

**EFFECT OF RADICAL SCAVENGERS ON THE PERFORMANCE  
OF ADVANCED OXIDATION PROCESSES**

129260

by

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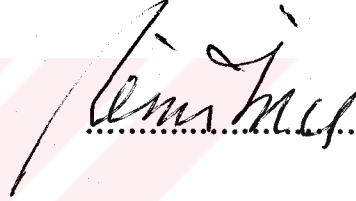
**Boğaziçi University**

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**APPROVED BY:**

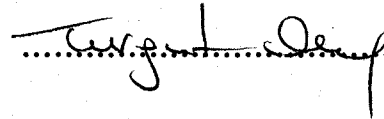
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***To my dear family,***

***With love...***

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## ABSTRACT

Advanced Oxidation Processes (AOPs) rely on the generation of short-lived, powerful and non-selective hydroxyl radicals ( $\bullet\text{OH}$ ) that are responsible for the destruction of a wide range of contaminants in wastewaters. The efficiency of AOPs depends on the production of  $\bullet\text{OH}$  and utilization of it effectively by the target contaminants. Non-target substances, or radical scavengers that exist in wastewaters reduce the efficiency of AOPs by consuming significant amounts of  $\bullet\text{OH}$ .

The purpose of this study was to investigate the kinetics of reactive dyestuff degradation by an advanced oxidation system using ultraviolet light (UV) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and the effect of  $\bullet\text{OH}$  scavenging species such as bicarbonate, carbonate and chloride on the efficiency of the process.

The method involved preparation of synthetic dye solutions using a reactive azo dye, Procion Red HE-7B, which was selected as a model compound for its wide use in the industry. The effectiveness of the employed system was tested by monitoring the degradation of color and organic carbon in the absence and presence of scavengers.

It was found that in the absence of scavengers, 15 minutes was sufficient for complete color removal, whereas 1 hour contact time was necessary for 92 per cent organic carbon degradation. In the presence of scavenging species, the rate of color removal was inhibited and the degree of inhibition increased with increasing concentrations of bicarbonate and carbonate species. It was further found that chloride inhibited the degradation of color only at 100-1250 mM chloride, and did not affect the rate at higher concentrations.

The rate of color and organic carbon degradation was found to follow first order kinetics with respect to concentration, and second order kinetics with respect to  $\bullet\text{OH}$ . The bimolecular color and organic carbon rate constants with  $\bullet\text{OH}$  was estimated by using a simplified kinetic model describing the reaction mechanism. The estimated constants were in good agreement with the published data for azo dyes.

## ÖZET

İleri Oksidasyon Prosesleri (İOP), atıksulardaki çeşitli kirleticilerin parçalanmasını sağlayan, kısa ömürlü, güçlü ve seçici olmayan hidroksil radikallerinin oluşumuna dayanmaktadır. İleri oksidasyon proseslerinin verimi, hidroksil radikallerinin üretimine ve bu radikallerin hedef kirleticiler tarafından etkili bir şekilde kullanımına bağlıdır. Atıksularda bulunan hedef kirletici dışındaki maddeler veya radikal yakalayıcılar, önemli miktarlarda hidroksil radikali tüketerek, ileri oksidasyon proseslerinin verimini düşürürler.

Bu çalışmanın amacı, ultraviyole ışık (UV) ve hidrojen peroksit ( $H_2O_2$ ) içeren ileri oksidasyon sistemi ile, reaktif boya parçalanma kinetiğinin ve bikarbonat, karbonat ve klorür gibi radikal yakalayıcılarının proses verimi üzerindeki etkilerinin incelenmesidir.

Kullanılan method, endüstrideki yaygın kullanımından dolayı reaktif azo boya olan Procion Red HE-7B kullanılarak sentetik boya çözeltilerinin hazırlanmasını içermektedir. Kullanılan sistemin verimliliği, radikal yakalayıcılarının yokluğunda ve varlığında, renk ve organik karbon giderimi izlenerek tespit edilmiştir.

Radikal yakalayıcılarının yokluğunda, rengin tümünün giderilmesi için 15 dakika yeterli iken, yüzde 92 organik karbon giderimi için bir saatin gerekli olduğu bulunmuştur. Radikal yakalayıcılarının varlığında, renk giderimi inhibe edilmiş ve inhibisyonun derecesi bikarbonat ve karbonatın artan konsantrasyonlarıyla artmıştır. Klorürün, renk giderimini 100 ile 1250 mM konsantrasyon aralığında inhibe ettiği ve daha yüksek konsantrasyonlarda renk giderimini etkilemediği bulunmuştur.

Renk ve organik karbon gideriminin konsantrasyona bağlı olarak birinci derece kinetiği, hidroksil radikaline bağlı olarak ikinci derece kinetiği izlediği bulunmuştur. Renk ve organik karbonun hidroksil radikali ile bimoleküler reaksiyon sabiti, reaksiyon mekanizmasını açıklayan basitleştirilmiş bir kinetik model ile hesap edilmiştir. Hesap edilen sabitler, azo boyalar için yayınlanmış data ile uyumludur.

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## 1. INTRODUCTION

Textile dyeing and finishing processes are among the major industrial water users and generate wastewaters that are difficult to treat satisfactorily by conventional treatment methods. Effluents of these processes are known to contain strong color and low biodegradability due to the complex structure of dyestuff and extensive use of dyeing additives.

The inadequacy of conventional treatment methods has led to the development of more effective and feasible technologies for color removal. Advanced Oxidation Processes (AOPs) are one of these alternative technologies that have gained widespread attention for the treatment of dyestuff.

AOPs rely on the generation of short-lived, highly oxidative hydroxyl radicals ( $\bullet\text{OH}$ ) which are responsible for the destruction of a wide range of contaminants in polluted water and wastewater. There has been so much research on the effect of operating parameters such as pH, oxidant dose, and ultraviolet light intensity to maximize the efficiency of AOPs. But, it is important to keep in mind that the efficiency of AOPs depends on the production and utilization of  $\text{OH}\bullet$ , and how effectively it attacks the target compound. Hence, the presence of non-target substances that may compete with the target contaminant for the  $\text{OH}\bullet$  must be taken into consideration. Peyton (1996) indicated that the effect of radical scavenging by non-target substances had more impact on AOP efficiency than the operating parameters.

In dyeing processes, large concentrations of auxiliary chemicals are used that end up in the dyeing wastewater effluents. Of these auxiliaries, sodium chloride ( $\text{NaCl}$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) are very common. While  $\text{NaCl}$  is used in excessive amounts to increase the fixation of dyes on the fibres,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  are used for the adjustment of pH. When  $\text{NaCl}$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  dissociate in the water, chloride ( $\text{Cl}^-$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions are formed which are known to be the strongest  $\text{OH}\bullet$  scavengers. Therefore, their impacts on the treatment efficiency must not be overlooked.

The purpose of this study was to investigate the kinetics of textile dye degradation by ultraviolet light (UV) / hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) homogeneous process, and the effect of  $\text{OH}\bullet$  scavenging species on the reaction rate.

The target contaminant was selected as a reactive azo dye, Procion Red HE 7B (Reactive Red 141), which is widely used in textile dyeing processes.

The method of study involved monitoring the degradation of the dye by means of the decay in its absorbance in the visible region, in the absence and presence of scavenging species.



## 2. THEORETICAL BACKGROUND

### 2.1. The Textile Industry

The textile industry is comprised of a diverse, fragmented group of establishments that produce and/or process textile-related products (fiber, yarn, fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establishments receive and prepare fibers; transform fibers into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and finish these materials at various stages of production (EPA, 1997).

Textile manufacturing begins with the production or harvest of raw fiber. Fibers used in textiles can be harvested from natural sources (e.g., wool, cotton) or manufactured from regenerative cellulosic materials (e.g., rayon, acetate), or it can be entirely synthetic (e.g., polyester, nylon). After the raw natural or manufactured fibers are shipped from the farm or the chemical plant, they pass through four different production stages as follows (EPA, 1997):

1. **Yarn formation:** Textile fibers are converted into yarn by grouping and twisting operations used to bind them together. Natural fibers such as cotton and wool are first cleaned to remove impurities and are then go through a series of preparation steps, including opening, blending, carding, combing, and drafting before they can be spun into yarn. Since manmade fibers are synthesized from organic chemicals, yarn formation of manmade fibres does not involve the extensive cleaning and combing procedures associated with natural fibres. Spinning, drawing and often texturizing processes are used to create yarns from manmade fibres.
2. **Fabric formation:** The major methods for fabric manufacture are weaving and knitting.
3. **Wet processing:** Wet processing enhances the appearance, durability, and serviceability of fabrics by converting undyed and unfinished goods, known as gray or greige goods, into finished consumers` goods. Wet processing consists of four stages including fabric preparation, dyeing, printing, and finishing. These stages involve treating gray goods with chemical baths and often require additional washing, rinsing, and drying steps.

4. Fabrication: Finished cloth is fabricated into a variety of apparel, household and industrial products.

Textile manufacturing is one of the largest industrial producers of wastewater. Types of wastewater include cleaning water, process water, noncontact cooling water, and stormwater. The amount of water used varies widely in the industry, depending on the specific processes operated at the mill, the equipment used, and the prevailing management philosophy regarding water use. Because of the wide variety of process steps, textile wastewater typically contains a complex mixture of chemicals (EPA, 1997).

Wet processing operations, including preparation, dyeing and finishing, generate the majority of the textile wastewater. Dyeing operations generate a large portion of the industry's total wastewater. The primary source of wastewater in dyeing operations is spent dyebath and washwater. Such washwater typically contains by-products, residual dye, and auxiliary chemicals (EPA, 1997).

#### **2.1.1. Dyeing Operations**

Dyeing operations are used at various stages of production (fibers, yarn, piece-dyeing) to add color and intricacy to textiles and increase product value. Textiles are dyed using a wide range of dyestuffs, techniques, and equipment. Dyes used by the textile industry are largely synthetic, typically derived from coal tar and petroleum-based intermediates. Some naturally occurring dyes, derived from animal or plant sources, are also used but are relatively unimportant commercially. Dyes are sold as powders, granules, pastes, and liquid dispersions, with concentrations of active ingredients ranging typically from 20 to 80 per cent (EPA, 1997).



### 2.1.2. Methods of Dyeing

Dyeing can be performed using continuous or batch processes. In batch dyeing, a certain amount of textile substrate, usually 100 to 1000 kilograms, is loaded into a dyeing machine and brought to equilibrium, or near equilibrium, with a solution containing the dye. Because the dyes have an affinity for the fibres, the dye molecules leave the dye solution and enter the fibres over a period of minutes to hours, depending on the type of dye and fabric used. Auxiliary chemicals and controlled dyebath conditions (mainly temperature) accelerate and optimize the action. The dye is fixed in the fiber using heat and/or chemicals, and the tinted textile substrate is washed to remove unfixed dyes and chemicals. Pad dyeing can be performed by either batch or continuous processes (EPA, 1997).

In batch dyeing, the objective is maximum exhaust and fixation of the dye to minimize carryover of unfixed dye into the washing stages. The maximum dye exhaust achievable is related to the affinity of the dye for the fiber and the bath ratio. Bath ratio is the ratio of the mass of the dyebath to the mass of the goods in the dyeing machine and typically ranges from five to 50 depending on the type of dye, dyeing system, and affinity of the dyes for the fibres (EPA, 1996).

In continuous dyeing processes, textiles are fed continuously into a dye range at speeds usually between 50 and 250 meters per minute. Continuous dyeing processes typically consist of dye application, dye fixation with chemicals or heat, and washing. Dye fixation is a measure of the amount of the percentage of dye in a bath that will fix to the fibres of the textile material. Dye fixation on the fiber occurs much more rapidly in continuous dyeing than batch dyeing (EPA, 1996).

## 2.2. Environmental Problems Associated with Dyeing

The environmental problems arising from dyeing processes can be summarized as follows (Tezcanlı, 1995):

- Wastage of large amounts of water
- Use of massive amounts of salt in cellulose dyeing
- Treatment difficulties for some metals which can be constituents of some dyes
- Interference of color (unfixed dye) with the transmission of light in receiving body, interrupting photosynthesis and aquatic life
- Wastage of numerous auxiliary chemicals.

Pollutants associated with dyeing may originate from the dyes themselves (e.g., toxicity, metals, color) or derive from auxiliary chemicals used during the dyeing processes (e.g., salts, surfactants, lubricants). Pollutant impacts are also associated with chemicals used during dyeing equipment and maintenance. Dyeing contributes essentially all of the salt and color in effluent from textiles operations (EPA, 1996).

Alkalinity of dyeing effluents is a further environmental concern. Dyeing operations are generally carried out in a range of neutral pH conditions to highly alkaline conditions. Alkali is introduced to cause the reaction between the dye and the fibre (Tezcanlı, 1995).

### 2.2.1. Sources of Color in Dyeing Wastewater

Dyes are the principal sources of color in dyeing wastewater. Dyes are highly colored materials used in relatively small quantities (a few percent or less of the weight of the substrate) to impart color to textile materials for aesthetic or functional purposes. In typical dyeing processes, 50 to 100 per cent of the color is fixed on the fiber and the remainder is discarded in the form of spent dyebaths or in wastewater from subsequent textile-washing operations (EPA, 1996).

Each dye class is generally applicable to (or has affinity for) specific types of fibers.

Table 2.1. Typical fixation rates for dyes of various classes (EPA, 1996)

Dye class	Typical Fixation (%)	Fibers Typically Applied to
Acid	80 to 93	Wool, nylon
Azoic	90 to 95	Cellulose
Basic	97 to 98	Acrylic
Direct	70 to 95	Cellulose
Disperse	80 to 92	Synthetic
Reactive	50 to 80	Cellulose
Vat	80 to 95	Cellulose

As represented in Table 2.1, the popular reactive dye classes fall in the lower range of the fixation scale. For these dyes, fixation is often less than 75 per cent. They require special attention to maximize fixation and therefore minimize waste color discharge. Important factors are bath ratio, optimized salt use, and adequate time for exhaustion (EPA, 1996).

### 2.2.2. Auxiliary Chemicals used in Dyeing

Auxiliary chemicals are used in extremely large quantities in textile dyeing operations; in some cases, the weight of chemicals may be as high as the weight of goods being dyed (EPA, 1996). Chemicals, which are most frequently used in dyeing, are listed in Table 2.2. This table indicates that a large range of substances other than dyes can be found in a dyeing effluent at any one time (Correia *et al.*, 1994).

Table 2.2. Most frequently auxiliary chemicals used in dyeing (Correia *et al.*, 1994)

Description	Composition	Function
Salts	Sodium chloride Sodium sulfate	Neutralize zeta potential of the fibre, Retarder
Acids	Acetic and sulphuric acid	pH control
Bases	Sodium hydroxide Sodium carbonate	pH control
Buffers	Phosphate	pH control
Sequestering agents	EDTA	Complex hardness, Retarder
Dispersing and surface active agents	Anionic, cationic and nonionic	Disperse dyes, Regulate dye application, Softeners
Oxidising agents	Hydrogen peroxide Sodium nitrite	Insolubilise dyes
Reducing agents	Sodium hydrosulphite Sodium sulphide	Solubilise dyes, Remove unreacted dye
Carriers	Phenyl phenols Chlorinated benzenes	Enhance absorption

### 2.2.3. Sources of Salt in Dyeing Wastewater

Several authors have identified salts in textile-dyeing wastewater as a potential problem area. Many types of salt are either used as raw materials or produced as by-products of neutralization or other reactions in textile wet processes. Salt is used mostly to assist the exhaustion of ionic dyes, particularly anionic dyes, such as direct and fiber reactive dyes on cotton. Typical cotton batch dyeing operations use quantities of salt that range from 20 per cent to 80 per cent of the weight of goods dyed, and the usual salt concentration in such wastewater is 2000 ppm to 3000 ppm (EPA, 1996).

Types of salts used in textile operations are listed in Table 2.3. Common salt (sodium chloride) and Glaubers salt (sodium sulfate) constitute the majority of total salt use. Other salts used as raw materials or formed in textile processes include Epsom salt (magnesium chloride), potassium chloride, and others in low concentrations (EPA, 1996).

Table 2.3. Types of salt used in textile operations (EPA, 1996)

Salt type	Typical use
Calcium chloride	Formed
Common salt	Dyeing
Epsom salt	Fixing
Glaubers salt	Dyeing
Magnesium chloride	Catalyst
Potassium chloride	Formed

Each dye class requires characteristic amounts of salt, and dyes within a class exhibit wide variances. In general, the salt requirements for batch dyeing of cotton with various dye classes are as shown in Figure 2.1.

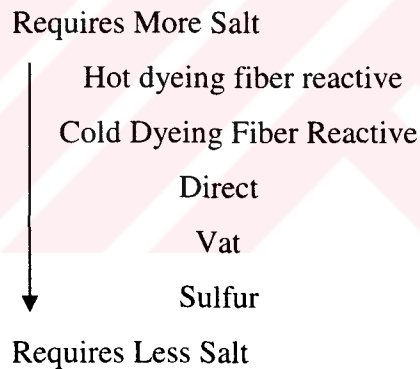


Figure 2.1. Salt requirements for various dye classes-batch dyeing of cotton (EPA, 1996).

### 2.3. Dyes

Dyes are generally small molecules comprising two key components: the chromophore, responsible for the color, and the functional group that allows dye fixation onto the fibers. There are hundreds of dyes reported in specialized literature, which are classified by their chemical structure or in terms of their application to the fiber type (Correia *et al.*, 1994).

In terms of chemical structure, the azo compounds represent the largest group of all textile dyestuffs produced. They derive the name from their characteristic azo group, consisting of two nitrogen atoms (-N=N-). In accordance with the number of such groups, the dyes are described as monoazo, disazo, triazo, tetrakisazo, etc. dyes (Rys and Zollinger, 1972).

