İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

EFFECT OF TEXTILE PREPARATION CHEMICALS ON THE H_2O_2/UV-C OXIDATION OF THE NONIONIC SURFACTANT NONYL PHENOL ETHOXYLATE

M.Sc. Thesis by
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Programme : Environmental Sciences and Engineering

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TEKSTİL HAZIRLAMA ÖN İŞLEMİNDE KULLANILAN KİMYASALLARININ NONİYONİK YÜZEY AKTİF MADDE NONİL FENOL ETOKSİLATIN H_2O_2/UV-C OKSİDASYONUNA ETKİLERİ

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FOREWORD

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May 2010 Sarina Shayin

Environmental Engineer

TABLE OF CONTENTS

Page

ABBREVIATIONS

ABS : Alkyl Benzene Sulfonates
AOC : Assimilable Organic Carbon
AOP : Advanced Oxidation Processes
APEO : Alkyl and Aryl Polyethoxylate
COD : Chemical Oxygen Demand
DTPMP : Diethylene Triamine Penta-Methylene Phosphonic Acid
EU : European Union
HEDP : 1-Hydroxy Ethylidene-1,1-Diphosphonic Acid
LAS : Linear Alkylbenzene Sulfonates
NOM : Natural Organic Matter
NPEO : Nonyl Phenol Ethoxylate
PAC : Powdered Activated Carbon
SDBS : Sodium Dodecylbenzene Sulfonate
TOC : Total Organic Carbon
UV-C : Ultraviolet C

LIST OF TABLES

LIST OF FIGURES

Page

EFFECT OF TEXTILE PREPARATION CHEMICALS ON THE H_2O_2/UV-C OXIDATION OF THE NONIONIC SURFACTANT NONYL PHENOL ETHOXYLATE

SUMMARY

The present experimental study aimed at investigating the effect of common salt (3 g/L chloride), soda ash (carbonate-bicarbonate system, 1-5 g/L), and two commercially important organic sequestering agents (0.5-2.5 g/L DTPMP, i.e. diethylene triamine penta-methylene phosphonic acid and 0.5-1.5 g/L HEDP; 1-hydroxy ethylidene-1,1-diphosphonic acid) employed at concentrations being typically found in textile preparation effluents, on the H_2O_2/UV-C degradation of the commercially important nonionic textile surfactant nonylphenol ethoxylate (NPEO), a 10-fold ethoxylated nonyl phenol formulation called NP-10 (NPEO=210 mg/L, corresponding to a COD of 450 mg/L). H_2O_2/UV-C experiments were conducted at an initial H_2O_2 concentration of 30 mM and an initial pH of 10.5 and 11.5, being typical for textile preparation effluents. Treatment efficiencies and degradation rates were comparatively evaluated in terms of parent pollutant (NPEO), COD and TOC abatements as well as pH changes and H_2O_2 consumption kinetics.

In the second part of the experimental study, the application of H_2O_2/UV-C treatment on effluents originating from four different simulated textile preparation effluents was investigated to apply H_2O_2/UV-C treatment to actual preparation wastewater. Experimental results have indicated that in the absence of any textile preparation chemical, NPEO degradation was complete in 15 min (rate coefficient: 0.2211 min^{-1}) accompanied with 78% COD and 57% TOC removals achieved after 60 min photochemical treatment time. H_2O_2 consumption rates were not significantly affected by the introduction of inorganic textile auxiliaries (average rate coefficient: 0.025 min^{-1}). Only elevated pH ($\geq$11.5) enhanced the dissociation of H_2O_2 to its conjugate base HO_2^-, whereas the organic sequestering agents competed for UV-C light absorption and $HO^\bullet$ radicals. H_2O_2/UV-C oxidation of the textile preparation effluent bearing 3 g/L Cl^-, 1.5 g/L NaOH and 1 g/L DTPMP resulted in the worst treatment performance because of its high pH and organic carbon content. For this textile preparation effluent, complete NPEO abatement required 100 min treatment (rate coefficient: 0.0183 min^{-1}), while COD and TOC removals decreased to only 16% and 8%, respectively, after 60 min photochemical treatment. The highest H_2O_2/UV-C treatment performance resulting in 34% COD and 28% TOC removals was obtained for the textile preparation effluent comprising of 3 g/L Cl^-, 1.5 g/L NaOH and 1.0 g/L HEDP. For this textile preparation effluent, NPEO degradation was complete after 50 min (rate coefficient 0.0612 min^{-1}) exposure to the H_2O_2/UV-C process.

