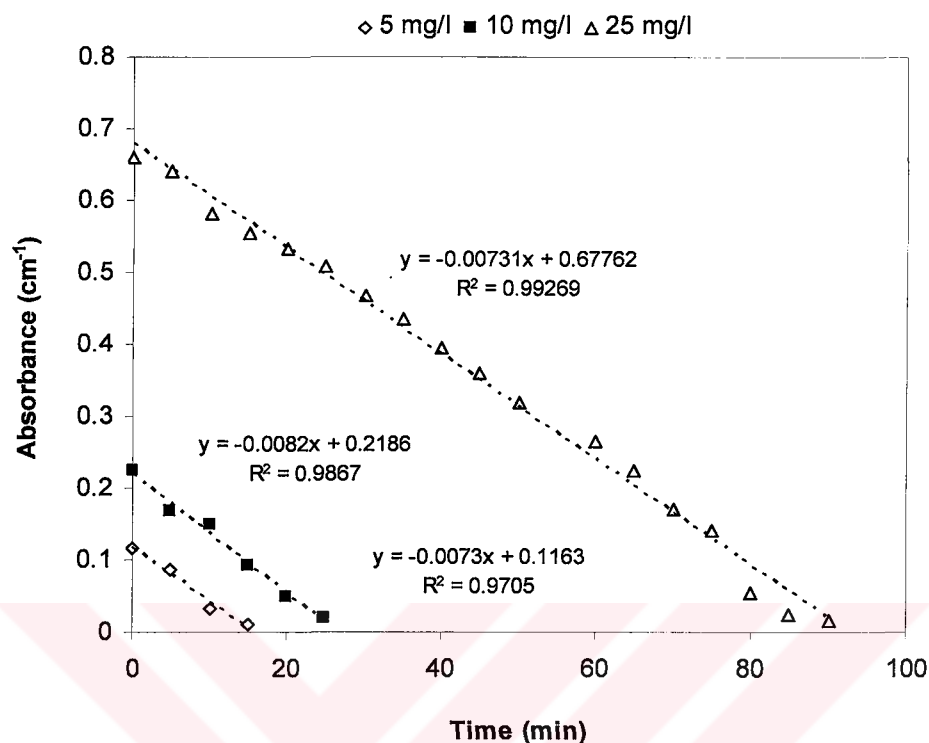


Figure B.1. PEC UV₂₅₄ degradation at different HA concentrations (1.25×10^{-2} M NaCl; E = +1 V vs SCE; pH = 3.0).