The second classification of dyes which is based on their mode of application distinguishes acid, reactive, metal-complex, disperse, vat, mordant, direct, basic and sulfur dyes. Most commonly in use today are the reactive and direct types for cotton dyeing, and disperse types for polyester dyeing (Snowden-Swan, 1995). Research on textile effluent decolorization has often focused on reactive dyes for the following reasons. First, reactive dyes represent an increasing market share due to the increasing use of cellulosic fibres. Second, these dyes have low fixation rates and this results in highly colored spent dyebaths whose treatment is inadequate in conventional wastewater treatment plants (Vandevivere *et al.*, 1998).

- **Fiber Reactive Dyes:** The most popular method of batch dyeing of cotton, especially cotton knits, is fiber reactive dyes. Fiber reactive dyes are water-soluble, anionic dyes that provide high wetfastness and relatively simple dyeing methods. They are mainly used for dyeing cellulosic fibers such as cotton and rayon but are also sometimes used for wool, silk, nylon, and leather. Fiber reactive dyes have largely replaced direct, azoic, and vat dyes and are the largest dye class in commercial value. Because of the bright shades available particularly orange, scarlet, and turquoise, they are popular choices for color fashion apparel (EPA, 1996).

Fiber reactive dyes combine covalently with the fibre. During the coloration process, the dye is first absorbed by the fibre and then reacts with it by either a substitution reaction or an addition reaction between the reactive system in the dye molecule and a suitable group in the fibre molecule, e.g. ionized hydroxy groups in cellulosic fibres (Nunn, 1979).

The characteristic structural features of a reactive dye are represented in Figure 2.2 (Rys and Zollinger, 1975).

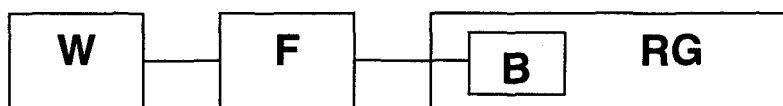


Figure 2.2. Characteristic features of a reactive dye.

RG is the reactive group, which is generally attached to the chromogen (F) by a bridging group (B) and W is the water solubilising group. The functional groups of fibres that react with reactive dyes to form covalent bonds are the hydroxyl group of cellulose and the amino, carboxyl, hydroxyl and thiol groups of wool and silk. All these residues have a nucleophilic character and therefore add to an electrophilic centre of the reactive group. The bridging group influences the reactivity, the degree of fixation, the stability and other dyeing characteristics. Chromogen is the colored part of the molecule, usually an azo, metal-complex azo, anthraquinone or phthalocyanine residue. As with other classes of dye, fastness to light and to chemical treatments are largely determined by the stability of the chromogen. Water solubility is generally conferred by sulphonic acid groups attached to the chromogen and/or, occasionally, to the reactive system (Rys and Zollinger, 1975).

The fundamental problem of reactive dyeing is that reaction of the reactive dye with water (hydrolysis) competes with the fixation reaction (formation of a covalent bond between the dye and the textile substrate). The hydrolysed dye cannot react with the fibre. A high ratio of fixation to hydrolysis is therefore an important prerequisite for high fixation and therefore for the practical usefulness of a reactive dye (Rys and Zollinger, 1972).

The major environmental concerns about fiber reactive dyes focus on color and salt, two pollutants that are receiving increased attention. Fiber reactive dyeing of cotton and other cellulose fibers cannot achieve the high fixation level of other fibers, which in wool and synthetics are typically in the range of 90 per cent or higher. To maximize fixation, fiber reactive dyes require the use of large amounts of salt, typically up to 100 grams per liter. Even with high levels of salt added and the use of new bifunctional reactive dyes which have two reactive groups that increase the efficiency of dye fixation, fixation in typical batch dyeing processes usually remains below 70 to 80 per cent. After dyeing, the fabric is

washed with an anionic surfactant to remove unreacted dye. This results in the discharge of large amounts of color to the wastewater. Decolorization of the effluent is difficult because of the low level of aerobic biodegradation and/or adsorption of the dye color onto activated sludge during treatment. Also, some jurisdictions are tightening salt limits to levels that may be difficult to meet because conventional treatment systems are not effective in removing salt (EPA, 1996).

#### **2.4. Conventional Treatment Methods for Textile Wastewater**

Wastewater discharges from dyeing and finishing processes of textile industries are of great concern, due to their negative impacts on environment. Effluents of such processes are known to contain considerable color, non-biodegradable organics, suspended solids, unstable pH and temperature and a high chemical oxygen demand (COD) (Ince *et al.*, 1997). The non-biodegradability of textile wastewaters is due to their high content of dyestuffs, surfactants and additives that are highly structured complex polymers (Moraes *et al.*, 2000).

Conventional wastewater treatment plants relying on activated sludge systems are not adequate for the treatment of textile mill effluents. Activated sludge and other types of bioreactor fail to remove sufficient color, COD, surfactants and other micropollutants present in textile effluents. Tertiary coagulation/flocculation is often used with variable results but at times near-complete decolorization and water reuse is possible; sludge disposal remains, however, a problem. Membrane filtration of process substreams may yield substantial cost savings by allowing water, chemicals and heat reuse. But, handling and disposal of the concentrate stream remains and this causes a severe limitation to filtration processes (Correia *et al.*, 1994). All these technologies are partially or ultimately effective for color removal but they transfer the contaminants from one medium to another, leaving the final environmental problem unsolved. Therefore, it is more and more necessary to develop destructive systems leading to complete mineralization or at least, to less harmful or easy-to-treat compounds. From this point of view, oxidation of organic pollutants is an attractive method (Colonna *et al.*, 1999). Goronszy *et al.* (1992) showed chemical oxidation as the most efficient and simplest pretreatment method for organics



using oxidants such as chlorine, ozone, hydrogen peroxide, potassium permanganate and chlorine dioxide to destroy odor-causing sulfur compounds, control bacterial growth, and reduce COD. On the other hand, conventional chemical oxidation has low removal rates for many environmental contaminants (EPA, 1998).

In recent years, advanced oxidation processes have emerged as an important class of technologies for accelerating the oxidation and hence destruction of a wide range of contaminants in polluted water and wastewater (Bolton *et al.*, 1996).

## 2.5. Innovative Treatment Methods: Advanced Oxidation Processes

AOPs have recently become essential counterparts of wastewater treatment plants due to increasing public concern for health related environmental problems, and the need for revision of effluent discharge standards (Ince and Apikyan, 2000).

The AOP technologies rely on the *in-situ* generation of short-lived, highly oxidative species, primarily the hydroxyl radical, to function as initiators. As implied by the term AOP, light energy is one of the essential components of an AOP technology. Depending on the type of AOP technology employed, ultraviolet radiation (of wavelengths from 100 to 400 nm) or visible radiation (400 to 700 nm) is used to produce  $\bullet\text{OH}$  (EPA, 1998).  $\bullet\text{OH}$  has a high oxidation-reduction potential (2.85 V) (Glaze *et al.*, 1987) and thus decomposes organic matter drastically with an extremely high rate constant of  $10^8\text{-}10^9 \text{ m}^3\text{kmol}^{-1}\text{s}^{-1}$  (Ingold, 1973).

The hydroxyl radical can be generated by a variety of methods as follows:

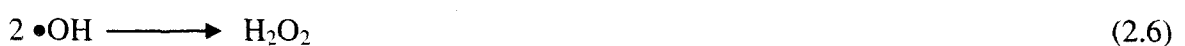
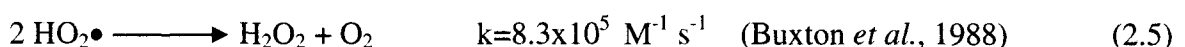
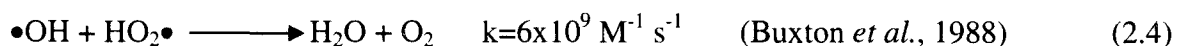
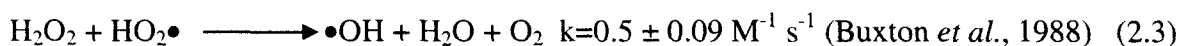
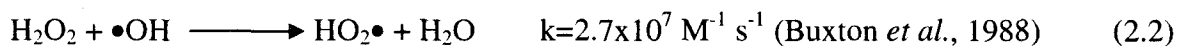
1. Homogeneous photolysis: These processes employ UV photolysis of hydrogen peroxide, ozone ( $\text{O}_3$ ) or both to generate  $\bullet\text{OH}$  and other radicals. The most common homogeneous processes are UV/ $\text{H}_2\text{O}_2$ , UV/ $\text{O}_3$  and UV/  $\text{H}_2\text{O}_2/\text{O}_3$  processes.
2. Dark homogeneous oxidation: These processes do not employ UV light; they usually involve the use of Fenton's reaction, ozone at high pH and  $\text{O}_3/\text{H}_2\text{O}_2$ .

3. Heterogeneous photolysis: Solid particles of the semiconductors absorb UV light and generate  $\bullet\text{OH}$  and other radicals in reactions on the surface of the particles. The process is heterogeneous because there are two active phases, solid and liquid. The most common of these processes is the UV/titanium dioxide ( $\text{TiO}_2$ ) system.
4. Radiolysis: A source of high-energy radiation is used to irradiate the wastewater.  $\bullet\text{OH}$ , hydrogen radicals ( $\bullet\text{H}$ ), hydrated electrons and other radicals are generated in the radiolysis of water.
5. Sonolysis: These processes involve exposing contaminated aqueous solutions to ultrasound.

### 2.5.1. UV/ $\text{H}_2\text{O}_2$ Process

The UV/ $\text{H}_2\text{O}_2$  system generates  $\bullet\text{OH}$  by photolyzing the peroxide HO-OH bond with UV light below 300nm (Bolton and Cater, 1994).

Several researchers have indicated that the following radical chain reactions occur in a hydrogen peroxide solution with UV-light irradiation (Alnaizy and Akgerman, 2000, Crittenden *et al.*, 1999, Huang and Shu, 1995, Ku *et al.*, 1998, Stefan *et al.*, 1996).



When  $\text{H}_2\text{O}_2$  solution is exposed to UV irradiation, hydroxyl radicals are formed which then undergo a series of chain reactions with the target organic compound (M), other organic compounds such as humic substances and inorganic compounds such as bicarbonate, carbonate and chloride ions. The compounds present in the solution instead of the target organic compound are called scavengers and will be discussed in the following sections. The  $\bullet\text{OH}$  attacks  $\text{H}_2\text{O}_2$ , leading to the formation of perhydroxyl radical ( $\text{HO}_2\bullet$ ). The  $\text{HO}_2\bullet$  may react with the target compound and other constituents in the solution, but at much slower rates than the hydroxyl radical. The chain reactions are terminated by the reaction of  $\bullet\text{OH}$  with  $\text{HO}_2\bullet$ , recombination reactions of  $\text{HO}_2\bullet$  and  $\bullet\text{OH}$  to regenerate  $\text{H}_2\text{O}_2$ , as presented in Equations 2.4, 2.5 and 2.6.

A comparative evaluation of Fenton's reaction,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  treatments coupled with ultraviolet light has shown that the UV/ $\text{H}_2\text{O}_2$  process has additional advantages in that there is no sludge production and high rates of COD removal can be achieved (Gregor, 1992). Hydrogen peroxide is easier to transport and store, and has almost infinite solubility in water when compared with ozone. Ozone is not a stable gas and must be generated and used on-site immediately. An ozone-water contacting device is needed that can adequately transfer ozone into the liquid phase which increases the capital cost in an UV/ $\text{O}_3$  system (Alfano *et al.*, 2001). Moreover, UV/ $\text{H}_2\text{O}_2$  process forms no vapor emission that can be a significant problem with the treatment of volatile organics in an UV/ $\text{O}_3$  system (Bolton and Cater, 1994).

The major drawback to the use of hydrogen peroxide is the relatively low molar extinction coefficient, which means that in waters with high inherent UV absorption the fraction of light absorbed by the hydrogen peroxide can be low unless prohibitively large concentrations are used. This results in higher operating cost for the treatment of contaminated water (Bolton and Cater, 1994).

### 2.5.2. UV/Ozone Process

The UV/O<sub>3</sub> process seems, at present, to be the most frequently applied AOP for a wide range of compounds. This is mainly due to the fact that ozonation is a well-known procedure in water and wastewater technology. The following radical chain reactions occur in an ozone solution with UV-light irradiation (Legrini *et al.*, 1993).



Photons react with ozone to produce oxygen and oxygen atom (O(<sup>1</sup>D)) which is the precursor of •OH. Hydrogen peroxide, produced after photolysis of ozone in aqueous solution, is subsequently photolyzed to •OH.

### 2.5.3. Fenton and Photo-Fenton Processes

The dark reaction of ferrous iron (Fe (II)) with H<sub>2</sub>O<sub>2</sub> is known as Fenton's reaction.



The •OH thus formed either can react with Fe (II) to produce ferric iron (Fe (III)) as shown in Equation 2.13 or can react with and initiate oxidation of organic pollutants present in a waste stream. This process is effective at pH levels less than or equal to 3 (EPA, 1998).



The rate of removal of organic pollutants and the extent of mineralization with the Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub> reagents are improved considerably by irradiation with near-UV radiation and visible light. This process is called the photo-Fenton reaction. Chemical reactions that occur in the photo-Fenton process are shown in Figure 2.3 (A refers to the target contaminant, A\* and A• refer to reaction intermediates).

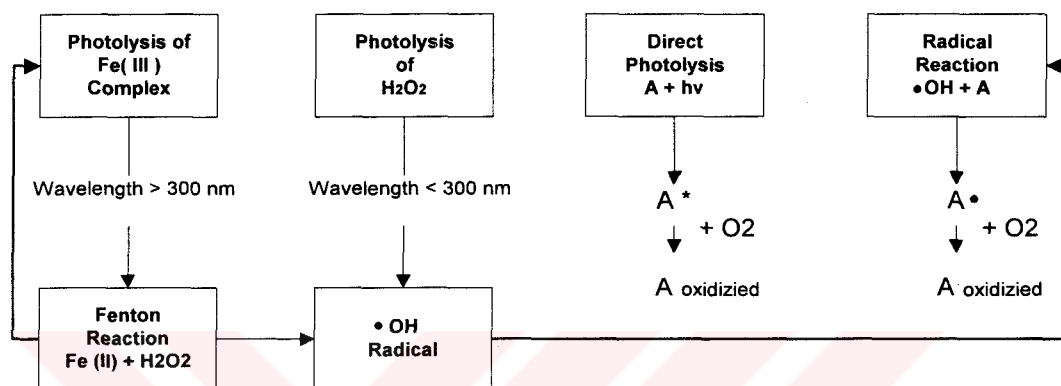


Figure 2.3. Scheme of chemical reactions in the photo-Fenton reaction (Kim *et al.*, 1997).

#### 2.5.4. Heterogeneous Photocatalytic Processes

Heterogeneous photocatalytic processes involve the degradation of organic pollutants by irradiated dispersions of semiconductors. Semiconductors are solids that have electrical conductivities between those of conductors and those of insulators. Semiconductors that have been used in environmental applications include TiO<sub>2</sub>, strontium titanium trioxide, and zinc oxide (ZnO). TiO<sub>2</sub> is generally preferred for use in commercial APO applications because of its high level of photoconductivity, ready availability, low toxicity, and low cost (EPA, 1998).

TiO<sub>2</sub> exhibits photoconductivity when illuminated by photons having an energy level that exceeds the TiO<sub>2</sub> band gap energy level of 3.2 eV. For TiO<sub>2</sub>, the photon energy required to overcome the band gap energy and excite an electron from the valence band to the conduction band can be provided by light of a wavelength shorter than 387.5 nm. When an electron in the valence band is excited into the conduction band, a vacancy or hole is left in the valence band. Such holes have the effect of a positive charge. The

combination of the electron in the conduction band ( $e^-_{CB}$ ) and the hole in the valence band ( $h^+_{VB}$ ) is referred to as an electron-hole pair. The electron-hole pair within a semiconductor band tends to revert to a stage where the electron-hole pair no longer exists because the electron is in an unstable, excited state; however, the band gap inhibits this reversal long enough to allow excited electrons and holes near the surface of the semiconductor to participate in reactions at the surface of the semiconductor (EPA, 1998).

The primary photocatalytic mechanism is believed to proceed as follows (EPA, 1998):



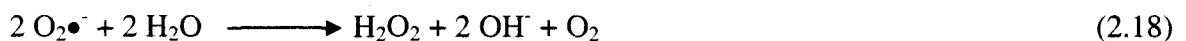
At the  $\text{TiO}_2$  surface, the holes react with either  $\text{H}_2\text{O}$  or  $\text{OH}^-$  from water dissociation to form  $\bullet\text{OH}$  as follows:



An additional reaction may occur if the electron in the conduction band reacts with  $\text{O}_2$  to form superoxide ions ( $\text{O}_2\bullet^-$ ) as presented in Equation 2.17.



The  $\text{O}_2\bullet^-$  can then react with  $\text{H}_2\text{O}$  to provide additional  $\bullet\text{OH}$ ,  $\text{OH}^-$ , and  $\text{O}_2$  as follows:



The  $\text{TiO}_2/\text{UV}$  process is known to have many important advantages, in particular: a large number of organic compounds dissolved or dispersed in water can be completely mineralized; the rate of reaction is relatively high if large surface areas of the photocatalyst

can be used;  $\text{TiO}_2$  can be recycled on a technical scale; UV lamps emitting in the spectral region required to initiate the photocatalytic oxidation are well known and are produced in various sizes (Legrini *et al.*, 1993).

#### 2.5.5. Vacuum Ultraviolet Photolysis

The high energy associated with UV radiation of a wavelength shorter than 190 nm can photolyze water to yield  $\bullet\text{OH}$  and  $\bullet\text{H}$ , a process referred to as VUV photolysis. Contaminant degradation in water and in a relatively high-humidity air stream can be accomplished through oxidation by  $\bullet\text{OH}$  or reduction by  $\bullet\text{H}$  because VUV photolysis of water produces powerful oxidizing species ( $\bullet\text{OH}$ ) and reducing species ( $\bullet\text{H}$ ) (EPA, 1998).