TEKSTİL HAZIRLAMA ÖN İŞLEMİNDE KULLANILAN KİMYASALLARININ NONİYONİK YÜZEY AKTİF MADDE NONİL FENOL ETOKSİLATIN H_2O_2/UV-C OKSİDASYONUNA ETKİLERİ

ÖZET

Bu deneysel çalışmada, klorürün (3 g/L), sodyum karbonatın (karbonat-bikarbonat sistemi, 1-5 g/L) ve iki organik yüzey aktif maddenin (0.5-2.5 g/L DTPMP, dietilen triamin penta metilen fosfonik asit, ayrıca 0.5-1.5 g/L HEDP; 1-hydroksi etiliden-1,1-difosfonik asit) tekstil elyafı hazırlama işleminde yoğun olarak tüketilen ve 10 etoksilat grubu içeren, noniyonik bir yüzey aktif madde nonil fenol etoksilatın (NFEO; NP-10) H_2O_2/UV-C arıtma prosesi ile ileri oksidasyonuna etkileri incelenmiştir.) H_2O_2/UV-C deneyleri, başlangıç konsantrasyonu 450 mg/L KOİ'ye eşdeğer 210 mg/L NPEO ile, başlangıç H_2O_2 konsantrasyonu 30 mM; tipik tekstil ön hazırlama işlemi pH'sı olan 10.5-11.5 ortak reaksiyon koşullarında gerçekleştirilmiştir. Tekstil yardımcılarının NPEO'ın fotokimyasal arıtma performansında neden oldukları değişiklikler, ana madde (NPEO), KOİ, TOK giderim verimleri ve kinetikleri, ayrıca pH değişimleri ve H_2O_2 tüketim hızı bazında değerlendirilmiştir.

Deneysel çalışmanın ikinci aşamasında ise H_2O_2/UV-C fotokimyasal arıtma prosesinin dört farklı tekstil ön hazırlama işleminden kaynaklanan sentetik olarak hazırlanmış atıksulara uygulanabilirliği karşılaştırmalı olarak araştırılmıştır. Deneysel sonuçlar, herhangi bir tekstil hazırlama yardımcı kimyasalın olmadığı durumda sulu NFEO'ın H_2O_2/UV-C prosesi ile 15 dakikalık bir süre içerisinde tamamen ayrıştığını (ayrışma hız sabiti: 0.2211 dak.$^{-1}$), bununla beraber %78 KOİ ve % 57 TOK gideriminin bir saatlik fotokimyasal arıtma süresi sonunda elde edildiğini göstermiştir. H_2O_2 tüketim hızının inorganik tekstil yardımcı kimyasalların ilavesiyle önemli derecede değişmediği (ortalama tüketim hız sabiti: 0.025 dak.$^{-1}$), sadece yüksek reaksiyon pH'sının ($\geq$11.5) H_2O_2'in konjüge bazı olan HO_2^- iyonuna iyonlaşmasını hızlandırdığını ve organik iyon tutucuların H_2O_2 ile UV-C ışığı ve $HO^\bullet$ radikalleri için rekabet ettiği sonucuna varılmıştır. H_2O_2/UV-C prosesi, 3 g/L Cl^-, 1.5 g/L NaOH and 1 g/L DTPMP içeren reçete için en kötü NFEO arıtma performansı ile sonuçlanmıştır. Bu tekstil ön hazırlama reçetesi için NFEO giderimi 100 dakikalık bir fotokimyasal oksidasyon süresine yükselmiştir (ayrışma hız sabiti: 0.0183 dak.$^{-1}$). Bununla birlikte bir saatin sonunda elde edilen KOİ ve TOK giderim verimleri ise sırasıyla %16 and %8 mertebelerine düşmüştür. En yüksek fotokimyasal arıtma performansı, 3 g/L Cl^-, 1.5 g/L NaOH ve 1.0 g/L HEDP içeren tekstil ön hazırlama reçetesi için elde edilmiştir. Söz konusu reçetenin kullanımından kaynaklanan sentetik atıksuda %100 NFEO giderimi 50. dakikanın (NFEO ayrışma hız sabiti: 0.0612 min^{-1}) sonunda elde edilmiştir. KOİ ve TOK giderim verimleri ise sırasıyla %34 ve %28 olarak bulunmuştur.