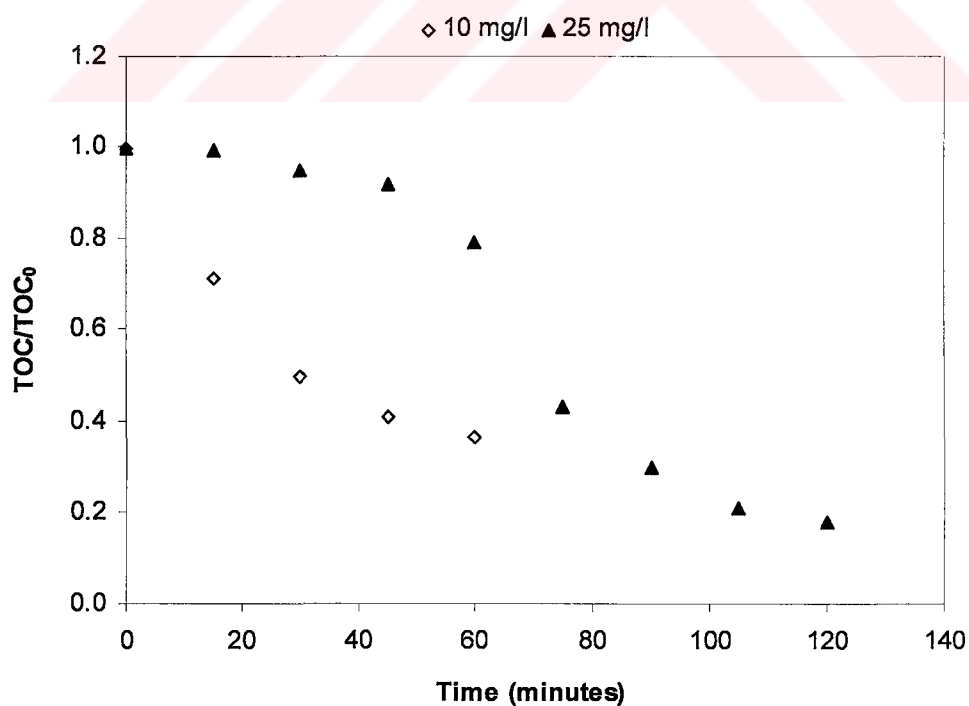


Figure B.2. TOC removal at different HA concentrations (1.25×10^{-2} M NaCl; E = +1 V vs SCE; pH = 3.0).

Appendix C. Effect of chloride on the PEC efficiency

Table C.1. Effect of chloride on the PEC UV₂₅₄ degradation (25 mgL⁻¹ HA; E = +1 V vs SCE; pH = 3.0).

Time (minutes)	Chloride (M)			
	0.0000	0.0050	0.0125	0.0500
0	0.659	0.659	0.659	0.659
15	0.610	0.537	0.554	0.530
30	0.498	0.487	0.467	0.496
45	-	-	0.359	-
60	0.344	0.307	0.266	0.298
75	0.198	0.1598	0.139	0.206
90	0.031	0.032	0.017	0.037

Table C.2. Effect of chloride on the PEC TOC removal (25 mgL⁻¹ HA; E = +1 V vs SCE; pH = 3.0).

Time (min)	Chloride (M)			
	0.000	0.0050	0.0125	0.0500
0	8.40	8.40	8.40	8.40
30	8.10	7.92	7.98	7.20
60	6.90	6.60	5.63	5.80
90	2.72	2.54	2.52	2.84
120	1.82	1.62	1.48	1.86

Appendix D. Effect of pH on the PEC HA degradation

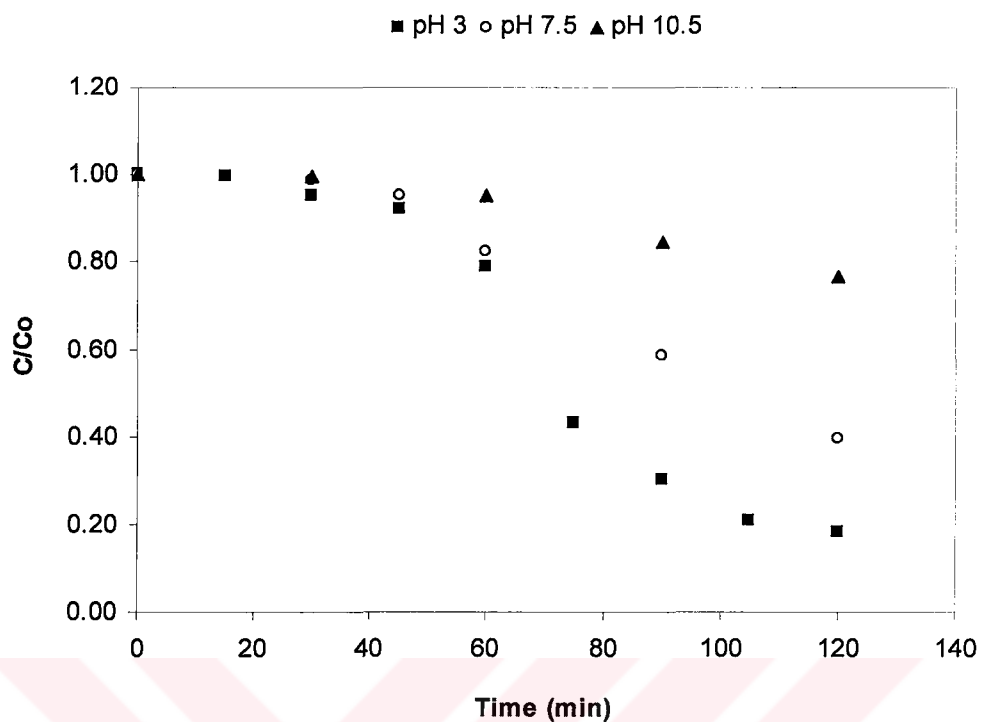


Figure D.1. Effect of pH on the PEC TOC removal (25 mgL^{-1} HA in $1.25 \times 10^{-2} \text{ M}$ NaCl; $E = +1 \text{ V}$ vs SCE).