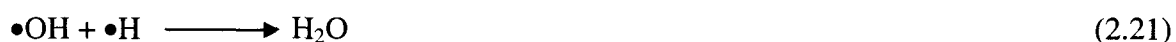
For applications in environmental protection engineering, degradation of organic material in condensed or gaseous phases are most interesting. Technical applications are so far limited to aqueous systems containing relatively low concentrations of organic pollutants. In general, the VUV process is very simple and has the particular advantage that no chemicals need to be added. The process represents a real challenge to other photochemical treatment processes (Legrini *et al.*, 1993).

#### 2.5.6. Sonolysis

Sonochemistry is defined as chemical reactivity induced and/or catalyzed by intense pressure waves in a liquid medium. Propagation of an ultrasound wave in aqueous solution leads to the formation of cavitation bubbles; a prerequisite for these bubbles is the presence of a dissolved gas (Suslick, 1990).

The phenomenon "acoustic cavitation" is the major step that influences the sonochemical process and consists of at least three distinct and successive stages: nucleation, bubble growth (expansion), and under proper conditions implosive collapse (Suslick, 1990). The collapse of the bubbles spawn extreme conditions such as very high temperatures and pressures, which in turn lead to the dissociation of  $\text{H}_2\text{O}$  and the production of radical species such as  $\bullet\text{OH}$ ,  $\bullet\text{HO}_2$  (Petrier *et al.*, 1994; Colarusso and Serpone, 1996).

Experience in homogeneous sonochemistry has shown that there are three potential sites for chemical reactions in ultrasonically irradiated liquids (Weavers *et al.*, 1998). The hydroxyl radicals generated by water sonolysis may either react in the cavitation bubble itself, or at the interfacial sheath between the gaseous bubble and the surrounding liquid and/or in the solution bulk to produce hydrogen peroxide and water as shown (Serpone *et al.*, 1994):



If the solution is saturated with oxygen, peroxy and more hydroxyl radicals are formed in the gas phase (upon the decomposition of molecular oxygen), and the recombination of the former at the cooler sites (interface or the solution bulk) produces additional hydrogen peroxide as shown below (Makkino *et al.*, 1982; Petrier *et al.*, 1994).





### 2.5.7. Scavenging Effects in AOPs

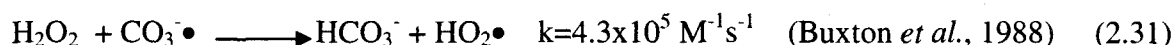
The efficiency of AOPs depends on the production and utilization of  $\text{OH}\bullet$ , and how effectively it attacks the target compound. A drawback resulting from the high reactivity and non-selectivity of  $\text{OH}\bullet$  is that it also reacts with “non-target” materials present in the water, such as carbonate and bicarbonate ions, humic substances, etc. which are referred to as radical “scavengers”. This results in higher  $\text{OH}\bullet$  demand to accomplish a desired degree of organic compound removal in solution. This, in turn, increases the oxidant consumption rate and thus the treatment cost associated with the process.

Both in wastewaters and natural waters, there exist various organic/inorganic substances and background impurities that usually reduce the oxidation efficiency of target pollutants by consuming significant amounts of  $\text{OH}\bullet$ . Humic acids are the most important organic substances that are found in surface and ground water supplies. Of the inorganic impurities, carbonate ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) ions are very common. Carbonate and bicarbonate ions are frequently found in natural waters, and chloride ion might exist in high concentrations in some effluents such as landfill leachate, tannery and dye manufacturing wastewaters. In some cases of wastewater treatment, bicarbonate species are added into a chemical coagulation unit to adjust or stabilize the solution pH for acquiring better treatment performance (Liao *et al.*, 2001).

Carbonate and bicarbonate ions are known as the strongest hydroxyl radical scavengers; therefore, a high alkalinity would be expected to adversely affect AOP treatment efficiency. The reaction of  $\text{OH}\bullet$  with  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  generates carbonate and bicarbonate radicals ( $\text{CO}_3^{\bullet-}$  and  $\text{HCO}_3\bullet$ ), that exhibit similar reactivities toward other species (Peyton *et al.*, 1998, Liao and Gürol, 1995).



The second-order rate constants of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  with  $\text{OH}\bullet$  are  $3.9 \times 10^8$  and  $8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  (Buxton *et al.*, 1988) respectively, showing that carbonate scavenges hydroxyl radicals 45 times faster than bicarbonate (Peyton *et al.*, 1998). On the other hand, the carbonate radical formed as a result of the reactions of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  with  $\text{OH}\bullet$  radical may generate  $\text{HO}_2\bullet$  by consuming the  $\text{H}_2\text{O}_2$  in the surrounding:



The  $\text{HO}_2\bullet$  may also oxidize the target contaminant, but at a much slower rate than  $\text{OH}\bullet$ . Moreover, the  $\text{CO}_3^{\bullet-}$  itself may act as an oxidant to degrade the target contaminant, however unlike  $\text{OH}\bullet$ , it is highly selective and reacts relatively slowly with organic compounds.

Chloride ions react with  $\text{OH}\bullet$  to form  $\text{HOCl}$  at a rate constant of  $4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  (Jayson *et al.*, 1973) according to Reaction 2.32. The  $\text{HOCl}$  may dissociate back to  $\text{OH}\bullet$  and chloride ions with a dissociation rate constant of  $6.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  (Jayson *et al.*, 1973), which is slightly larger than the  $\text{OH}\bullet$  scavenging reaction of  $\text{Cl}^-$ .



## 2.6. Advanced Oxidation Processes for the Treatment of Textile Dyeing Effluents and the Effect of Scavenging Agents: Literature Review

### 2.6.1. Color removal by AOPs

•**UV/ $\text{H}_2\text{O}_2$  Process:** Ince and Gönenç (1997) studied the treatability of a textile azo dye, Remazol Black B, by UV/ $\text{H}_2\text{O}_2$  process. They found that a contact time of 10 minutes was sufficient for complete color removal but it was meaningless in terms of total organic carbon (TOC) reduction. They also found that 28 per cent COD removal was achieved in 65 minutes. They performed experiments in the dark to test the influence of UV radiation and it was found that no degradation of the dye occurred over 24 hours. They observed that excess  $\text{H}_2\text{O}_2$  dosing beyond the effective concentration produced an inhibitory effect on the rate of color removal.

Colonna *et al.* (1999) studied the photodegradation of some azo and anthraquinone dyes in the presence of hydrogen peroxide. They found that UV alone or  $H_2O_2$  in the absence of UV light had no effect on dye degradation. They observed that at least 90 per cent mineralization was obtained in no more than 3 hours. It was observed that color removal and TOC decay followed first-order-kinetics. They studied the effect of  $H_2O_2$  concentration on dye degradation and found that faster dye degradation occurred until a  $[H_2O_2]/[dye]$  ratio of 400 and it was observed that at higher ratios, the degradation process became slower.

Shu *et al.* (1994) investigated the photooxidation of two non-biodegradable azo dyes, acid red 1 and acid yellow 23, by UV/ $H_2O_2$  process. It was observed that the decomposition of both azo dyes was pseudo-first order with respect to the dye concentrations. They found that neither hydrogen peroxide nor UV radiation alone could decompose the dyes. However, by combining UV radiation and  $H_2O_2$ , they observed relatively high degradation rates. They studied the effect of  $H_2O_2$  dosage on the decolorization rates and concluded that beyond the optimum  $H_2O_2$  concentration, the rates decreased significantly. They observed that at higher pH values, the decolorization rates decreased due to the decomposition of  $H_2O_2$  into water and oxygen rather than hydroxyl radicals in alkaline media. They further found that increasing the initial dye concentration decreased the rate of decolorization. They also observed that decolorization rates increased with increasing light intensities.

•**Fenton and Photo-Fenton Oxidation Processes:** Solozhenko *et al.* (1995) studied the decolorization of azo dye solutions by Fenton's oxidation. They observed 95-97 per cent decolorization by  $H_2O_2/Fe(II)$  process at the minimum  $H_2O_2$  concentration of 17 mg/L. Experimental results showed that decolorization occurred effectively only in an acidic medium. They also found that decolorization proceeded more effectively at higher temperatures and increasing the temperature from 25°C to 45°C, decreased the time taken for 95 per cent decolorization from 80 minutes to 17 minutes.

Ince and Tezcanlı (1999) investigated the treatability of textile dye-bath effluents by photo-Fenton process, using a reactive azo dye Procion Red HE 7B and typical dye bath constituents. They found that complete color removal and 79 per cent TOC degradation

were achieved in 20 minutes UV irradiation, at a temperature of 40°C, pH = 3, and with a H<sub>2</sub>O<sub>2</sub>/Fe(II) molar ratio of 20:1. They implied that an appropriate coagulation/membrane system was necessary to make the effluent reusable.

Liao *et al.* (1999) studied the simultaneous removal of COD and color from dye manufacturing process wastewater using photo-Fenton oxidation process. They found that in the presence of 680 mg/L H<sub>2</sub>O<sub>2</sub> and 140 mg/L Fe(II), increasing the UV light intensity increased the removal rates of COD and color. They observed that without ferrous ions, UV/ H<sub>2</sub>O<sub>2</sub> process resulted in 67 per cent and 87 per cent removal in 2 hours for COD and color, respectively whereas these values increased to 76 per cent and 93 per cent in the combined process. Experimental results showed that within the pH range of 2-5, the best COD removal occurred at pH = 3 over the reaction period of 90 minutes. As for the color removal, pH = 4 was found to be the optimal value.

•**Ozone and UV/Ozone Processes:** Wu and Wang (2001) studied the ozonation of aqueous azo dye, Reactive Black 5 in a semi-batch reactor. They observed that decolorization of the azo dye by ozone was a pseudo-first-order reaction with respect to dye. The decolorization rate constant was found to increase with increasing applied ozone dose and increasing temperature, however, decreased with initial dye concentration. They further observed that ozonation reduced COD and enhanced the biodegradability of the wastewater.

Shu and Huang (1995) studied the degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process. The degradation rate of azo dyes was observed to be first order with respect to both dye and ozone concentrations. For acid orange 10, they observed that the concentration decreased from 42.25 mg/L to less than 0.1 mg/L in 16 minutes by ozonation. They also examined the effect of chemical structure of the dyes and concluded that dyes with more azo links were more difficult to degrade by ozone than monoazo dyes. No significant enhancement was observed between ozonation and UV/ozone processes. This was interpreted as partial evidence that the UV light was strongly absorbed by azo dyes rather than ozone and as a result •OH was produced weakly.

•**Photocatalytic Oxidation Processes:** Poullos and Aetopoulou (1999) studied the photocatalytic oxidative degradation of a synthetic textile azo dye, Reactive Orange 16, in the presence of TiO<sub>2</sub> suspensions, under artificial and natural illumination. They observed that after 40 minutes illumination, complete decolorization was achieved with both, however, the decomposition rate of the dye in sunlight was 2.3 times lower than in artificial illumination. They studied the photocatalytic degradation of the dye in the presence of H<sub>2</sub>O<sub>2</sub> and found that there was an optimum H<sub>2</sub>O<sub>2</sub> concentration beyond which the decomposition rate decreased. Below pH = 6, strong adsorption (70-90 per cent) of the dye onto the TiO<sub>2</sub> surface was observed, especially between pH 1-3, as a result of the electrostatic attraction of the positively charged TiO<sub>2</sub> with the fully ionized sulfonic and ethylsulphonic groups in the dye.

Tanaka *et al.* (2000) studied the degradation of seven azo dyes by illumination with near-UV light ( $\lambda > 310$  nm) in TiO<sub>2</sub> suspensions. They observed that lowering pH accelerated the degradation due to the increase in the positive charge of TiO<sub>2</sub> and this promoted the adsorption of dye to TiO<sub>2</sub>. The results of the study revealed that diazo dyes were less degradable than monoazo dyes.

•**Ultrasound:** Vinodgopal *et al.* (1998) studied the degradation of a reactive textile azo dye, Remazol Black B in oxygen saturated aqueous solution using a high frequency ultrasonic generator (640 kHz). They found that after 90 minutes of sonication, the visible absorption of the dye had completely disappeared. They observed 65 per cent TOC removal in 6 hours of sonication.

Ince and Tezcanlı (2001) studied the degradation of Remazol Black B by combined sonolysis (520 kHz) and ozonation. They found that color removal in 15 minutes with the combined system was twice as fast as than that with ozone alone, while no significant removal was observed by ultrasound alone. The lack of color degradation by ultrasound was attributed to the shortness of the contact period. They observed that total mineralization over 1 hour in ultrasound alone, ozone alone and in the combined scheme were 2, 50 and 76 per cent, respectively. They implied that longer contact time was necessary for appreciable conversion of TOC to CO<sub>2</sub> by ultrasonic treatment alone.

## 2.6.2. Effect of Scavengers on AOPs

2.6.2.1. Degradation of Dyes: Arslan and Balcioglu (2000) investigated the ozonation of Procion Yellow HE4R and Remazol Black SB in actual dye rinse waters and simulated exhausted dye bath liquors. They found that in the ozonation of hydrolyzed dyestuff, color and  $UV_{254}$  disappeared quickly, whereas COD and TOC removals were incomplete even after 60 minutes of treatment, for both dyes. In the ozonation of simulated Remazol Black SB dye-bath effluents, they studied the separate and combined effect of  $70 \text{ gL}^{-1} \text{ NaCl}$  and  $5 \text{ gL}^{-1} \text{ Na}_2\text{CO}_3$ . They observed that the addition of NaCl and  $\text{Na}_2\text{CO}_3$  had no negative impact on decolorization kinetics. On the other hand, a two-fold decrease in  $UV_{254}$  and TOC removals were observed which implied that  $\text{OH}\bullet$  effect of soda became particularly pronounced at high pH values ( $> 10.3$ ). It was further found that NaCl did not affect the rate of dye-bath oxidation. It was also observed that the simultaneous addition of both salt and soda did not result in a synergy between the introduced chemicals. For the ozonation of actual reactive dye rinse baths, it was observed that 10-20 times higher ozone doses were required for the decolorization of Remazol Black SB rinse water. It was further found that the decolorization time was proportional to the pollution strength of the rinse water.

Neppolian *et al.* (2002) investigated the influence of carbonate and chloride ions on the photocatalytic degradation of a textile dye, Reactive Blue 4. They found that the degradation of the dye decreased with increasing carbonate ion concentration. This was attributed to the hydroxyl radical scavenging property of carbonate ions. They examined the effect of chloride ion by adding sodium chloride to the dye solution in the range of  $0.25\text{-}2 \text{ g L}^{-1}$ . They observed that increasing the chloride ion concentration decreased the rate of degradation. The decrease in the presence of chloride ions was due to the hole scavenging properties of chloride ion. The reaction of dye with the holes competed with the reaction of chloride ions with the holes and this resulted in lower dye degradation.

Kiwi *et al.* (2000) studied the oxidation of Orange II by photoassisted Fenton process in the presence of chloride ions. They observed that the oxidation of the dye was possible in the presence of high  $\text{Cl}^-$  concentrations. They explained that the intermediate radicals that were formed in the presence of chloride ions ( $\text{Cl}_2\bullet^-$ ,  $\text{Cl}\bullet$ , and  $\text{HOCl}\bullet$ ) were also responsible for the oxidation of the dye instead of hydroxyl radicals. They found that the



concentrations of  $\text{Cl}\cdot$  and  $\text{HOCl}\cdot$  were 2 orders of magnitude lower than the concentration of  $\text{Cl}_2\cdot$ . On the other hand, the concentration of  $\text{OH}\cdot$  was found to be 3 orders of magnitude below the concentration of  $\text{Cl}_2\cdot$ . The rate constants for the reaction of  $\text{OH}\cdot$  and  $\text{Cl}_2\cdot$  radicals with Orange II were determined by laser kinetic spectroscopy and found as  $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $3.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

Sökmen and Özkan (2002) investigated the effect of different inorganic anions ( $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , acetate and citrate) on the photocatalysis of an acidic cationic dye, Astrazone Orange G. They found that the presence of anions except for  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$  inhibited the rate of color removal in the first 10-20 minutes of illumination. On the other hand, they observed that 90-95 per cent color removal was still achieved after 20 minutes illumination whether anionic species were present or not. Inhibition effects of anions except for  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$  were attributed to the scavenging of holes by the anions. They explained that the anions were adsorbed on the  $\text{TiO}_2$  surface and competed with the dye for the photo-oxidizing species on the surface and thus prevented the photocatalytic degradation of Astrazone Orange.

2.6.2.2. Degradation of Other Contaminants: Liao *et al.* (2001) studied the scavenging role of chloride and bicarbonate ions in the UV/  $\text{H}_2\text{O}_2$  process at different pH values and different molar ratios of chloride/carbonate species ( $\text{Cl}^-/\text{C}_\text{T}$ ) using n-chlorobutane (BuCl) as the probe of  $\cdot\text{OH}$ . They found that BuCl and  $\text{H}_2\text{O}_2$  were found to disappear by following the first-order reaction and this result was found to be independent of pH variation or concentration change of chloride and bicarbonate species. They also found that the stripping effect of BuCl was insignificant as compared to oxidation by  $\cdot\text{OH}$ .  $\text{H}_2\text{O}_2$  decomposition was found to follow first-order reaction for all the cases. They observed that in the presence of chloride alone, the steady-state  $\cdot\text{OH}$  concentration increased with increasing pH significantly within the pH range of 2-6 and it then remained a plateau at  $\text{pH} > 6$ . They further examined that, in the presence of both chloride and bicarbonate species, optimum pH to obtain the maximum of  $\cdot\text{OH}$  concentration shifted toward a higher one as the molar ratio of  $\text{Cl}^-/\text{C}_\text{T}$  increased. The results showed that the optimum pH value was 4, 5, and 5-7 for the molar ratios of 1, 10, and 100 respectively. They also found that, without bicarbonate species, the increase of chloride concentration up to 1250 mM led to a significant decrease in  $\cdot\text{OH}$  concentration, however, it remained rather unchanged when

the chloride concentration was larger than 1250 mM. In contrast, in the presence of both chloride and bicarbonate species, the  $\bullet\text{OH}$  concentration was found to decrease significantly when the chloride concentration reached to a level as high as 250 mM. It was observed that  $\text{H}_2\text{O}_2$  decomposition rate remained the same regardless of pH values and concentrations of chloride and bicarbonate species.