1. INTRODUCTION

Nonylphenol ethoxylates (NPEOs) are produced in large quantities for application in many different industries including textile preparation and dyeing processes (scouring, bleaching, mercerizing, dyeing, etc.), pulp & paper processing, paint and resin formulation, oil and gas recovery, steel manufacturing, pest control and power generation (Van de Plassche et al., 1999; Utsunomiya et al., 1997). More recently, many countries, large companies, environmental protection agencies and scientific entities have classified metabolites of NPEOs and other alkylated polyethoxylates (APEOs) as harmful, since they enter the aquatic and terrestrial environment at concentrations and/or conditions that might have immediate or long-term negative impacts (Renner, 1997; APE Research Council, 2001; Environment Canada, 2002; EU, 2002; U.S. EPA, 2004). Many companies even voluntarily stopped using APEO-based chemicals in their application and massive productions. This is so because it has been recently recognized that their use is creating long-term concerns and potential risks for the ecosystem (Procter and Gamble, 2005). On the other hand, APEOs are still being used in several industrial applications where they cannot not be replaced yet by another alternative chemical due to technical as well as economical reasons.

It has been demonstrated that primary NPEO biodegradation at domestic and/or industrial wastewater treatment plants produces metabolites that are generally more hydrophobic, toxic, persistent and/or estrogenic as compared to the original compound (Thiele et al., 1997; Bokern et al., 1997; Servos, 1999; EU, 2002). The generally accepted biodegradation pathway was proposed by Ahel et al. (1994) and begins with the simultaneous ω-oxidation of the ethoxy chain and the α–, β–, or ω-oxidation of the alkyl chain prior to ether hydrolysis (Di Corcia et al., 2000). The metabolites formed are short-chain APEOs which are subsequently transformed to the corresponding alkyl phenol polyethoxylates as well as carboxyalkylphenol polyethoxylates under aerobic, and to alkyl phenols under anaerobic conditions (Jonkers et al., 2001; Zhang et al., 2008; Montgomery-Brown et al., 2008). It has been estimated that at least 60-65% of all nonylphenolic compounds that have entered the sewage, are discharged into receiving water bodies in the environment, mainly in the form of their acidic and neutral degradation products (Ahel et al., 1994). For instance, NPEOs are easily degraded to their main metabolite, e.g. nonyl phenol (NP) under anaerobic conditions, that is known to disrupt normal hormonal functions in the body (Dachs et al., 1999; Johnson and Sumpter, 2001) and thus is considered as an endocrine disrupting chemical. Moreover, the formation of NP cannot be ruled out under “oxic conditions”, since some scientific evidence has been reported recently for its presence in aerobic environments (Montgomery-Brown et al., 2008). NPEOs may undergo complete primary biodegradation in the presence of oxygen; this type of oxidation is attributable to the degradation of the alkyl chain, but little evidence was observed for degradation of the aromatic ether bond (Scott and Jones, 2000). Former studies revealed that though rapid primary NPEO degradation takes place, degradation products are not available to microorganisms (Ahel et al., 1994). Consequently, its degradation via alternative chemical oxidation methods has become a major challenge for future investigations.

Considering the characteristics of textile preparation wastewater (i.e. its H_2O_2 content used for fabric bleaching purposes, low suspended solids content and hence low turbidity, medium strength COD, aliphatic, polymeric organic carbon content that does not absorb UV light above 230 nm, etc.), UV-driven photochemical oxidation processes might be a potential option for their full and efficient treatment. Our previous studies have demonstrated that anionic and anionic/nonionic textile surfactant formulations could be successfully degraded by employing advanced oxidation processes; i.e. AOPs (Arslan-Alaton et al., 2007; Arslan-Alaton and Erdinc, 2006). Photochemical AOPs are ambient temperature, but also energy-intensive (electrically driven) processes based on the formation of free radicals (in particular $HO^{\bullet -}$ oxidation potential: + 2.8 eV; $HO_2^{\bullet -}$ oxidation potential: + 1.7 eV) that vigorously and almost indiscriminately attack all organic as well as inorganic water constituents (Glaze et al., 1995; Legrini et al., 1993). Hence, AOPs are usually employed for the destructive treatment of hazardous, toxic and/or refractory pollutants (Parsons, 2004). Among them, the H_2O_2/UV-C treatment process is a relatively known and well-established homogenous advanced oxidation system that does not produce volatile or solid emission/residues and is also not very sensitive to the reaction pH (CCOT, 1995; Ince, 1999; Parsons, 2004). In addition, ethoxylate-based nonionic surfactants do not significantly absorb UV light above 240 nm and thus do not seriously compete with H_2O_2 for UV-C light irradiation (Legrini et al., 1993). Consequently, one of the major limitations of the H_2O_2/UV-C oxidation process, e.g. the low extinction coefficient of H_2O_2 at 254 nm wavelength ($\varepsilon_{H2O2,254\ nm} = 19.6\ M^{-1}\ cm^{-1}$) can be overcome when textile surfactants are subjected to photochemical treatment (Baxendale and Wilson, 1957; Arslan-Alaton and Erdinc, 2006). On the other hand, textile preparation effluent contains significant concentrations of hydrogen peroxide, soda-ash, caustic soda, organic sequestering agents as well as chloride (IPPC, 1998) that may hinder effective UV light absorption by H_2O_2 and/or scavenge the in-situ produced free radicals (Buxton et al., 1989).