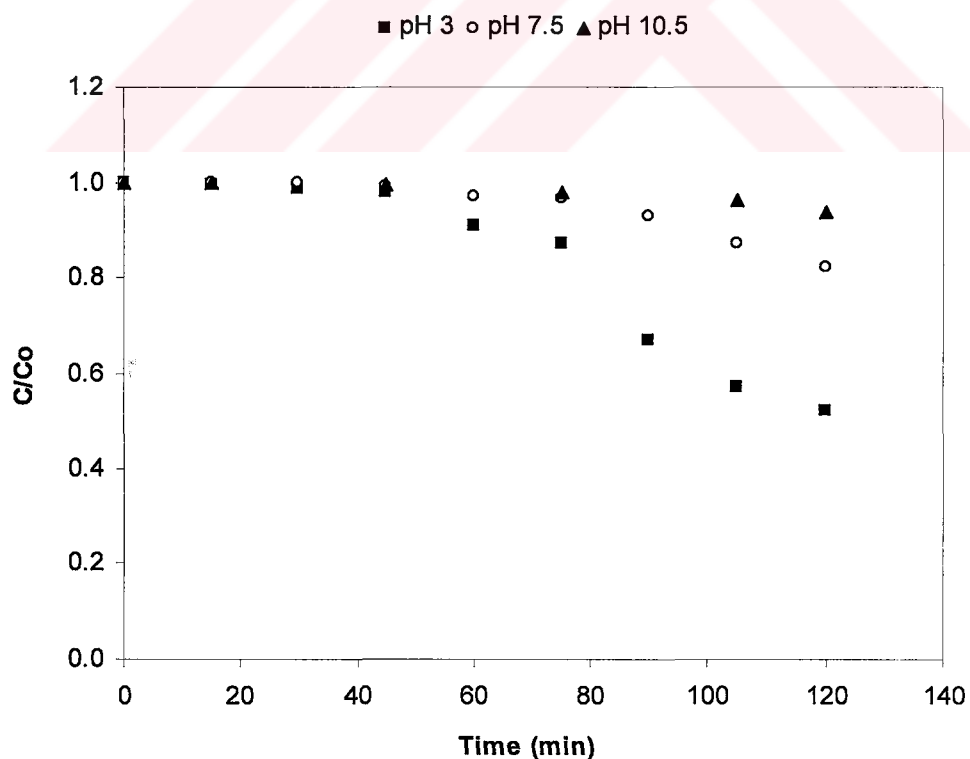


Figure D.2. Effect of pH on the PC TOC removal (25 mgL^{-1} HA in $1.25 \times 10^{-2} \text{ M}$ NaCl; $E = +1 \text{ V}$ vs SCE).