Wang *et al.* (2001) investigated the effect of bicarbonate and carbonate ions on the photodegradation of humic acids by UV/ $\text{H}_2\text{O}_2$  using three different  $\text{HCO}_3^-/\text{CO}_3^{2-}$  concentrations, 0, 1.29 mM and 2.5 mM. They observed that higher content of carbonate species led to higher residual of humic acid throughout the reaction period. In the absence of carbonate species, the pseudo-first order rate constant for humic acid removal was found to be  $0.0256 \text{ min}^{-1}$ . This value was decreased to  $0.0155 \text{ min}^{-1}$  and  $0.0133 \text{ min}^{-1}$  for  $\text{HCO}_3^-/\text{CO}_3^{2-}$  concentration of 1.29 mM and 2.5 mM. They also found that the decomposition of  $\text{H}_2\text{O}_2$  was increased in the presence of carbonate species due to the reaction of  $\text{H}_2\text{O}_2$  with carbonate radicals.

Wang *et al.* (2000) studied the UV-catalyzed hydrogen peroxide oxidation of natural organic matter (NOM) in drinking water. They found that the humic acid decay was fastest ( $k=0.037 \text{ min}^{-1}$ ) when UV/quartz was used as the light source. It was observed that humic acid decomposed at a much slower rate with UV/Pyrex ( $k=0.0025 \text{ min}^{-1}$ ) and sunlight ( $k=0.0007 \text{ min}^{-1}$ ). They also examined that the destruction rate of humic acid increased with increasing  $\text{H}_2\text{O}_2$  concentration up to 2.94 mM and then decreased with further increases. They further investigated the effect of bicarbonate/carbonate ions with the initial carbonate concentration of 100-400 mg/l as  $\text{CaCO}_3$ . It was found that a 22 and 70 % reduction in the humic acid removal ( $k=0.029 \text{ min}^{-1}$  and  $k=0.011 \text{ min}^{-1}$ , respectively) were observed with the initial bicarbonate and carbonate concentrations of 96 mg/l and 124 mg/l, respectively.

Liao and Gurol (1995) investigated the UV/ $\text{H}_2\text{O}_2$  oxidation of BuCl in the presence of carbonate/bicarbonate ions. They observed that the effect of carbonate ions on BuCl removal became more pronounced at lower BuCl concentrations. They also found that the decomposition rate of  $\text{H}_2\text{O}_2$  remained rather constant for carbonate concentration up to 90 mM.



### 3. MATERIALS AND METHODS

#### 3.1. Materials

##### 3.1.1. Dye

Procion Red HE-7B (Reactive Red 141) (MW=1781 g mol<sup>-1</sup>) was purchased from BASF-Istanbul in 75 % purity. The chemical structure of the dye is represented in Figure 3.1. The characteristics of the dye are as follows:

Type: Reactive azo dye (Reactive Red 141)

Formula: C<sub>52</sub>H<sub>34</sub>O<sub>26</sub>S<sub>8</sub>N<sub>14</sub>Cl<sub>2</sub> (as sodium salt)

Color content: approximately 75 %

$\lambda_{\max}$  : 544 nm

MW: 1781 g mol<sup>-1</sup>

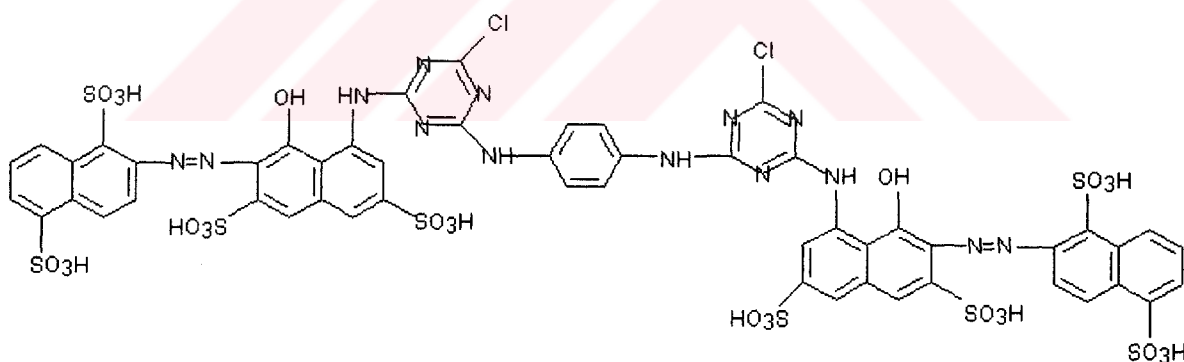


Figure 3.1. The chemical structure of Procion Red HE-7B

##### 3.1.2. Hydrogen Peroxide

Reagent grade hydrogen peroxide (35 %, w/v) was obtained from Merck.

### **3.1.3. Sodium Hydroxide and Hydrochloric Acid**

Reagent grade NaOH (Merck) and HCL (37 %, Merck) were used for pH adjustment.

### **3.1.4. Sodium Bicarbonate**

Reagent grade sodium bicarbonate ( $\text{NaHCO}_3$ , Merck) was used to simulate background impurities of bicarbonate ions.

### **3.1.5. Sodium Carbonate**

Reagent grade sodium carbonate ( $\text{Na}_2\text{CO}_3$ , Merck) was used to simulate background impurities of carbonate ions.

### **3.1.6. Sodium Chloride**

Reagent grade sodium chloride ( $\text{NaCl}$ , Riedel) was used to simulate background impurities of chloride ions.

### **3.1.7. Analytical Equipment**

Unicam-He $\lambda$ ios-Alpha/Beta Double Beam Spectrophotometer was used for the determination of color, hydrogen peroxide and for monitoring the breakdown of the oxidation intermediates.

Sartorius Balance was used for weighing the dye. Oven was used for drying the glassware. All glassware was rinsed first with tap water and then deionized water before use.

## 3.2. Methods

### 3.2.1. Experimental Set-up

The experiments were carried out in a four-liter plexy glass batch reactor, equipped with four Philips 15-Watt low-pressure mercury UV lamps, emitting monochromatic light at 253.7 nm. The lamps were located at the top of the reactor with a perpendicular distance of 5 cm from the surface of the solution. Contents of the reactor were stirred with three magnetic stirrers, located at the bottom of the reactor, to obtain a homogeneous mixture. The schematic diagram of the reactor is given in Figure 3.2.

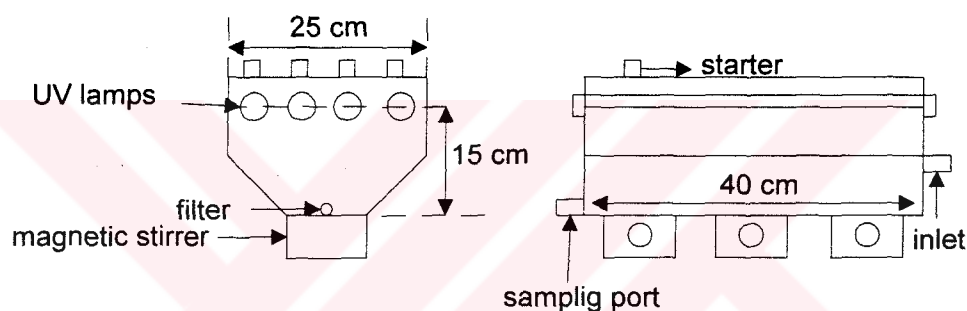


Figure 3.2. The schematic diagram of the photoreactor

### 3.2.2. Experimental Procedure

Procion Red HE-7B was chosen as a model compound in this study to represent reactive azo dyes, which is widely used in textile dyeing operations. Stock dye solutions were prepared by dissolving the dye in deionized water and stirring for 6 hours at 80 °C at a pH value of 10.6 to obtain 100% hydrolysis. The reactor was filled with 3 liters of 25 mg/L of Procion Red HE-7B solution to simulate typical dyebath effluent concentrations.

The experimental scheme consisted of monitoring the degradation of Procion Red under UV radiation alone,  $\text{H}_2\text{O}_2$  alone and UV/ $\text{H}_2\text{O}_2$  combined system.

The optimum pH of the system was selected by irradiation of the dye solutions in the presence of  $\text{H}_2\text{O}_2$  at a pH of 2, 3, 5, 7, 9, and 11. The changes in pH during treatment were also recorded.

The effect of initial dye concentration on the rate of decolorization was determined by exposing 5, 12.5, 25, and 50 ppm Procion Red to UV/ H<sub>2</sub>O<sub>2</sub> oxidation.

The optimum H<sub>2</sub>O<sub>2</sub> concentration in the reactor was determined by monitoring the rate of color degradation at increasing concentrations of H<sub>2</sub>O<sub>2</sub>. The decomposition of H<sub>2</sub>O<sub>2</sub> in the UV/H<sub>2</sub>O<sub>2</sub> system, in the presence and absence of the dye was also monitored.

Varying concentrations of bicarbonate, carbonate and chloride ions were added to the reactor to investigate the scavenging effects. In these experiments, pH was not adjusted.

Samples were withdrawn periodically to analyze color and H<sub>2</sub>O<sub>2</sub> residuals. The color of the samples was monitored at the maximum absorption wavelength of the dye at 544 nm. Hydrogen peroxide residuals were monitored by spectrophotometry at 351 nm based on the reaction of hydrogen peroxide with iodide catalyzed by molybdate (Klassen *et al.*, 1994). The absorbance of the samples was measured at 254 nm to observe the effectiveness of the UV/H<sub>2</sub>O<sub>2</sub> system in the mineralization of the dye since this wavelength is accepted as indicative of organic species having double bonds and/or an aromatic structure (Ravikumar and Gurol, 1994).

The intensity of the light source was determined by a chemical actinometer. The actinometer consisted of a well-oxygenated aqueous solution containing potassium peroxodisulphate (0.01 mol/L) and tert-butanol (0.1 mol/L) which upon irradiation with 254 nm light produced sulphuric acid. Upon photolysis of this solution, hydrogen ions (H<sup>+</sup>) were generated whose formation could be followed with a pH meter. The drop in pH as a function of irradiation time was recorded. The quantum yield of H<sup>+</sup> formation is defined as the ratio of the number of H<sup>+</sup> ions formed per the number of photons absorbed. When the pH data were converted into [H<sup>+</sup>] (pH = - log [H<sup>+</sup>]), and then plotted versus the irradiation time, a linear relationship was obtained.

The quantum yield of  $H^+$  formation ( $\Phi(H^+)$ ) is expressed by Equation 3.1.

$$\Phi(H^+) = \frac{[H^+] \times N_L \times V_{tot} \times 10}{t \times I_{abs} \times M} \quad (3.1)$$

where  $V_{tot}$  denotes the total volume ( $cm^3$ ) of the solution in the reactor,  $M$  is the surface area of the solution ( $cm^2$ ),  $t$  is the irradiation time and  $I_{abs}/N_L$  ( $N_L$ , Avogadro number) is the absorbed fluence rate in terms of Einsteins  $m^{-2} s^{-1}$ .  $[H^+]/t$  value was obtained from the slope of  $[H^+]$  vs.  $t$  plot. Absorbed fluence rate was calculated by using the constant values of  $\Phi(H^+)$ ,  $M$  and  $V_{tot}$ . A reference value of 1.8 was used for  $\Phi(H^+)$ . Incident fluence rate was calculated by Equation 3.2.

$$I_{abs} = I_0 (1 - 10^{-\epsilon \cdot c \cdot l}) \quad (3.2)$$

where  $I_{abs}$  is the absorbed photon fluence rate,  $I_0$  is the incident photon fluence rate,  $l$  is the pathlength,  $\epsilon$  and  $c$  are the molar extinction coefficient ( $20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and concentration of potassium peroxodisulphate, respectively (Mark *et al.*, 1990).

The molar extinction coefficient of the dye at 544 nm and 254 nm was calculated by using the Lambert-Beer equation as represented in Equation 3.3.

$$A = \epsilon \times C \times b \quad (3.3)$$

where  $A$  is the absorbance of the dye solution at time zero,  $C$  is the concentration of the dye expressed in terms of moles per liter and  $b$  is the pathlength.

## 4. RESULTS AND DISCUSSION

### 4.1. Light Intensity

Light intensity was measured by peroxodisulphate/tert-butanol chemical actinometer as described in section 3.2.2. The drop in pH was converted into the increase in  $H^+$  concentration and then plotted versus the irradiation time as shown in Figure 4.1. From the slope of this line ( $[H^+]/t = 5 \times 10^{-6} \text{ M s}^{-1}$ ), the absorbed fluence rate was calculated as  $8.41 \times 10^{-5} \text{ Einsteins m}^{-2} \text{ s}^{-1}$  ( $39.7 \text{ Watts m}^{-2}$ ) by using Equation 3.1, which was 91.3 per cent of the incident fluence rate ( $9.21 \times 10^{-5} \text{ Einsteins m}^{-2} \text{ s}^{-1} = 434.712 \text{ Watts m}^{-2}$ ).

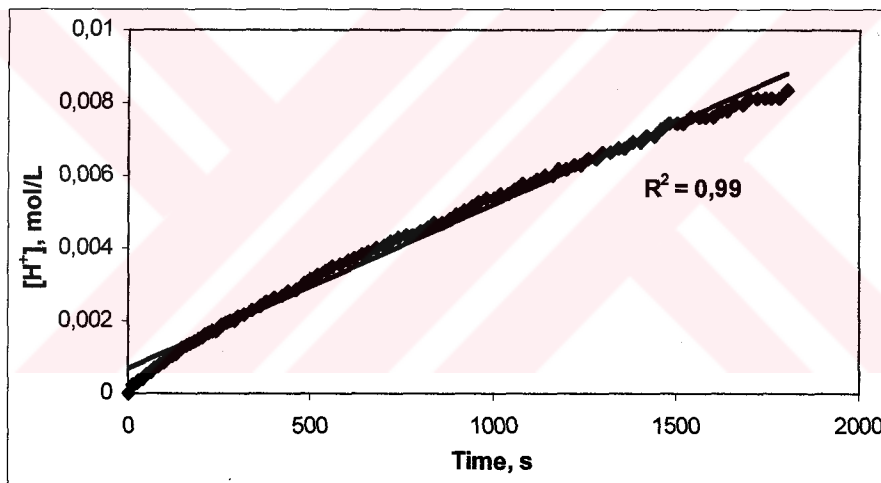
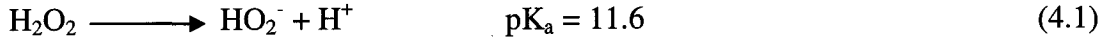


Figure 4.1. UV-light-induced increase in the  $H^+$  concentration in a solution of  $10^{-2} \text{ mol/L K}_2\text{S}_2\text{O}_8$  and  $10^{-1} \text{ mol/L t-butanol}$  vs. irradiation time

### 4.2. Effect of pH on Color Degradation

The effect of pH on the decolorization of Procion Red is illustrated in Figure 4.2. It was found that the rate of color degradation was fastest at  $\text{pH} = 7$ . At  $\text{pH} = 2$  and  $\text{pH} = 11$ , the system was found to be less effective. The less effectiveness under alkaline conditions was attributed to the decomposition of  $\text{H}_2\text{O}_2$  into peroxide anion ( $\text{HO}_2^-$ ) and hydrogen ion ( $\text{H}^+$ ) with a maximum rate at the pH of its  $\text{pK}_a$  value as presented in Equation 4.1. This

resulted in lower  $\bullet\text{OH}$  formation to attack Procion Red due to the decreased  $\text{H}_2\text{O}_2$  concentration.



Furthermore, the molar extinction coefficient of  $\text{HO}_2^-$  ( $240 \text{ M}^{-1} \text{ cm}^{-1}$ , Buxton *et al.*, 1988) is more than ten times greater than that of the  $\text{H}_2\text{O}_2$  ( $19.6 \text{ M}^{-1} \text{ cm}^{-1}$ , Bolton and Cater, 1994). As a consequence,  $\text{HO}_2^-$  might absorb more light and decrease the rate of absorption of UV by  $\text{H}_2\text{O}_2$ . In addition,  $\text{HO}_2^-$  reacts with  $\bullet\text{OH}$  more than two orders of magnitude than  $\text{H}_2\text{O}_2$  does as presented in Equation 4.2. This might also have lowered the concentration of  $\bullet\text{OH}$  in the solution resulting in a lower color degradation rate at  $\text{pH}=11$ .

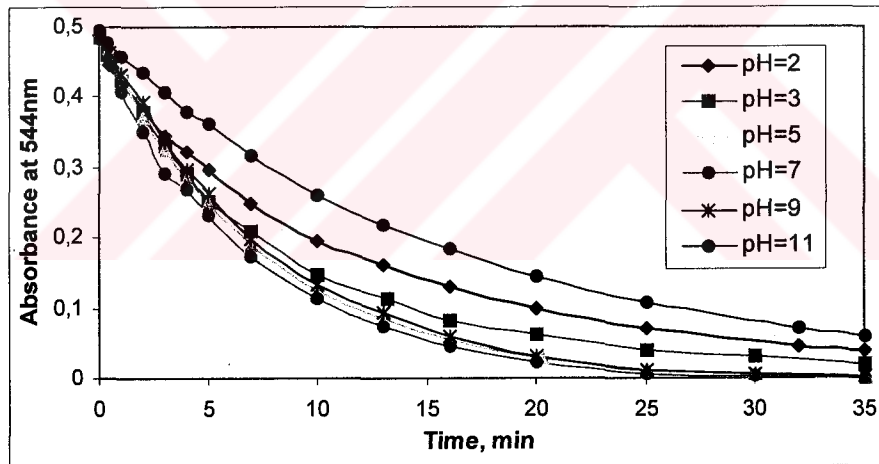
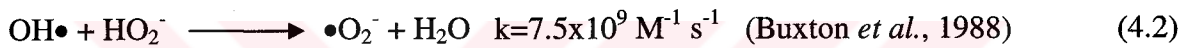


Figure 4.2. Effect of pH on the decolorization of Procion Red (Procion Red=25 ppm,  $\text{H}_2\text{O}_2=1.36 \text{ mM}$ )

### 4.3. Effect of Initial Dye Concentration on Color Degradation

To investigate the effect of initial dye concentration on the rate of decolorization, UV/ $\text{H}_2\text{O}_2$  experiments were carried out with 5, 12.5, 25 and 50 ppm Procion Red. It was found that increasing the dye concentration decreased the rate of color removal. The rate of decolorization at varying concentrations of Procion Red is presented in Figure 4.3.