Considering the above mentioned facts, the present work aimed at investigating the effect of common salt, soda ash (carbonate-bicarbonate system), and two commercially important sequestering agents (DTPMP, i.e. diethylene triamine penta-methylene phosphonic acid and HEDP; 1-hydroxy ethylidene-1,1-diphosphonic acid) at concentrations being typically found in textile preparation effluent, on the H_2O_2/UV-C degradation of NP-10, a 10-fold ethoxylated nonyl phenol formulation. In the first part of the experimental work, special emphasis was given to the scavenging properties of chloride as well as the binary impact of the chloride-carbonate scavengers at acidic and alkaline pH values. Treatment efficiencies and degradation rates were evaluated in terms of parent pollutant (NPEO), COD and TOC abatements as well as changes in pH and H_2O_2 consumption kinetics.

In the second part of the experimental study, the application of H_2O_2/UV-C treatment on effluents originating from four different simulated textile preparation effluents was comparatively evaluated. The difference of these textile preparation recipes were the pH buffering agent type (soda-ash or caustic soda) and hence effluent pH (10.5 or 11.5) as well as the organic sequestering agent type (DTPMP or HEDP). By the help of the obtained advanced photochemical oxidation kinetics and efficiencies, not only the most appropriate textile preparation recipe for application of the H_2O_2/UV-C treatment process to textile preparation effluent could be recommended, but also the effect of free radical scavengers in complex configurations and real industrial wastewater matrices could be highlighted.

2. THEORETICAL BACKGROUND

2.1 Textile Industry Overview

The textile industry is one of the longest and most complicated industrial chains in manufacturing industry. It is a fragmented and heterogeneous sector dominated by a majority of Small and Medium Enterprises, with a demand largely driven by three main end-uses: clothing, home furnishing and industrial use.

The textile industry is a significant contributor to many national economies, encompassing both small and large-scale operations worldwide. In terms of its output or production and employment, the textile industry is one of the largest industries in the world (IPPC, 2003).

The importance of the textile (and clothing) industry in the European economy is shown in Table 2.1. The figures in the table cover only a part of the total number of manufacturing companies in 2000 (i.e. they only cover companies with more than 20 employees).

This part of the industry represented that 3.4 % of EU manufacturing, 3.8 % of the added valued and 6.9 % of industrial employment.

Table 2.1: Share of the textile-clothing industry in the manufacturing industry in 2000 (only companies with > 20 employees; EURATEX, 2002)

Manufacturing type	**Turnover** EUR Billion	**Added value at f.c.***EUR Billion	**Employment million**	**Turnover %**	**Added value %**	**Employment %**
Textile	100.5	31.2	0.89	2.1	2.4	3.8
Clothing	61.5	18.2	0.73	1.3	1.4	3.1
Total	162	49.4	1.62	3.4	3.8	6.9
manufacturing	4756.8	1308.0	23.62	100	100	100

f.c.: factor costs

The textile manufacturing process is characterized by the high consumption of resources like water, fuel and a variety of chemicals in a long process sequence that generates a significant amount of waste. The common practices of low process efficiency result in substantial wastage of resources and a severe damage to the environment. The main environmental problems associated with textile industry are typically those associated with water body pollution caused by the discharge of untreated effluents. Other environmental issues of equal importance are air emission, notably Volatile Organic Compounds (VOC)'s and excessive noise or odor as well as workspace safety.

Textile fibers are categorized into two principal groups; natural and manmade. Natural fibers - cotton, wool, hemp, linen, jute, silk - are products of agriculture. Manmade fibers encompass both purely synthetic materials, e.g. nylon, polyester derived from petrochemicals, and regenerative cellulose materials, e.g. rayon and acetate, manufactured from wood fibers. Both types of man-made fibers are typically extruded into continuous filaments, which may then undergo treatment to impart texture to the fibers. The continuous filaments may be spun into yarn directly, or they may be cut into staple length and then spun in a process resembling that used for wool or cotton.

2.1.1 Textile preapration

The term "Preparation" has two implications in textile processing. In greige manufacturing, it is used to describe the processes which prepare yarns for weaving and knitting. Mostly, it is used to describe slashing operations that ready warp yarns for weaving. In dyeing and finishing, the term is used to describe those processes that ready fabrics for the steps that follow, coloration and finishing. Fabric preparation is the first of the wet processing steps where greige fabric is converted into finished fabric. The steps that follow, dyeing or printing and finishing, are greatly influenced by how the fabric is prepared.