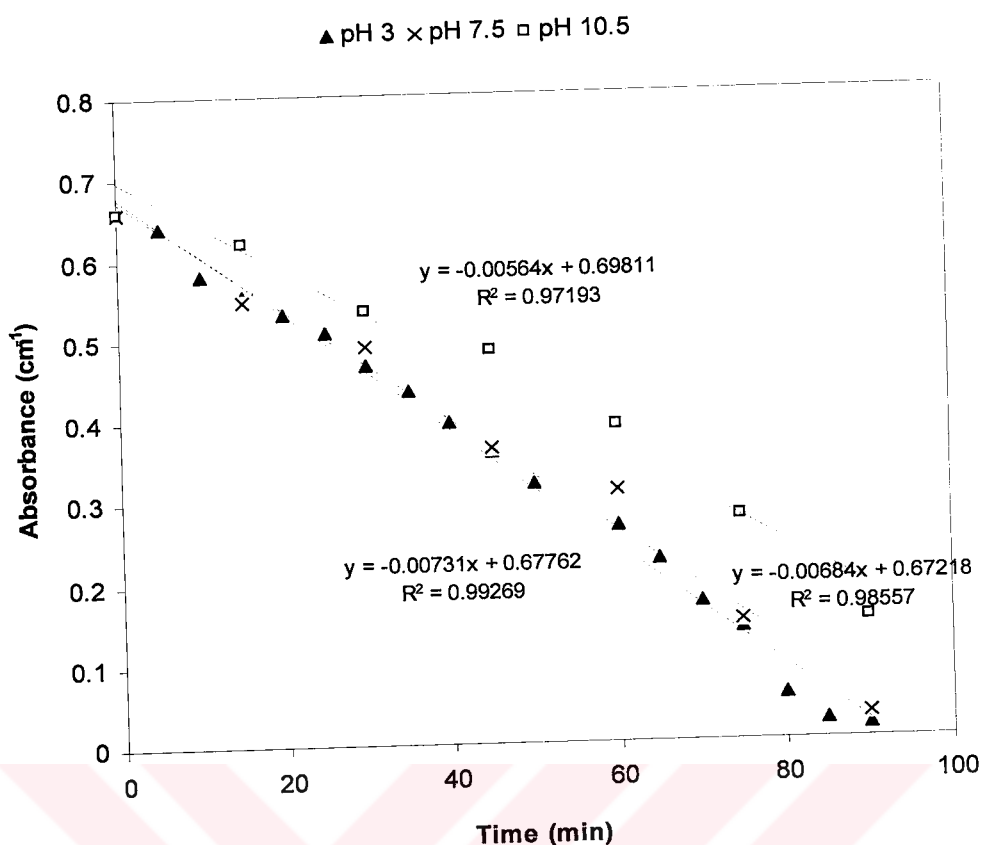


Figure D.3. Effect of pH on the PEC UV_{254} degradation (25 mgL^{-1} HA in 1.25×10^{-2} M NaCl; $E = +1 \text{ V}$ vs SCE).

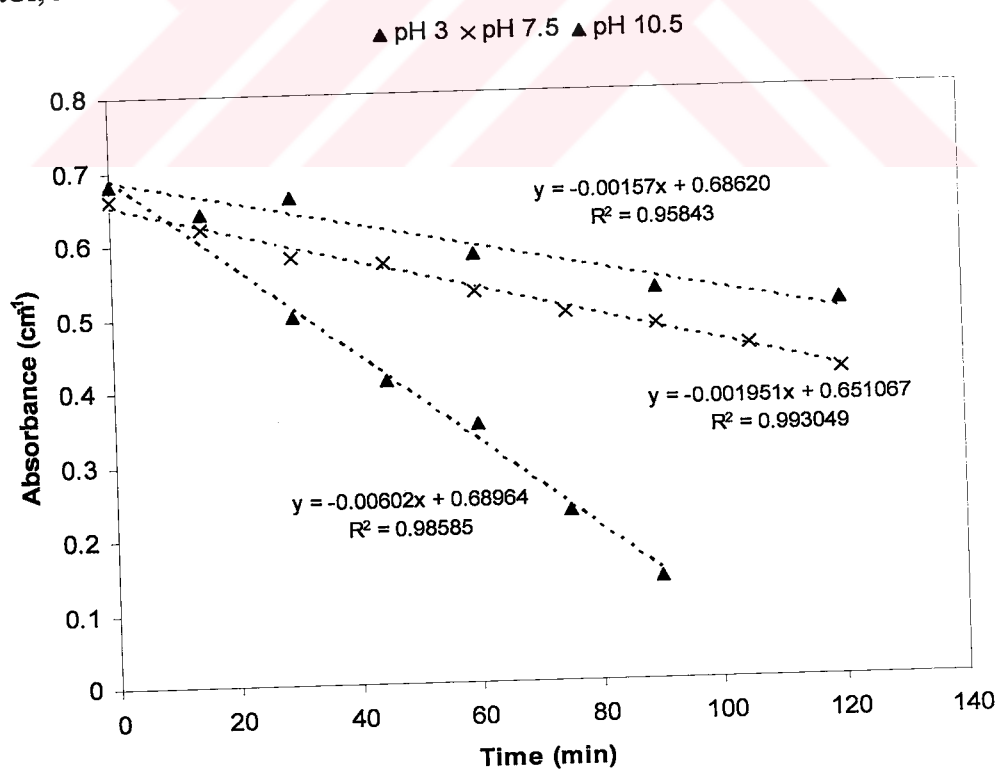


Figure D.4. Effect of pH on the PC UV_{254} degradation (25 mgL^{-1} HA in 1.25×10^{-2} M NaCl; $E = +1 \text{ V}$ vs SCE).

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