(Pseudo-first order decolorization rate constants for different concentrations of Procion Red are given in Figure 4.3.)

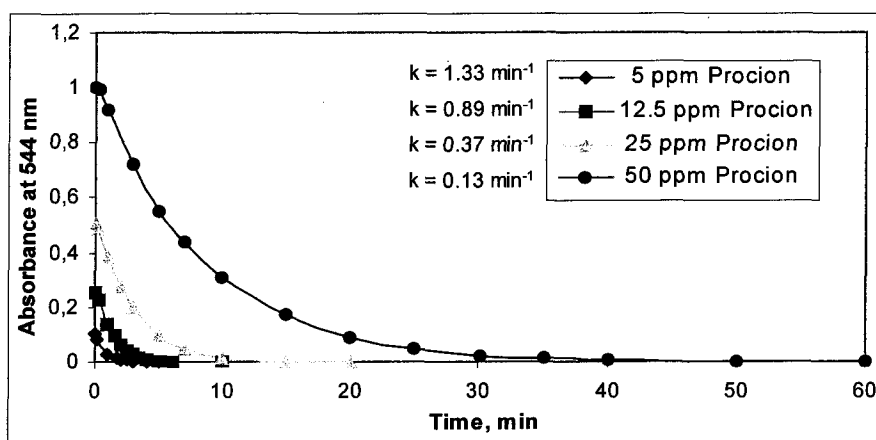


Figure 4.3. Effect of initial dye concentration on the rate of decolorization ( $H_2O_2=4.1$  mM)

## 4.4. Degradation of Procion Red

### 4.4.1. Spectral Changes

Time dependent changes in the absorption spectra of the dye solution between 200-800 nm band were monitored as presented in Figure 4.4. It was found that the absorption peak at 544 nm was removed in 10 minutes.

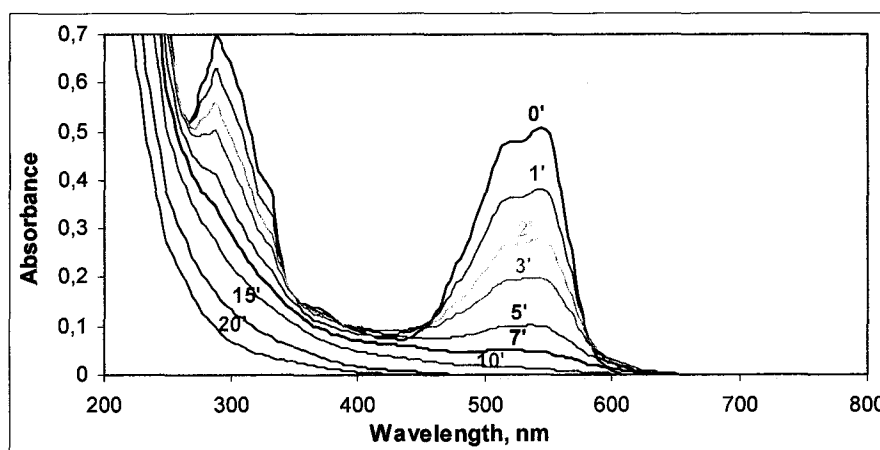


Figure 4.4. Changes in the absorption spectra of 25 ppm Procion Red exposed to UV/ $H_2O_2$  oxidation ( $pH_0 = 7$ ,  $H_2O_2 = 4.1$  mM)



#### 4.4.2. pH changes

The formation of organic acids led to a decrease in the solution pH during treatment. Initial pH of the solution was 7 and within 20 minutes of irradiation, this value decreased to 3.5 and then remained nearly constant up to 60 minutes as represented in Figure 4.5.

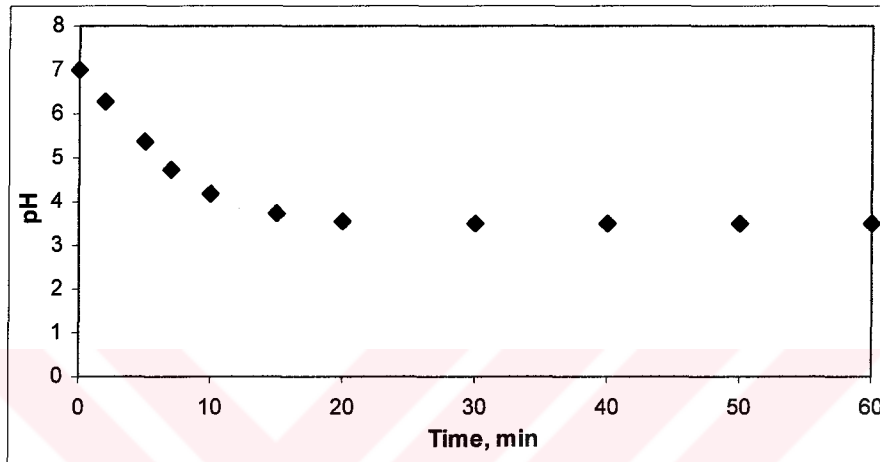


Figure 4.5. pH changes with time during UV/H<sub>2</sub>O<sub>2</sub> treatment (pH<sub>0</sub> = 7, Procion Red = 25 ppm, H<sub>2</sub>O<sub>2</sub> = 4.1 mM)

#### 4.4.3. Rate of color degradation

Color degradation was found to follow first order kinetics as represented by Equation 4.3.

$$dC/dt = k' C \quad (4.3)$$

where,  $C$  is the concentration of the dye (mass/volume) and  $k'$  is the pseudo-first-order reaction rate constant ( $\text{time}^{-1}$ ). Upon integration of Equation 4.3, the following equation is obtained.

$$\ln (C_t/C_0) = -k' t \quad (4.4)$$

where,  $t$  is the irradiation time ( $\text{min}^{-1}$ ),  $C_0$  and  $C_t$  are the concentration of Procion Red at time zero and at time  $t$ , respectively. Absorbance values were used instead of concentration as presented in Equation 4.5.

$$\ln (A_t/A_0) = -k' t \quad (4.5)$$

where,  $A_0$  and  $A_t$  are the absorbance of Procion Red at 544 nm at time zero and at time  $t$ , respectively.

Complete decolorization was achieved in 15 minutes of UV/ $\text{H}_2\text{O}_2$  treatment. Time related absorbance decay of Procion Red by UV/ $\text{H}_2\text{O}_2$  system is presented in Figure 4.6.

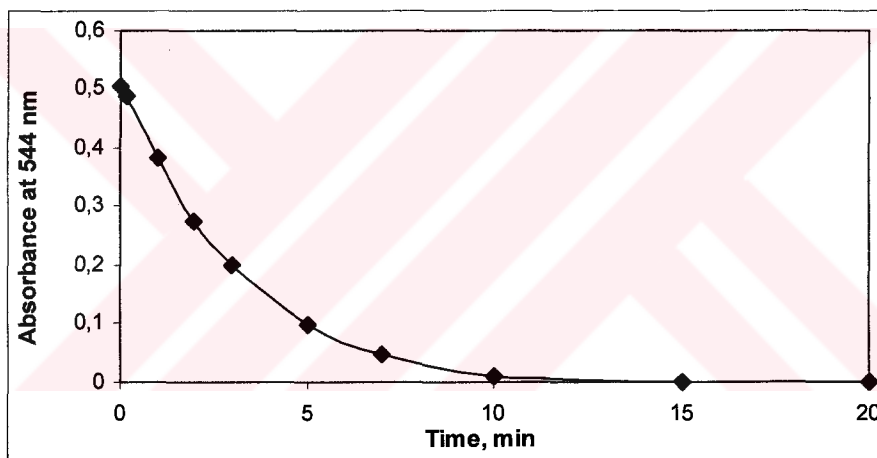


Figure 4.6. Degradation of 25 ppm Procion Red by UV/ $\text{H}_2\text{O}_2$  system ( $\text{H}_2\text{O}_2=4.1$  mM,  $\text{pH}_0=7$ )

The pseudo-first order color degradation rate constant was determined by Equation 4.5. Estimation of the first order color degradation rate constant by linear regression is represented in Figure 4.7.

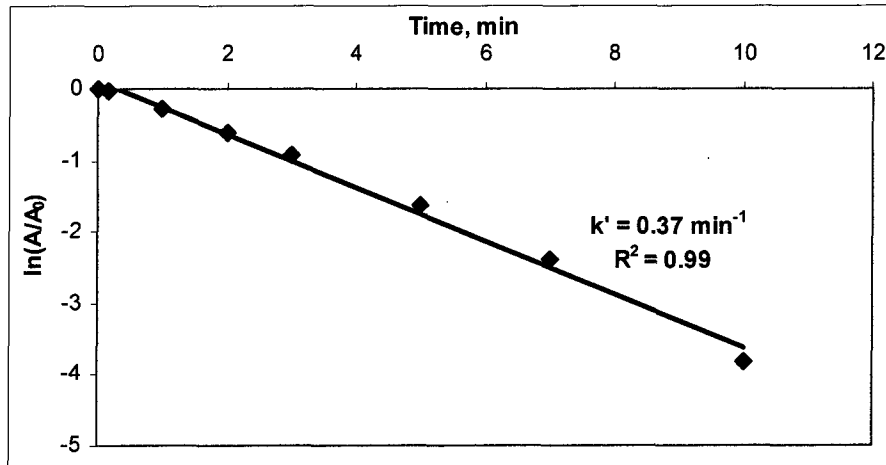


Figure 4.7. Estimation of the pseudo-first order color degradation rate constant by linear regression

#### 4.4.4. Degradation by UV alone and H<sub>2</sub>O<sub>2</sub> alone

Experiments were performed in the presence of UV alone and H<sub>2</sub>O<sub>2</sub> alone to investigate their individual effect on the rate of decolorization. A slight UV irradiation effect was observed on color removal with a rate constant of 0.0025 min<sup>-1</sup>. However, the color still remained unchanged when H<sub>2</sub>O<sub>2</sub> alone was applied in the reaction mixture. These results indicated that the hydroxyl radicals generated by the photodissociation of H<sub>2</sub>O<sub>2</sub> were the main responsible species for the degradation of Procion Red. The decay of absorbance by UV alone and H<sub>2</sub>O<sub>2</sub> alone is presented in Figure 4.8.

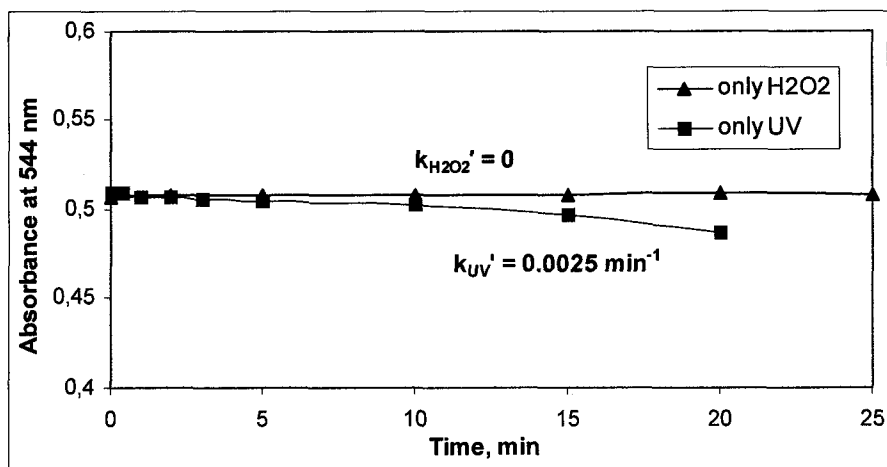
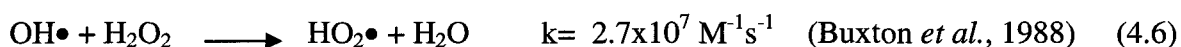


Figure 4.8. Decolorization by UV alone and H<sub>2</sub>O<sub>2</sub> alone

#### 4.5. Effect of initial H<sub>2</sub>O<sub>2</sub> Concentration on Color Degradation

The effect of initial H<sub>2</sub>O<sub>2</sub> concentration on the rate of color degradation was investigated by inputting various concentrations of H<sub>2</sub>O<sub>2</sub> and estimating the first-order color decay constants. The plot of  $k'$  against H<sub>2</sub>O<sub>2</sub> input concentrations is presented in Figure 4.9. It was found that the rate constant increased with increasing H<sub>2</sub>O<sub>2</sub> dose, up to a threshold value beyond which it was inhibited with further increases in H<sub>2</sub>O<sub>2</sub> concentration. This is not unusual, for the fact that H<sub>2</sub>O<sub>2</sub> itself acts as a scavenger of OH• in accordance with the reaction below (Buxton *et al.*, 1988):



When the concentration of H<sub>2</sub>O<sub>2</sub> is in excess, that is, it remains in solution long enough to exhibit a hydroxyl demand, the availability of hydroxyl radicals to supply the demand of the dye molecule is limited (Ince and Gönenç, 1997).

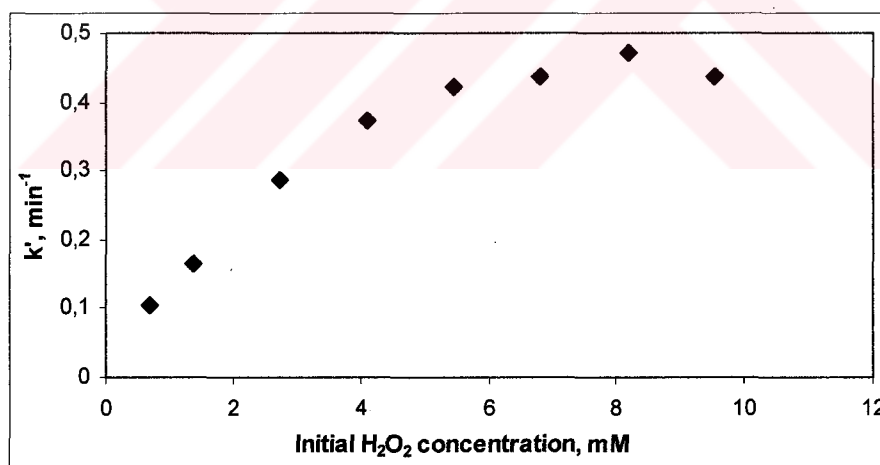


Figure 4.9. Effect of initial H<sub>2</sub>O<sub>2</sub> concentration on the rate of color degradation

When 5.45 mM, 6.81 mM and 8.18 mM H<sub>2</sub>O<sub>2</sub> concentrations were used, the color degradation rate constants were 0.42 min<sup>-1</sup>, 0.43 min<sup>-1</sup> and 0.47 min<sup>-1</sup>, respectively. On the other hand, it was found that the time taken for 100 per cent decolorization was 15 minutes for the H<sub>2</sub>O<sub>2</sub> concentrations of 4.1, 5.45, 6.81 and 8.18 mM. For considering the cost of the oxidant, the optimum H<sub>2</sub>O<sub>2</sub> concentration in this study was selected as 4.1 mM which yielded a degradation rate constant of 0.37 min<sup>-1</sup>.

#### 4.6. Decomposition of Hydrogen Peroxide

The photolysis of  $\text{H}_2\text{O}_2$  was investigated by monitoring its concentration during 120 min irradiation of 4.1 mM  $\text{H}_2\text{O}_2$  in deionized water. The effect of the presence of the dye on the rate of photolysis was investigated by running the test in a solution containing 25 ppm Procion Red. It was found that nearly 98 per cent of  $\text{H}_2\text{O}_2$  dissociated within the contact period in the presence and absence of Procion Red. However, the rate of photolysis was 1.55 times slower in the presence of the dye. This was attributed to the partial absorption of the UV light by the dye (Ince *et al.*, 1997). The rate of  $\text{H}_2\text{O}_2$  photolysis in the presence and absence of Procion Red is presented in Figure 4.10. It was also observed that the concentration of  $\text{H}_2\text{O}_2$  remained constant when there was no UV irradiation as shown in Figure 4.10.

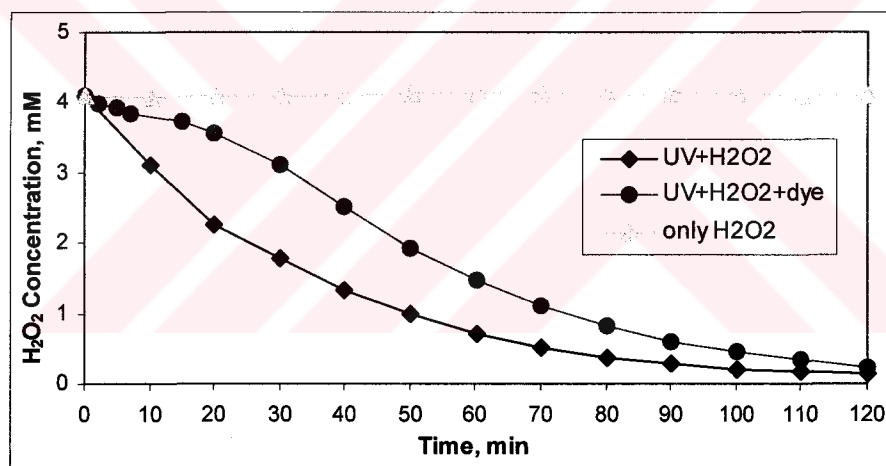


Figure 4.10. Photolysis of  $\text{H}_2\text{O}_2$  in the presence and absence of Procion Red ( $\text{H}_2\text{O}_2=4.1$  mM, Procion Red=25 ppm)

$\text{H}_2\text{O}_2$  photodissociation was found to fit first-order kinetics. Estimation of  $\text{H}_2\text{O}_2$  photodissociation rate constants in the presence and absence of Procion Red by non-linear regression is represented in Figure 4.11.  $\text{H}_2\text{O}_2$  photodissociation rate constants in the absence and presence of Procion Red were found as  $0.029 \text{ min}^{-1}$  and  $0.0187 \text{ min}^{-1}$ , respectively.