In wet processing it is generally recognized that the steps encompassing preparation are:

Singeing: A process where loose fibers and fuzz is burned away to yield a clear and clean fabric surface.

Desizing: A process where warp size is removed.

Scouring: A process where mill and natural dirt, waxes and grease are removed.

Bleaching: A process where color bodies are destroyed and the fabric is whitened.

Mercerizing: Caustic treatment of cellulosic fabrics improving luster, water absorbance, dye yield and fiber strength.

Carbonizing: Acid treatment of wool for removing vegetable matter.

Heat Setting: Heat treatment of fabrics containing thermoplastic synthetic fibers. Stabilizes fabric by reducing shrinkage and distortion.

2.2 Surfactants

Surfactants are a diverse group of chemicals with unique cleaning and/or solubilisation properties. They usually consist of a polar (hydrophilic) and a nonpolar (hydrophobic) group (Schwartz et al., 1977). Due to their amphiphilic nature they are widely used in household cleaning agents (detergents), personal care products, textiles, paints, inks, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery as well as pulp and paper industries (DiCorcia et al, 1998; Ying, 2006). Surfactants enter the environment mainly through the discharge of sewage effluents into natural water and the application sewage sludge on land for soil fertilizing purposes (Petrovic et al., 2004). Many commercial surfactants used today by different industries are only partially biodegradable and tend to sorb and hence accumulate on sludge and soil sediments (Swisher, 1987; Staples et al., 2001). As such, they cause a potential ecotoxicological risk in the environment. Moreover, the metabolites of some alkyl phenol ethoxylates have recently been declared as endocrine disrupting compounds (Jobling et al. 1993; White et al. 1994; Routledge et al., 1996 and Isidori et al., 2006). In conclusion, the efficient management and treatment of surfactants remains a major ecological and environmental problem. As such, more effective and at the same time economically feasible abatement processes have to be developed to alleviate the problem of surfactants in the environment. In particular, Advanced Oxidation Processes (AOP) have proven to be good candidates for the destructive treatment of toxic and/or recalcitrant pollutants and research is continuing in this field for more than three decades. Studies devoted to the treatment of surfactants by employing by chemical and photochemical AOP have been briefly and comparatively reviewed with an emphasis on combined/integrated chemical-biological or eventually photochemical-biological treatment approaches, electrical energy consumption rates of photochemically driven AOP, identification of advanced oxidation intermediates as well as changes in toxicity during application of AOP towards different test organisms.

2.2.1 General Properties & Types

The most conventional and scientifically accepted surfactant classification is based on their ionic (dissociation) properties in aqueous medium. Four main groups can be differentiated; namely anionic, cationic, nonionic and amphoteric (zwitterionic) ones. These four classes of surfactants will be briefly introduced in the forthcoming sections (Ying, 2006).

2.2.1.1 Anionic Surfactants

Anionic surfactants ionize in water to an anion and a cation that is in most cases an alkali metal (Na, K) or a quaternary ammonium ion. Anionic surfactants are the most widely used type of surfactants. These include alkylbenzene sulfonate, used as soaps (sodium or potassium salt of a fatty acids), di-alkyl sulfosuccinates, employed as wetting agent, lauryl sulfates, used as foaming agents, and lignosulfonates, used as dispersing agents). Anionic surfactants account for at least 50 % of the total surfactant production globally (Schwartz et al., 1977).

In the 1940-50's, synthetic detergents displaced soaps specially in the use of washing machines due to their higher tolerance to hard water, better cleaning properties and lower price. However, their frequent and ever increasing use brought about serious environmental problems that were in particularly noticed in industrialized regions of high population density. Surfactants were quickly noticed due to the appearance of persistent foam being aesthetically objectionable. Wastewater loaded with alkyl benzene sulfonates (ABS) was discharged into natural water bodies (creeks, lakes and rivers) where they could not be degraded by microorganisms and accumulated in the water environment as well as soil sediments. In the late 1960's, the use of branched alkylated detergents became banned by law and ABS were quickly replaced by linear alkylbenzene sulfonates (LAS) which were relatively expensive but readily biodegradable (Salager, 1999).

Today, LAS production is inexpensive and LAS still account for an integral proportion of detergents available in the market. LAS have an alkyl chain length in the C10-C16 range with a benzene ring generally attached to the C6-C8 position of the linear alkyl chain. The maximum effect as a cleaning agent is achieved with a C12-13 chain length. The chain length determines whether LAS is used as a wetting agent, tension lowering agent or an emulsifier (Schwartz et al., 1977).