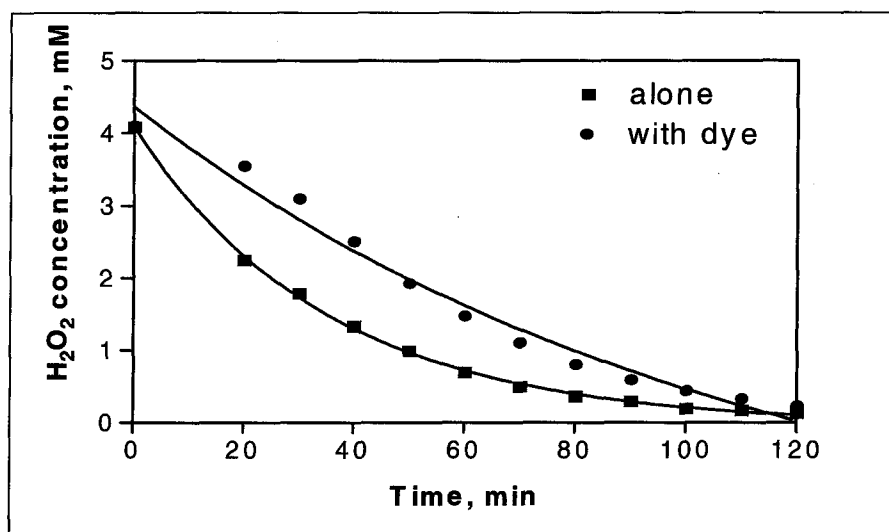


Figure 4.11. Estimation of the H<sub>2</sub>O<sub>2</sub> decomposition rate constants in the presence and absence of 25 ppm Procion Red by non-linear regression (H<sub>2</sub>O<sub>2</sub>=4.1 mM) The solid lines represent the fit of experimental data to  $(H_2O_2)_t = (H_2O_2)_0 e^{-kt}$

#### 4.7. Degradation of Organic Carbon

The absorbance of the samples was measured at 254 nm to observe the effectiveness of the UV/H<sub>2</sub>O<sub>2</sub> system in the mineralization of the dye since this wavelength is accepted as indicative of organic species having double bonds and/or an aromatic structure (Ravikumar and Gürol, 1994). In 15 minutes, at which the dye was completely decolorized, only 49.8 per cent organic carbon removal was observed. It was found that 91.7 per cent removal was achieved in 60 minutes. The changes in the absorbance at 254 nm with time are illustrated in Figure 4.12. Organic carbon degradation was also found to follow first order kinetics. Figure 4.13 represents the estimation of the rate of organic carbon degradation by linear regression.

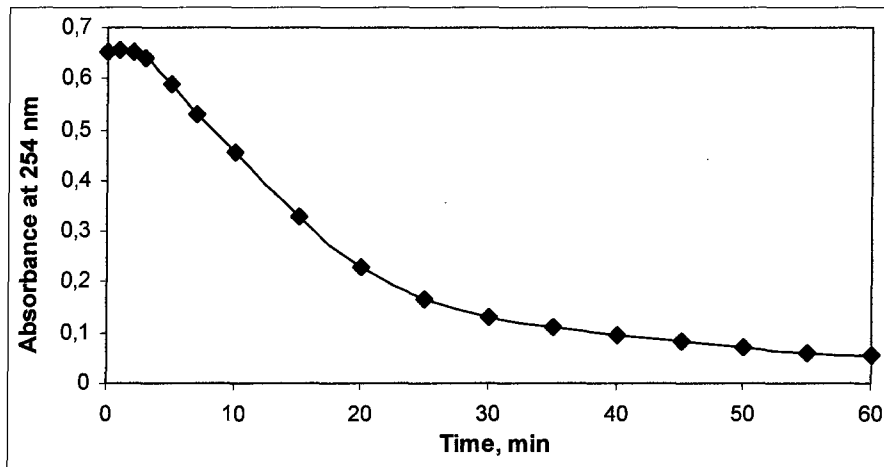


Figure 4.12. Degradation of organic carbon (Procion Red = 25 ppm,  $\text{H}_2\text{O}_2 = 4.1$  mM)

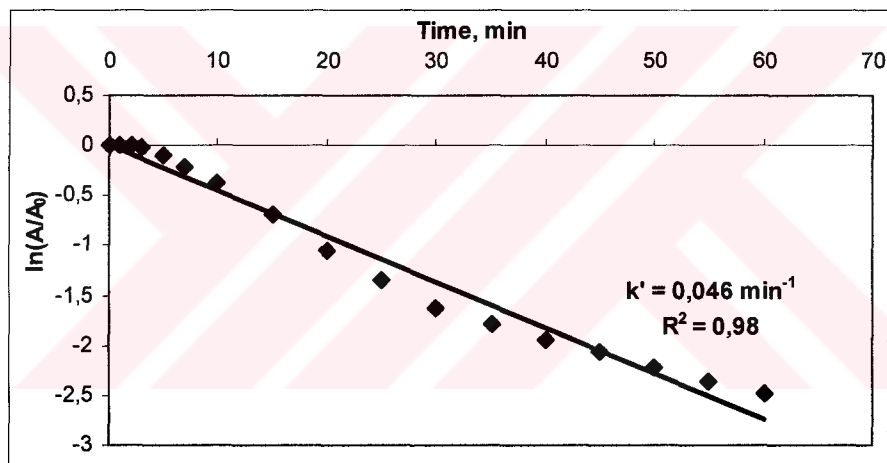


Figure 4.13. Estimation of the organic carbon degradation rate by linear regression

## 4.8. Effect of Scavengers

### 4.8.1. Carbonate species

The concentrations of bicarbonate and carbonate ions are directly related to the pH of the water, and the total inorganic carbonate ( $c_T$ ) concentration because of the dissociation of carbonic acid ( $H_2CO_3^*$ ). Since carbonic acid is a diprotic acid, it will dissociate in two steps, first to bicarbonate then to carbonate. The first dissociation of carbonic acid can be represented as in Equation 4.7.



Equation 4.8 presents the second dissociation of carbonic acid which is from bicarbonate to carbonate.



Equation 4.7 and Equation 4.8 are pH dependent and even small pH variations affect these reactions because of the change in carbonate/bicarbonate ion distribution (Tchobanoglous and Schroeder, 1985).

The  $c_T$  concentration can be written as follows:

$$c_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (4.9)$$

Figure 4.14 is a concentration diagram showing the relative distribution of carbonate species with respect to pH. It is obvious that at higher pH, the equilibrium between bicarbonate and carbonate species shifts towards carbonate ion, which has a higher reactivity with  $OH\bullet$  ( $k=3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) than the bicarbonate ion ( $k=8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ). As the pH falls below 5, the  $OH\bullet$  scavenging becomes negligible since the equilibrium shifts to the carbonic acid, which has a very low reactivity with  $OH\bullet$  (Liao and Gürol, 1995).



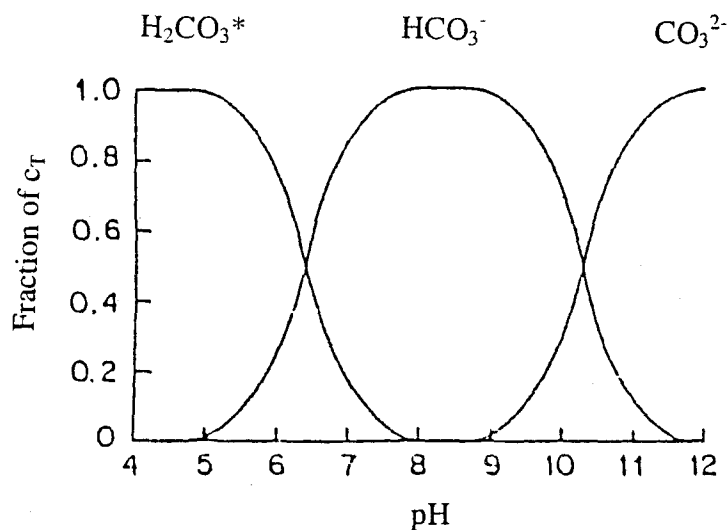


Figure 4.14. Distribution of total inorganic carbonate species in water (Schock, 1971)

4.8.1.1. Effect of bicarbonate ions on color degradation: The effect of bicarbonate ions on the degradation of Procion Red was investigated by incremental increases in  $HCO_3^-$  concentrations within 2.5-100 mM.

The influence of  $HCO_3^-$  addition on the removal of color was investigated by monitoring the dye spectrum during 35 minutes exposure to UV/ $H_2O_2$  in the presence of 100 mM  $HCO_3^-$ . The data are shown in Figure 4.15. When compared to the spectral changes of the dye in the absence of  $HCO_3^-$  (Figure 4.4), it is obvious that the rate of color degradation is inhibited by  $OH\bullet$  scavenging effect of  $HCO_3^-$ . In the absence of  $HCO_3^-$ , the color was almost removed in 10 minutes, whereas, in the presence of 100 mM  $HCO_3^-$ , 56 per cent of color remained unremoved at the end of 10 minutes.

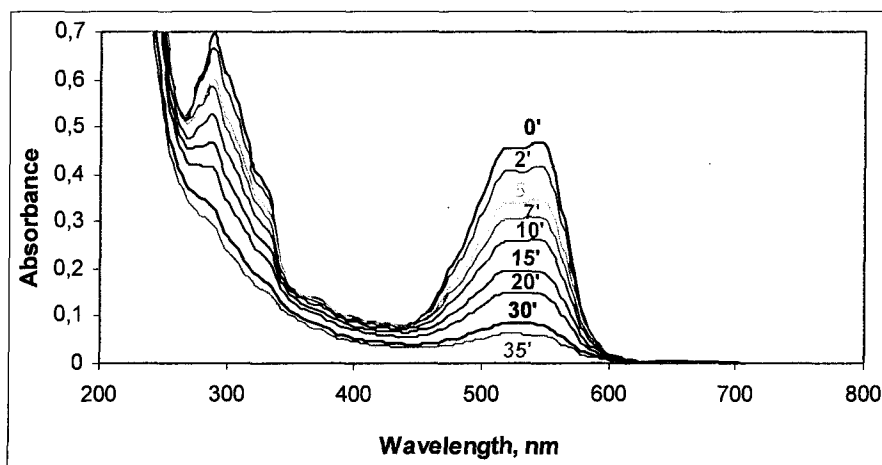


Figure 4.15. Changes in the absorption spectra of the dye solution in the presence of 100 mM  $\text{HCO}_3^-$  exposed to UV/ $\text{H}_2\text{O}_2$  oxidation (Procion Red = 25 ppm,  $\text{H}_2\text{O}_2$  = 4.1 mM)

Figure 4.16 shows the relative rates of color removal in the presence of various concentrations of bicarbonate species. At low concentrations of  $\text{HCO}_3^-$  (2.5 and 5 mM), radical scavenging effects were negligible and the dye was 100 per cent decolorized in 15 minutes as it was in the absence of  $\text{HCO}_3^-$ . At concentrations higher than 5 mM, the scavenging effects began to be apparent, inhibiting the rate significantly with increased concentrations. When 10, 20, 50 and 100 mM  $\text{HCO}_3^-$  concentrations were added to the solution, the pH ranged between 8.6 and 8.7, which showed that  $\text{HCO}_3^-$  species were dominant. It was found that pseudo-first order color degradation rate constant decreased from  $0.33 \text{ min}^{-1}$  to  $0.06 \text{ min}^{-1}$  as the bicarbonate concentration was increased from 2.5 mM to 100 mM, respectively. Although 100 per cent color removal was observed in 15 minutes in the presence of 2.5 mM and 5 mM  $\text{HCO}_3^-$ , only 57 per cent removal was accomplished in the presence of 100 mM  $\text{HCO}_3^-$  in 15 minutes.

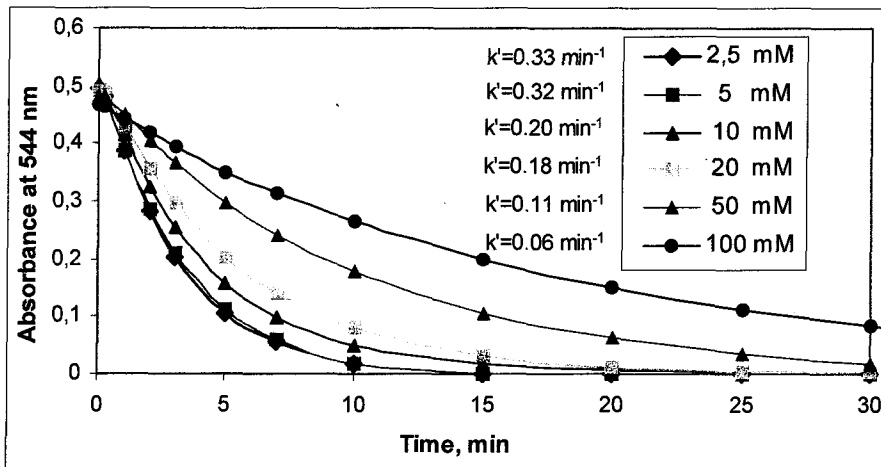


Figure 4.16. Dependence of color degradation on the concentration of  $\text{HCO}_3^-$  in the UV/ $\text{H}_2\text{O}_2$  system (Procion Red= $25 \text{ mg l}^{-1}$ ,  $\text{H}_2\text{O}_2=4.1 \text{ mM}$ )

The effect of increasing concentrations of bicarbonate on the rate of color removal is presented in Figure 4.17.

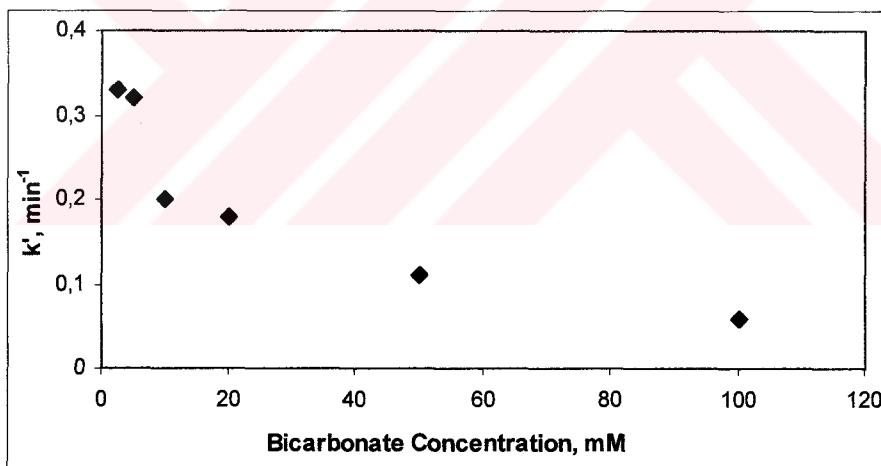


Figure 4.17. Effect of  $\text{HCO}_3^-$  concentration on the color degradation rate constant

**4.8.1.2. Effect of carbonate ions on color degradation:** The effect of carbonate addition was examined by monitoring the rate of dye degradation in the presence of 1, 2.5, 5 and 10 mM  $\text{CO}_3^{2-}$ , respectively.

Figure 4.18 shows the changes in the absorption spectra of the dye solution during 40 minutes of exposure to UV/ $\text{H}_2\text{O}_2$  in the presence of 5mM  $\text{CO}_3^{2-}$ . Although absorption peak at 544 nm was completely removed in 15 minutes in the absence of any scavengers, there

was still absorbance at 544 nm at the end of 40 minutes in the presence of 5mM  $\text{CO}_3^{2-}$ . This was the result of lowered concentration of hydroxyl radicals in the system due to the scavenging of  $\text{OH}\bullet$  by carbonate ions.

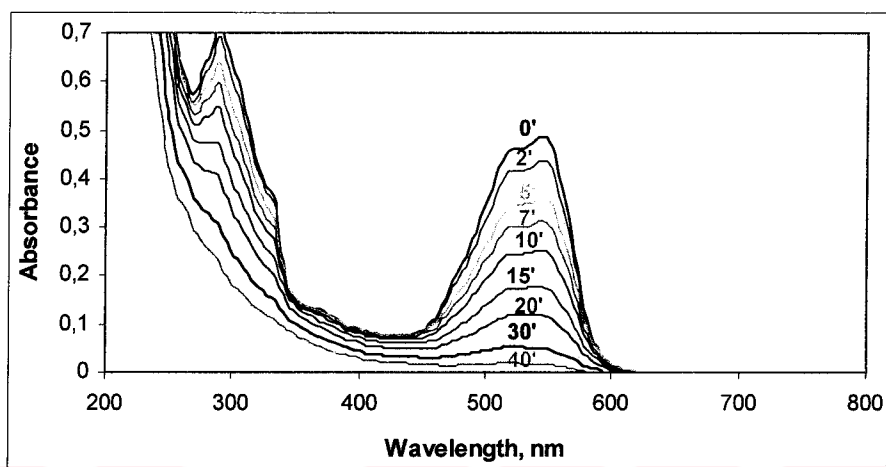


Figure 4.18. Changes in the absorption spectra of the dye solution in the presence of 5 mM  $\text{CO}_3^{2-}$  exposed to UV/ $\text{H}_2\text{O}_2$  oxidation (Procion Red=25 ppm,  $\text{H}_2\text{O}_2$ =4.1 mM)

It was found that higher content of  $\text{CO}_3^{2-}$  ions led to higher residuals of color in the effluent. When 1, 2.5, 5 and 10 mM  $\text{CO}_3^{2-}$  concentrations were added to the solution, 85, 74, 63, and 53 per cent color removal was achieved, respectively. The pH ranged between 10.4 and 11 with increasing concentrations of carbonate which showed that  $\text{HCO}_3^-$  species were still present as represented by Figure 4.14. As pH was increased, the equilibrium between  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  species shifted towards  $\text{CO}_3^{2-}$  ion, and the rate was lowered due to the higher reactivity of  $\text{CO}_3^{2-}$  with  $\text{OH}\bullet$  than  $\text{HCO}_3^-$ . The effect of  $\text{CO}_3^{2-}$  concentration on the rate of color degradation is presented in Figure 4.19.

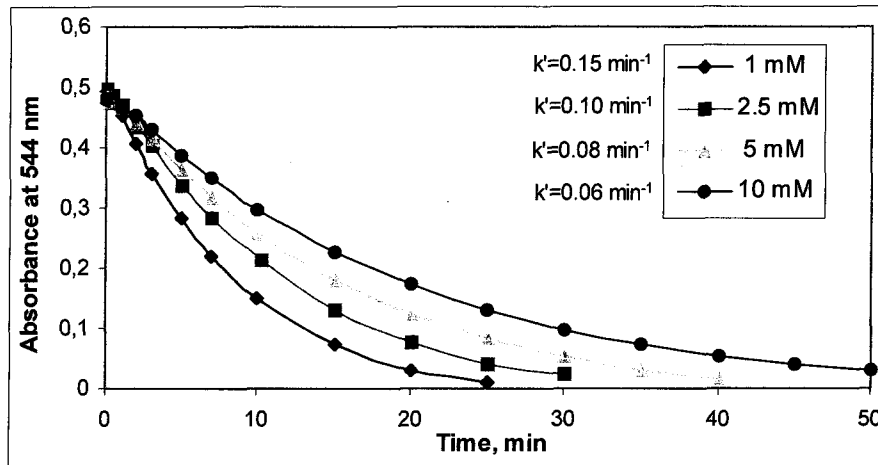


Figure 4.19. Dependence of color degradation on the concentration of  $\text{CO}_3^{2-}$  in the UV/ $\text{H}_2\text{O}_2$  system (Procion Red= $25 \text{ mg l}^{-1}$ ,  $\text{H}_2\text{O}_2=4.1 \text{ mM}$ )

The effect of increasing concentrations of carbonate on the rate of color removal is presented in Figure 4.20.

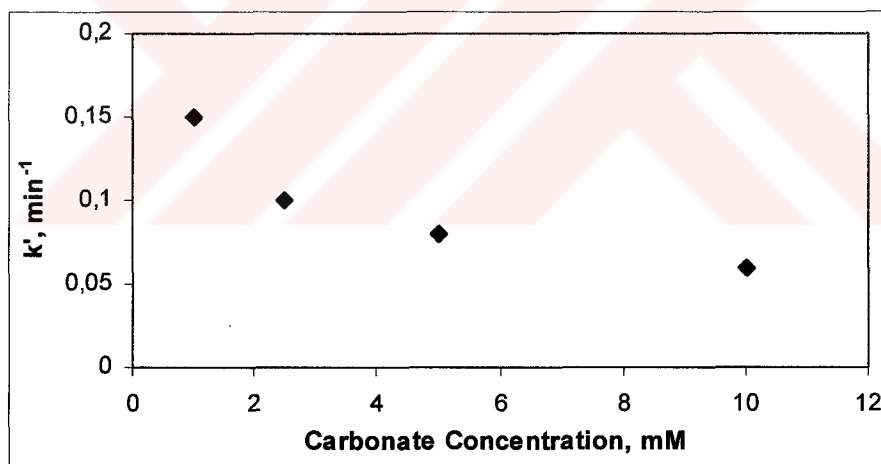


Figure 4.20. Effect of  $\text{CO}_3^{2-}$  concentration on the color degradation rate constant

#### 4.8.2. Chloride species

The effect of chloride ion on the degradation of Procion Red was investigated by adding increasing concentrations of  $\text{Cl}^-$  within 2.5-2000 mM, and monitoring color of the effluents. The pH of the solution ranged between 5.7 and 6.4 with increasing concentrations of chloride.

Time dependent changes in the absorption spectra of the dye solution during 25 minutes of exposure to UV/ $\text{H}_2\text{O}_2$  in the presence of 1000 mM  $\text{Cl}^-$  are presented in Figure 4.21. This concentration was selected because it is a typical value in Procion dyeing baths. It was found that 25 per cent of color remained unremoved in 15 minutes in the presence of 1000 mM  $\text{Cl}^-$ , whereas complete decolorization was accomplished in 15 minutes in the absence of chloride species.

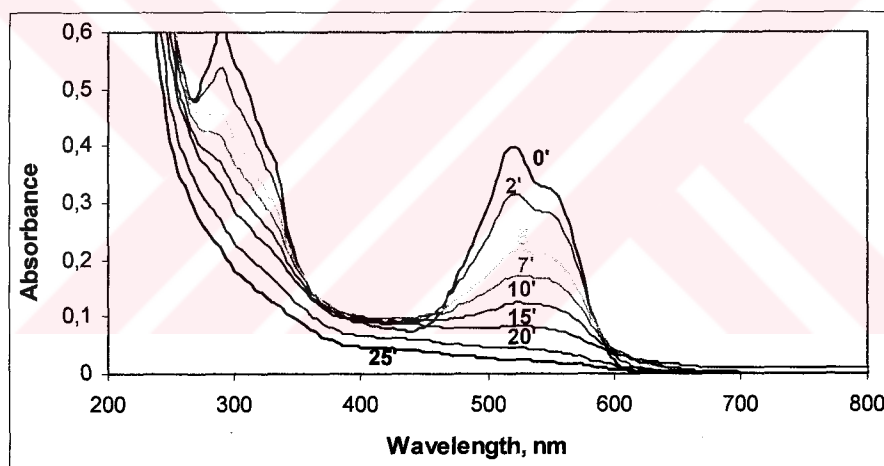


Figure 4.21. Changes in the absorption spectra of the dye solution in the presence of 1000 mM  $\text{Cl}^-$  exposed to UV/ $\text{H}_2\text{O}_2$  oxidation (Procion Red=25 ppm,  $\text{H}_2\text{O}_2$ =4.1 mM)

It was found that  $\text{Cl}^-$  decreased the rate only slightly up to a concentration of 100 mM. The color degradation rate constant reduced from  $0.35 \text{ min}^{-1}$  to  $0.31 \text{ min}^{-1}$  as the  $\text{Cl}^-$  concentration was increased from 2.5 mM to 100 mM, respectively. At concentrations higher than 100 mM, the increase in  $\text{Cl}^-$  concentration led to a significant decrease in the color degradation rate constant up to 1250 mM, but remained almost unchanged for the concentrations higher than 1250 mM. The data are presented in Figure 4.22. A similar result was observed by Liao *et al.* (2001). They found that the concentration of  $\text{OH}^\bullet$  remained unchanged for  $\text{Cl}^-$  concentrations higher than 1250 mM.

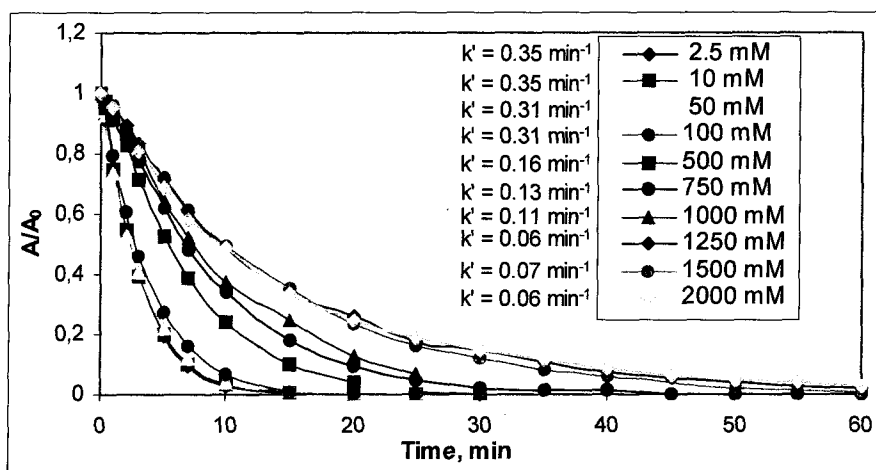


Figure 4.22. Dependence of color degradation on the concentration of  $\text{Cl}^-$  in the  $\text{UV}/\text{H}_2\text{O}_2$  system (Procion Red= $25 \text{ mg l}^{-1}$ ,  $\text{H}_2\text{O}_2=4.1 \text{ mM}$ )

The effect of increasing concentrations of chloride on the rate of color removal is presented in Figure 4.23.

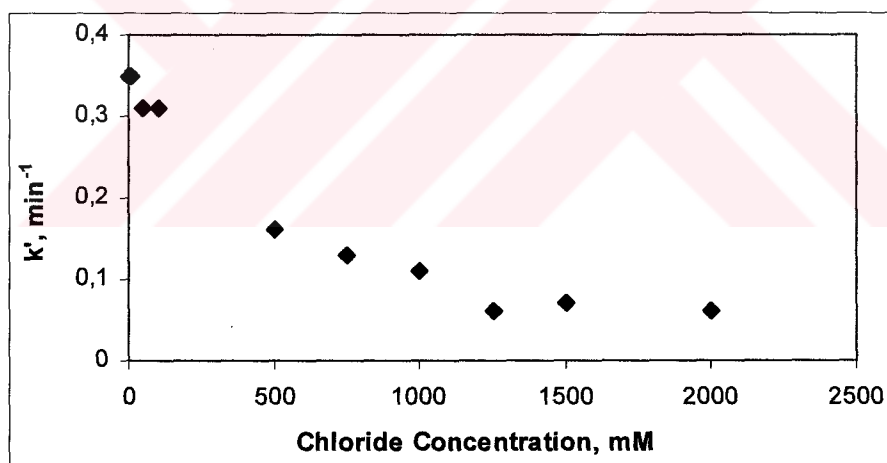


Figure 4.23. Effect of  $\text{Cl}^-$  concentration on the color degradation rate constant

#### 4.8.3. Combined presence of bicarbonate and carbonate species

The combined effect of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions on color removal was investigated using three different molar ratios of  $\text{HCO}_3^-/\text{CO}_3^{2-}$ . While  $\text{CO}_3^{2-}$  concentration was fixed at 10 mM,  $\text{HCO}_3^-$  concentrations of 10, 50, and 100 mM were added to the solution. Initial pH of the solution increased from 9.1 to 10.1 with decreasing  $\text{HCO}_3^-$  concentrations, which showed that there was no carbonic acid in the solution. The first order color degradation rate constants were found to be  $0.046 \text{ min}^{-1}$ ,  $0.038 \text{ min}^{-1}$  and  $0.033 \text{ min}^{-1}$  for  $C_T$  concentrations of 20 mM ( $\text{HCO}_3^-/\text{CO}_3^{2-}=1$ ), 60 mM ( $\text{HCO}_3^-/\text{CO}_3^{2-}=5$ ), 110 mM ( $\text{HCO}_3^-/\text{CO}_3^{2-}=10$ ), respectively. The dependence of color removal on the combined presence of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions is represented in Figure 4.24.

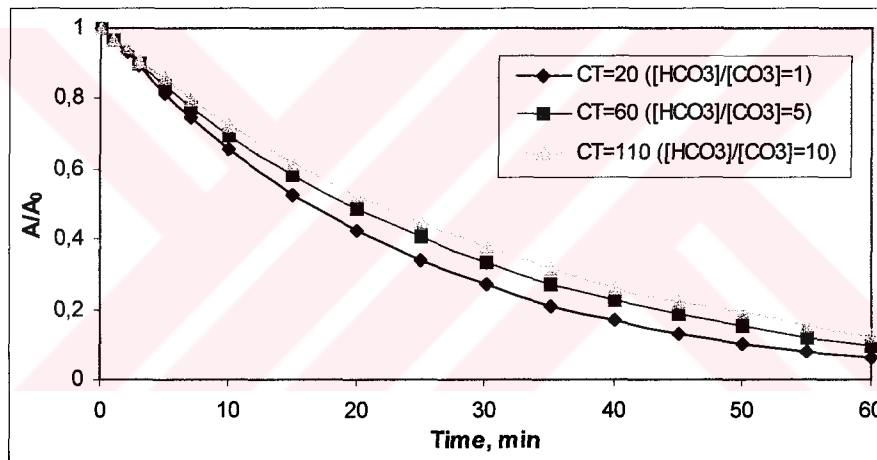


Figure 4.24. Dependence of color removal on  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  concentrations (Procion Red= $25 \text{ mg l}^{-1}$ ,  $\text{H}_2\text{O}_2=4.1 \text{ Mm}$ )

#### 4.8.4. Combined presence of bicarbonate, carbonate and chloride species

Bicarbonate, carbonate and chloride ions were added to the dye solution simultaneously to investigate if there was any synergy. The addition scheme was to hold two species constant and change the other. In all cases, increasing one of the ions' concentration resulted in a lower color removal rate. The data are presented in Figure 4.25. Note that only in one case, the concentration of  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  were 100 mM and 5 mM, respectively.



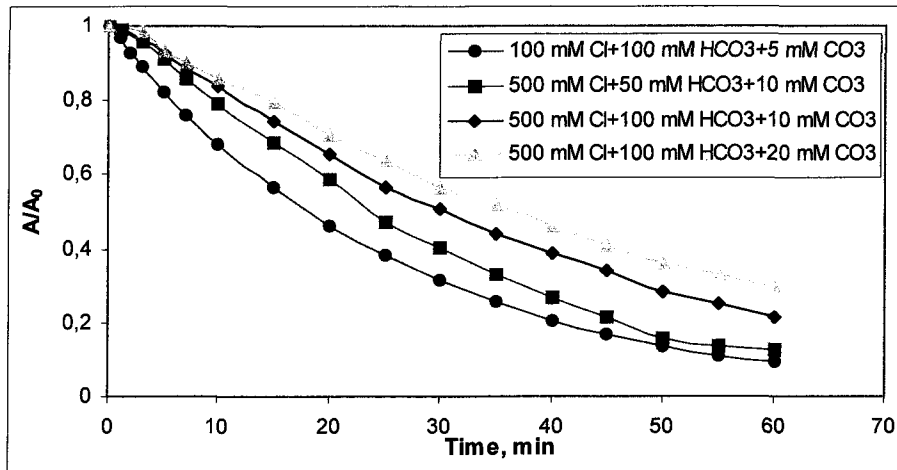


Figure 4.25. Dependence of color removal on  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  concentrations (Procion Red= $25 \text{ mg l}^{-1}$ ,  $\text{H}_2\text{O}_2=4.1 \text{ mM}$ ,  $\text{pH}=9.08-10.08$ )

#### 4.8.5. Comparison of changes in absorption spectra

The changes in the absorption spectra of the dye solution between 200-800 nm band in the absence of scavengers and presence of 100 mM  $\text{HCO}_3^-$  and 1000 mM  $\text{Cl}^-$ , at time zero, at 5 and 10 minutes were compared as presented in Figure 4.26, Figure 4.27 and Figure 4.28. It was found that at time zero, a higher peak was observed in the absence of scavengers and the peak in the presence of 1000 mM  $\text{Cl}^-$  was lower than in the presence of 100 mM  $\text{HCO}_3^-$ . The lower peak was due to the more turbid sample in the presence of 1000 mM  $\text{Cl}^-$ .