2.2.1.2 Cationic Surfactants

Cationic surfactants **(**with a market share around 5%) are ionized in water into a cation and a halogenated anion. The cation is most of the time a quaternary ammonium ion with one or multiple alkyl chains usually originating from natural fatty acids. Although cationic surfactants are not good detergents or foaming agents, they exhibit a perfect adsorption capacity on negatively charged substrates as most surfaces are in aqueous medium at neutral pH’s. This capacity renders them a softening action for fabric and hair rinsing. The positive charge also enables them to be used as floatation collectors, hydrophobating agents, corrosion inhibitors as well as dispersing agents (Salager, 1999). Quaternary ammonium - based cationic surfactants are widely employed as fabric softeners or disinfectants. They are also used as emulsifying agents in inks and coatings. More important is their use as bactericides; cationic surfactants are used to aseptize surgery hardware as well as in disinfectant formulations for domestic and hospital use (Lewis et al., 1983; Giolando et al., 1995). Another specific application is for sterilization purposes of bottles and containers in the dairy and beverage industries. Because their production is more costly than that of most anionics and nonionics, their application is very limited to the applications mentioned above (Salager, 1999). Among the surfactant classes, they impart the highest aquatic toxicity and hence have to be used with special caution (Ying, 2006).

2.2.1.3 Nonionic Surfactants

Nonionic surfactants account for more than 40-45% of the total industrial production worldwide and their production and use has an increasing tendency. These surfactants do not ionize in water due to their nonpolar chemical structure. In other words, nonionic surfactants do not dissociate in aqueous medium (Ying, 2006). Consequently, they are excellent candidates to enter complex solvent mixtures, as found in many commercial products. They are much less sensitive to hardness causing divalent cations than ionic surfactants, and thus can be used in high salinity/hard water (Ying, 2006). Nonionic surfactants have good cleaning, foaming, wetting and emulsifying properties. Most categories sold today have a very low mammal toxicity level and are hence used in pharmaceutical, cosmetic and food products. Nonionic surfactants are made hydrophilic by a polymeric ethylene glycol chain being obtained as a polycondensation product of ethylene oxide. These are alkyl and aryl polyethoxylates (APEO). Recently, the benzene group in APEO has been removed due to its toxic/mutagenic/endocrine disrupting properties. Surfactants with an aromatic content (APEO) are more and more being replaced by aliphatic ethoxylates.

2.2.1.4 Amphoteric (Zwitterionic) Surfactants

These are surfactants with a market share of less than 2% and according to the operating conditions (e.g. water pH) may act as an anionic or eventually cationic surfactant. Near their “isoelectric point” these surfactants display both negative and positive charges and act as real amphoters often accompanied with a minimum interfacial activity and maximized water solubility (Salager, 1999). As in the case of cationic surfactants, their application range is very limited to a few specific cases (cosmetics) where biocompatibility and low toxicity is of integral importance (Schwartz et al., 1977).

2.2.2 Environmental Characteristics of Surfactants, Including Biodegradability And Toxicity

The biodegradability and toxicity of surfactant classes are briefly addressed in the forthcoming sections according to their chemical classification.

2.2.2.1 Anionic Surfactants

Among the most important and well studied anionic surfactants, LAS can be mentioned on the first place. LAS are readily degradable in activated sludge as well as attached (fixed film) growth reactors with half lives of less than 3-4 days. The major detectable degradation intermediate of LAS are mono- and dicarboxylic sulfophenyl acids having an alkyl chain length of 4 to 13 (Gonzalez-Mazo et al. 1997; Yadav et al., 2001). Desulfonation and aromatic ring cleavage follow in the biodegradation pathway of LAS. Due to the fact that aromatic ring oxidation and rupture requires the involvement of molecular oxygen, aromatic anionic surfactants cannot be degraded anaerobically (De Wolf et al., 1998; Krueger et al., 1998). Incomplete removal of such kind of surfactants results in bioaccumulation of partially degraded metabolites in sewage sludge and later on in river and lake sediments. Water hardness and salinity factors have serious impact on the biodegradation rate of surfactants (Krueger et al., 1998).

For anionic surfactants, EC_{50} values were often found far above 1 mg/L, indicating that the acute toxic effect of anionic surfactants is not very dramatic. According to acute toxicity studies carried out with the freshwater cladoceran *Daphnia magna*, the toxic effect of LAS increases with the alkyl chain length and molecular weight (Verge et al., 2000). But no estrogenic effects were observed for LAS by two in-vitro assays, namely the yeast estrogen receptor and the vitellogenin assay carried out with cultured trout hepatocytes. From the terrestrial toxicity data available, LAS cannot be considered as seriously toxic to terrestrial organisms (e.g. plants).