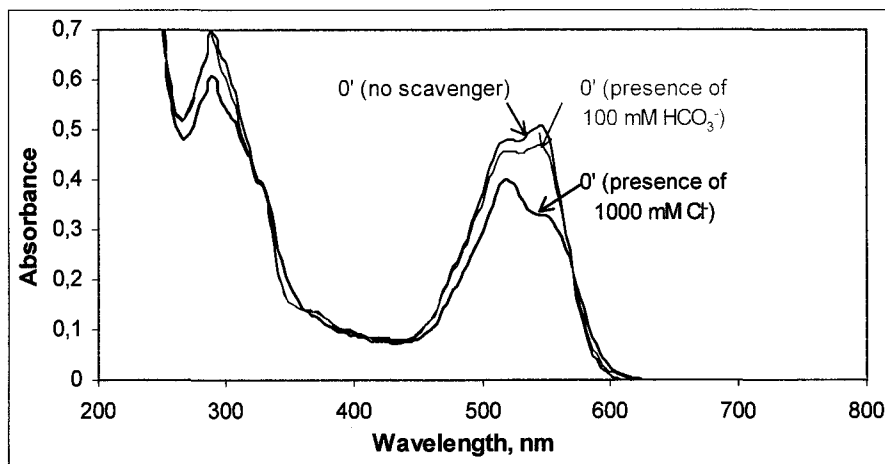


Figure 4.26. Changes in the absorption spectra of the dye solution at time zero in the absence of scavengers and presence of 100 mM  $\text{HCO}_3^-$  and 1000 mM  $\text{Cl}^-$  exposed to UV/ $\text{H}_2\text{O}_2$  oxidation (Procion Red= $25 \text{ ppm}$ ,  $\text{H}_2\text{O}_2=4.1 \text{ mM}$ )

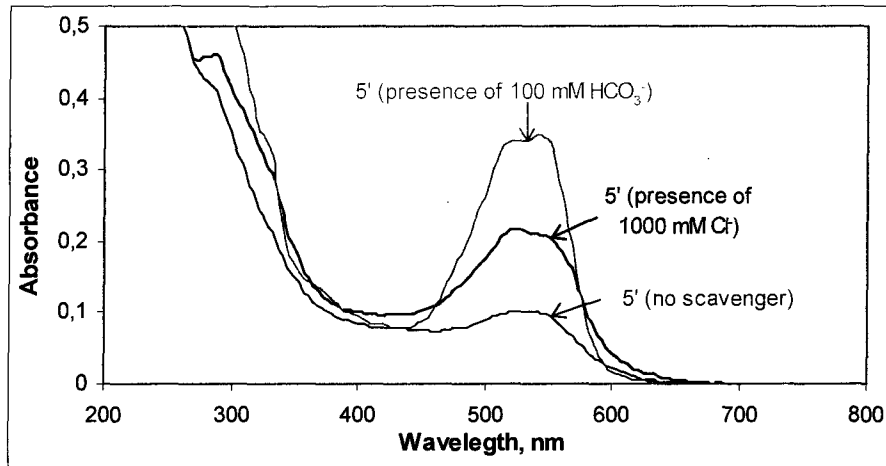


Figure 4.27. Changes in the absorption spectra of the dye solution at 5 minutes in the absence of scavengers and presence of 100 mM  $\text{HCO}_3^-$  and 1000 mM  $\text{Cl}^-$  exposed to UV/ $\text{H}_2\text{O}_2$  oxidation (Procion Red=25 ppm,  $\text{H}_2\text{O}_2=4.1$  mM)

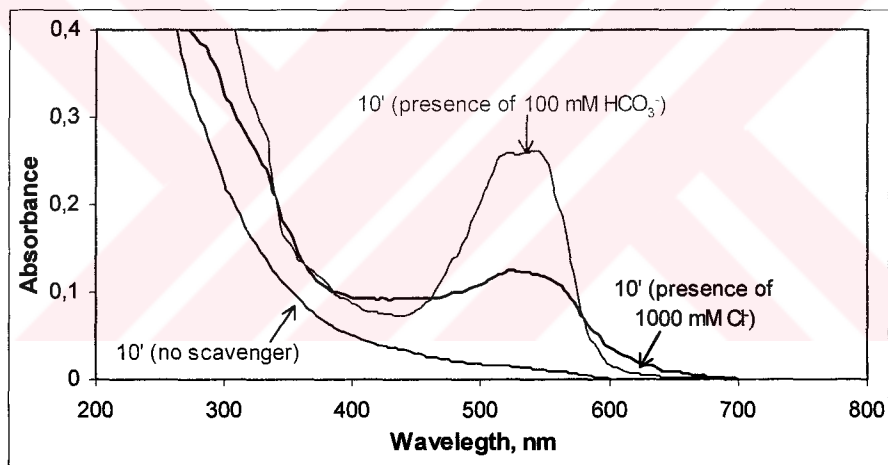
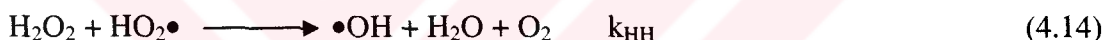


Figure 4.28. Changes in the absorption spectra of the dye solution at 10 minutes in the absence of scavengers and presence of 100 mM  $\text{HCO}_3^-$  and 1000 mM  $\text{Cl}^-$  exposed to UV/ $\text{H}_2\text{O}_2$  oxidation (Procion Red=25 ppm,  $\text{H}_2\text{O}_2=4.1$  mM)

#### 4.9. Kinetic Modelling of Dye Degradation

A simple model was developed to describe the kinetics of dye degradation by the UV/H<sub>2</sub>O<sub>2</sub> system employed in this study. The chemical reactions used for the development of the model are summarized below:



The first reaction describes the photolysis of H<sub>2</sub>O<sub>2</sub> by UV irradiation (hν), with a reaction rate of r<sub>0</sub>. The second and third reactions together are a simplified representation of the •OH dependent degradation of the dye with respect to color and organic content, with rate constants k<sub>C</sub> and k<sub>R</sub>, respectively. The fourth reaction shows an additional pathway of •OH utilization or scavenging (other than by dye components), and the last one is an additional route (other than photolysis) for H<sub>2</sub>O<sub>2</sub> utilization. Note that the presence of carbonates and chloride is not included in the overall scheme. Values of k<sub>H</sub> and k<sub>HH</sub> are available in literature sources as 2.7x10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>, and 0.5 M<sup>-1</sup> s<sup>-1</sup>, respectively (Buxton *et al.*, 1988). Since k<sub>HH</sub> is much too small relative to k<sub>H</sub> and the observed rate constants of organic dyes with OH radicals (10<sup>8</sup>-10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> (Buxton *et al.*, 1988)), Reaction 4.14 was neglected in the modelling process.

In accordance with the above reaction scheme, in which •OH was considered to be the only oxidizing agent effecting the degradation of the dye, the kinetics of dye degradation can be expressed as:

$$-\frac{d[\text{dye}]}{dt} = k'' [\text{OH}\cdot][\text{dye}] \quad (4.15)$$

where,  $k''$  is the second order rate constant of the dye with hydroxyl radical, and  $[\text{OH}\cdot]$  and  $[\text{dye}]$  are the molar concentrations of hydroxyl radical and the dye at time  $t$ , respectively.

The dye is made of two major components, the chromophoric group consisted of double bonded nitrogen atoms connected to aromatic rings, and the non-chromophoric part made of aromatic rings or unsaturated organic carbons. Hence, dye concentration at time  $t$  can be expressed as the sum of these two molecular components by:

$$[\text{dye}] = [\text{chromophoric components} + \text{aromatic components}] \quad (4.16)$$

It is of common knowledge that priority of  $\text{OH}\cdot$  is to attack the chromophoric components, i.e., the  $\text{N}=\text{N}$  bonds. The overall degradation of the dye for organic components, therefore, is accelerated only after decolorization is fairly complete. As indicated in Section 4.7, the total absorbance of the dye solution at 254 nm was reduced only by 49.8 per cent at 15 minutes, at which the absorbance at the visible band was totally removed. Thus, the dye concentration at time  $t$  can be estimated using the absorbance of the solution at 544 nm and 254 nm by reference to Lambert-Beer Law:

$$c_{544} = \frac{A_{544}}{\epsilon_{544} \times b} \quad (4.17)$$

$$c_{254} = \frac{A_{254}}{\epsilon_{254} \times b} \quad (4.18)$$

where  $A_{544}$  and  $A_{254}$  are the absorbance of the solution at time  $t$  at 544 nm and 254 nm,  $\epsilon_{544}$  and  $\epsilon_{254}$  are the molar extinction coefficients of color and aromatic components at 544 nm and 254 nm, and  $b$  is the optical path length. The values of  $b$ ,  $\epsilon_{544}$ ,  $\epsilon_{254}$  are 1 cm,  $7.41 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $1.78 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively.

In accordance, Equation 4.15 is rearranged to yield:

$$-\frac{d[\text{dye}]}{dt} = k_C [\text{OH}\bullet] [\text{DYE}_C] + k_R [\text{OH}\bullet] [\text{DYE}_R^*] \quad (4.19)$$

where,  $k_C$  and  $k_R$  are second order rate constants for the reaction of color and aromatic components of the dye with hydroxyl radicals, and  $[\text{DYE}_C]$ ,  $[\text{DYE}_R^*]$  are the molar concentrations of color and aromatic components, respectively.

If it is assumed that there is a steady state concentration of hydroxyl radicals in the reactor, a mass balance analysis will yield:

$$0 = -\frac{d[\text{OH}\bullet]}{dt} = r_0 - k_C [\text{OH}\bullet] [\text{DYE}_C] - k_R [\text{OH}\bullet] [\text{DYE}_R^*] - \sum k_i [S_i] [\text{OH}\bullet] \quad (4.20)$$

where,  $r_0$  is the photolysis rate of hydrogen peroxide ( $\text{M s}^{-1}$ ) by which OH radicals are generated,  $k_i$  is the second order rate constant between hydroxyl radical and any OH• scavengers, and  $[S_i]$  is the molar concentration of any scavenger at time  $t$ . Since the only •OH scavenger in the model is  $\text{H}_2\text{O}_2$ ,  $S_i$  represents the concentration of  $\text{H}_2\text{O}_2$  at time  $t$ , and therefore the term  $\sum k_i [S_i] [\text{OH}\bullet]$  is equivalent to  $k_H [\text{OH}\bullet] [\text{H}_2\text{O}_2]$ ,  $k_H$  as defined previously.

It was found that the rate of color and organic carbon degradation both followed first order kinetics with respect to the corresponding concentrations as:

$$-\frac{d[\text{DYE}_C]}{dt} = k'_C [\text{DYE}_C] \quad (4.21)$$

$$-\frac{d[\text{DYE}_R^*]}{dt} = k'_R [\text{DYE}_R^*] \quad (4.22)$$

where  $k'_C$  and  $k'_R$  are the pseudo-first order rate constants of the corresponding reactions, respectively. Moreover, the rates are second order with respect to the  $\bullet\text{OH}$  concentration, i.e.

$$-\frac{d[\text{DYE}_C]}{dt} = k_C [\text{DYE}_C] [\bullet\text{OH}] \quad (4.23)$$

$$-\frac{d[\text{DYE}_R^*]}{dt} = k_R [\text{DYE}_R^*] [\bullet\text{OH}] \quad (4.24)$$

Equating Equations 4.21 and 4.23, and Equations 4.22 and 4.24, and solving for  $k_C$  and  $k_R$ , respectively, one finds:

$$k_C = \frac{k'_C}{[\bullet\text{OH}]} \quad (4.25)$$

$$k_R = \frac{k'_R}{[\bullet\text{OH}]} \quad (4.26)$$

Substituting these values into Equation 4.20, and rearranging yields:

$$-\frac{d[\text{OH}\bullet]}{dt} = r_0 - \frac{k'_C}{[\bullet\text{OH}]_t} [\bullet\text{OH}]_{ss1} [\text{DYE}_C] - \frac{k'_R}{[\bullet\text{OH}]_t} [\bullet\text{OH}]_{ss2} [\text{DYE}_R^*] - k_H [\text{H}_2\text{O}_2] [\bullet\text{OH}] \quad (4.27)$$

where  $[\bullet\text{OH}]_{ss1}$  and  $[\bullet\text{OH}]_{ss2}$  refer to the steady state hydroxyl radical concentrations during the first 15 min of irradiation and during the total contact time, respectively. The quantity  $[\bullet\text{OH}]_t$  may be assumed to be equal to the corresponding  $[\bullet\text{OH}]_{ss}$ , so that Equation 4.27 is simplified as:

$$[\bullet\text{OH}]_{ss} = \frac{r_0 - k'_C [\text{DYE}_C] - k'_R [\text{DYE}_R^*]}{k_H [\text{H}_2\text{O}_2]_t} \quad (4.28)$$

The quantity  $r_0$ , or the rate of photolysis of  $\text{H}_2\text{O}_2$  is dependent on the incident light intensity and the fraction of light absorbed by  $\text{H}_2\text{O}_2$ , and defined by (Liao and Gürol, 1995):

$$r_0 = (2.303 \Phi_T \epsilon p I_0 \eta) [\text{H}_2\text{O}_2] \quad (4.29)$$

where,  $\Phi_T$  is the overall quantum yield ( $1 \text{ mol E}^{-1}$ ),  $\epsilon$  is the molar extinction coefficient of  $\text{H}_2\text{O}_2$  at 254 nm ( $19.6 \text{ M}^{-1} \text{ cm}^{-1}$ ),  $p$  is the pathlength between the light source and the solution surface (5.3 cm),  $I_0$  is the incident light intensity ( $3.04 \times 10^{-6} \text{ E s}^{-1} \text{ l}^{-1}$ ), and  $\eta$  is the fraction of light absorbed by  $\text{H}_2\text{O}_2$ .

The rate of decomposition of hydrogen peroxide was found to follow first order kinetics with respect to its concentration, so that:

$$r_0 = (2.303 \Phi_T \epsilon b I_0 \eta) [\text{H}_2\text{O}_2] = k' [\text{H}_2\text{O}_2] \quad (4.30)$$

where,  $k'$  is the pseudo-first order decomposition rate constant of  $\text{H}_2\text{O}_2$  (assuming that decomposition occurs via photolysis alone, found as  $0.0187 \text{ min}^{-1}$ ). Hence, the fraction of light absorbed by  $\text{H}_2\text{O}_2$  ( $\eta$ ) can be estimated by:

$$\eta = \frac{k'}{2.303 \Phi_T \epsilon b I_0} \quad (4.31)$$

$\eta$  was calculated as 0.66 which showed that only 66 per cent of the incident light was absorbed by  $\text{H}_2\text{O}_2$ .

The solution of Equation 4.28 for the steady state hydroxyl radical concentration  $[\bullet\text{OH}]_{ss}$  was carried out using the data set presented in Table 4.1. The calculated value of  $[\bullet\text{OH}]_{ss}$  was then substituted into Equation 4.25 and Equation 4.26 to estimate the values of  $k_C$  and  $k_R$ , respectively. The results are presented in Table 4.2.

Table 4.1. List of parameters used in the kinetic model

Time, min	H <sub>2</sub> O <sub>2</sub> , mM	[DYE <sub>C</sub> ], M	[DYE <sub>R</sub> <sup>*</sup> ], M
0	4.1	6.83 x 10 <sup>-6</sup>	3.68 x 10 <sup>-6</sup>
2	3.975	3.72 x 10 <sup>-6</sup>	3.66 x 10 <sup>-6</sup>
5	3.936	1.35 x 10 <sup>-6</sup>	3.3 x 10 <sup>-6</sup>
7	3.828	0.63 x 10 <sup>-6</sup>	2.98 x 10 <sup>-6</sup>
10	3.791	0.15 x 10 <sup>-6</sup>	2.54 x 10 <sup>-6</sup>
15	3.730	0	1.84 x 10 <sup>-6</sup>
20	3.552	0	1.29 x 10 <sup>-6</sup>
30	3.099	0	0.72 x 10 <sup>-6</sup>
40	2.509	0	0.52 x 10 <sup>-6</sup>
50	1.928	0	0.39 x 10 <sup>-6</sup>
60	1.476	0	0.3 x 10 <sup>-6</sup>

Table 4.2. Estimated parameters in the model

[•OH] <sub>ss</sub>	k <sub>C</sub>	k <sub>R</sub>
1.15 x 10 <sup>-11</sup> M	5.4 x 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup>	6.67 x 10 <sup>7</sup> M <sup>-1</sup> s <sup>-1</sup>

The calculated second order rate constant  $k_C$  is in good agreement with the observed rate constants of azo dyes with hydroxyl radicals. The value of  $k_R$ , corresponding to the rate of intermediate product destruction is approximately 10 fold lower, which is reasonable because the rate of absorbance decay at 254 nm was much slower than that of 544 nm.

Consequently, the effect of carbonate and chloride species in solution can easily be predicted by the proposed model upon the addition of their reaction rates with •OH into the last term of Equation 4.20.



## 5. CONCLUSIONS

The purpose of this study was to investigate the kinetics of dye degradation by UV/H<sub>2</sub>O<sub>2</sub> and the effects of bicarbonate, carbonate and chloride ions on the rate of color removal. The method involved exposure of a reactive azo dye, Procion Red to UV/H<sub>2</sub>O<sub>2</sub> in the absence and presence of scavengers, and monitoring the absorbance of the solution at 544 nm and 254 nm.

The results of the study are summarized below:

1. The rate of decolorization of Procion Red was fastest at pH=7 in the absence of scavengers.
2. Application of the UV/H<sub>2</sub>O<sub>2</sub> system resulted in a pH reduction during treatment due to the destruction of Procion and formation of organic acids.
3. The degradation of Procion Red followed first order kinetics. The degradation process was insignificant in the presence of UV alone, and no degradation occurred in the presence of H<sub>2</sub>O<sub>2</sub> alone.
4. Application of the UV/H<sub>2</sub>O<sub>2</sub> system in the absence of scavengers showed that Procion Red was completely decolorized in the first 15 minutes of treatment, which corresponded to 49.8 per cent organic carbon degradation.
5. Color degradation was considerably enhanced by increasing H<sub>2</sub>O<sub>2</sub> concentration up to a level (8.18 mM), beyond which the rate was inhibited.
6. It was found that hydrogen peroxide was removed from solution at a faster rate (1.55 times) in the absence of Procion Red than in its presence. The rate of H<sub>2</sub>O<sub>2</sub> take up was found to decrease during decolorization of Procion Red. These findings indicated that Procion Red and H<sub>2</sub>O<sub>2</sub> competed for UV light, thus the photolysis of H<sub>2</sub>O<sub>2</sub> was partly inhibited.

7. Aromatic degradation was found to follow first order kinetics and 91.7 per cent removal was achieved in 60 minutes.

8. At low concentrations of bicarbonate ion (2.5 and 5 mM), the dye was 100 per cent removed by color in 15 minutes as it was in the absence of  $\text{HCO}_3^-$ . With further increases in  $\text{HCO}_3^-$  concentration above 5 mM, inhibition in color degradation became more pronounced.

9. At all concentrations of carbonate ions, the rate of color removal was inhibited. The degree of inhibition increased with increased  $\text{CO}_3^{2-}$  concentration.

10. Chloride ion slightly decreased the rate of color removal up to a concentration of 100 mM. Further increases in  $\text{Cl}^-$  concentration up to 1250 mM led to a significant decrease in the color degradation rate constant. At  $\text{Cl}^-$  concentrations larger than 1250 mM, the rate of color removal was unaffected.

11. A kinetic model was proposed neglecting the effects of hydroxyl radical scavengers, by which the hydroxyl radical steady state concentration, second order rate constants of the color and aromatic components with  $\bullet\text{OH}$  were estimated as  $1.15 \times 10^{-11}$  M,  $5.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , and  $6.67 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  respectively. The calculated rate constants are in agreement with the reference data for azo dyes.

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