2.2.2.2 Cationic Surfactants

Cationic surfactants strongly sorb onto suspended solids such as activated sludge as a consequence of the electrostatic attraction of opposite charges. Most cationic surfactants are readily biodegradable under aerobic conditions. In the degradation of n-alkyl, n-methyl ammonium halides trimethylamine, dimethylamine and methylamine were identified as the main intermediates in sewage sludge (Nishiyama et al., 1995). Even long chain alkyl trimethyl ammonium salts are completely biodegradable under aerobic conditions. Especially primary biodegradation has been reported to occur promptly with half lives of only a few hours, whereas ultimate oxidation may take several days to weeks for some cationic surfactants. Quaternary ammonium salts are commonly used as biocides. Consequently, they are more biotoxic than other surfactant types. Again, the physicochemical properties (e.g. alkyl chain length, aromaticity) of a surfactant determine the fate and effects of these compounds in the environment (Garcia et al., 2001). Under anaerobic conditions, cationic surfactants exhibit only poor biodegradation and have no evidence of mineralization (Garcia et al., 2001). Primary biodegradation (removal of the parent compound under anaerobic conditions (during sludge digestion)) was found below 40% even for the simplest representatives. For this particular reason (low or no biodegradability under anoxic/anaerobic conditions), a cationic surfactant called "ditallow dimethyl ammonium chloride", that was the main cationic surfactant used as the active substance in most fabric softener formulations globally for over 30 years, has been replaced by diethyl ester dimethyl ammonium chloride. The new cationic surfactant is completely biodegradable under aerobic as well as anaerobic conditions; due to its short half life even in sewage sludge (< 1 d), it is practically completely removed (> 99%) in standard laboratory screening tests.

The acute toxicity of cationic surfactants is generally speaking highest for cationic surfactants (Ying, 2006). EC_{50} values can be < 0.2 mg/L, speaking for fairly high toxicity values. Acute toxicity tests carried out with *Daphnia magna* and Photobacterium phosphoreum for different quaternary ammonium surfactants revealed that in particular substitution of a methyl group with a benzyl group increased the toxicity of the cationic surfactant, whereas no significant (incremental) difference was obtained with increasing alkyl chain length. This can be attributed to the lower bioavailability of the longer chain homologues as a consequence of their decreased solubility. As a result, reduced water solubility (increasing hydrophobicity) accounts for lower biotoxicity (Giolando et al., 1995).

2.2.2.3 Nonionic Surfactants

Among the nonionic surfactants, the fatty alcohol ethoxylates are easily biodegradable under aerobic and anaerobic conditions and do not accumulated in aerobic sludge-amended soils. For two important metabolites, namely polyethlene glycol and free fatty alcohol, high primary biodegradation was observed accompanied with high concentrations of metabolites. In contrast to aerobic biodegradation of fatty alcohol ethoxylates, where central cleavage dominates, the first stage of anaerobic microbial attack is the cleavage of the terminal ethoxy unit, releasing acetaldehyde stepwise, and shortening the ethoxy chain until the lipophilic component is reached (Huber et al., 2000).

APEO belong to one of the most frequently used classes of nonionic surfactants and are nowadays detectable in most natural waters around the world (Giger et al., 1984). Their metabolites nonylphenol and octyl phenol have recently attracted lots of scientific attention because of their estrogenic effects and their ability to bioaccumulate in biota, sludge and sediments (Ying et al., 2002). Their relatively high K_{ow} ($\log K_{ow} = 4.0$-4.5) value and low water solubility (5-15 mg/L) enhances their tendency to bioaccumulate in the environment. It has been reported that most alkylphenols are rapidly metabolized by enzymatic actions to their corresponding glucuronide conjugates and different hydroxylated compounds as identified via GC/MS analysis (Lee, 1999). Related studies have indicated that alkylphenols are enzymatically metabolized and eliminated in body tissues via rapid conjugation but at the same time high amounts of the parent compound remain intact and tend to bioaccumulate. During the biodegradation of APEO at sewage treatment works short-chain ethoxylates. The complete elimination of the ethoxylate component is only possible under anaerobic conditions (Prats et al., 1999). The most intermediates reported for APEO are reported as alkylphenols; short-chain alkylphenol ethoxylates and/or ether carboxylates including alkylphenoxy acetic acid and alkylphenoxy ethoxy acetic acid (Ying, 2006). Extensive degradation to carboxylates is only possible under aerobic conditions (Ying, 2006). In natural waters and conventional treatment plants only partial degradation occurs. On the other hand, in appropriately treated (composted, digested) sludge practically complete degradation occurs under aerobic conditions; primary degradation occurs within a few days, whereas partial mineralization required several weeks. Degradation rates and efficiencies are temperature-, acclimation period and water salinity-dependent.

As has been mentioned above, one of the most frequently employed nonionic surfactants were nonylphenol ethoxylates (NPEO) for a long time. Concentrations of NPEO in wastewater up and down stream of effluent treatment plants ranged from 30 - 400 µg/L and non-detect to 300 µg/L, respectively. For the main anaerobic metabolite, nonylphenol, the concentrations in influent and effluent were approximately 10-15 times less (Snyder et al., 1999; DiCorcia et al., 2000). Concentrations of nonylphenol in biosolids were measured to be in the range of some hundred mg/kg (Brunner et al., 1988; Ejlertsson et al., 1999). Several studies concluded that the major sources of nonylphenol in the environment are urban wastewater treatment plants, natural waters near wastewater discharge (outfalls) and soils/sediments close to urban and industrialized areas (Ying, 2006).

Because (anaerobic/anoxic/aerobic) biological wastewater treatment can result in the production and elimination of undesirable alkyl phenols, it is often difficult to determine the actual removal efficiency/concentration of these compounds in wastewater treatment plant influent and effluent. In addition, most alkyl phenols (e.g. nonylphenol) can volatilize and/or preferentially adsorb onto solids (Ahel et al., 1993) making it very difficult to determine whether biological treatment is even occurring. The only information that can be gathered from the difference between influent and effluent concentration of APEO's is the elimination rate under specified conditions (e.g. in engineered treatment systems). From the above information, it is clear that alternative analytical measurement/treatment methods have to be developed to understand the fate and abtiotic/biotic removal mechanisms of APEO in the environment.

In acute toxicity assays, fathead minnows were especially sensitive to the effect of fatty alcohol alkyl ethoxylates on egg production and larval survival. APEO were found much less acutely toxic than their degradation products (metabolites), for instance nonylphenol or octyl phenol, on aquatic test organisms (Naylor, 1995). The toxicity generally decreases with an increase in the alkyl chain length of the APEO.

2.3 Textile Auxiliaries-Sequestering Agents

The principles behind sequestration is the formation of a water soluble complex between a sequestering agent and a polyvalent metal ion. The technique can be used for softening water; however, it is more often used as a component in many textile wet processing steps to remove metallic ions that interfere with the process (Tomasino,1992).

2.3.1 General properties and synthesis

2.3.1.1 Amino polycarboxylates

Amino polycarboxylates have the structure and features of a tertiary nitrogen atom in a central position in the molecule and acidic groups bound at alkyl residues around them. At least four functional groups, which possess donor properties, are spatially arranged in such a way that they can usually form 1:1 complexes. In this way, five-membered or six-membered rings are formed with multiplychargedmetal ions.

The commercial synthesis of the various amino polycarboxylates is based on the transformation of ethyl diamine to a cyanomethyl derivative, followed by hydrolysis (Thomas, 2003).

2.3.1.2 Hydroxy carboxylates

The hydroxy carboxylates HEDTA and HEIDA are chemically quite similar to the amino carboxylates EDTA and NTA. They also differ chemically in that one carboxylate group is replaced by a hydroxy group. The partially higher water solubilities of their salts compared to those of EDTA and NTA under acidic conditions can offer advantages (Thomas, 2003).

2.3.1.3 Organophosphonates

One or more nitrogen atoms in an amino polyphosphonate molecule can abstract a proton. This leads to a separation of the charge between the nitrogen atoms and the carboxyl and/or groups of phosphonic acids, thereby resulting in a betaine structure. Most organophosphonates with more than one phosphonate group bind bivalent metal ions similarly to, or better than, NTA. In addition to the amino polyphosphonates, the polyphosphonates have also attained a certain importance.

HEDP and PBTC, their structure is similar to that of the amino phospho-nates without the central nitrogen atoms. The synthesis of most organophosphonates is performed by reaction of phosphonic acid, formaldehyde and either ammonium ions to form ATMP or amines to form EDTMP, HDTMP (hexamethylene diaminotetra (methylene phosphonic acid)) and DTPMP. HEDP is made directly from PCl_3 and acetic acid (Deskundigen, 1997).

2.4 Other Auxiliaries

These auxiliaries are mainly used in pretreatment operations (scouring, mercerising, and bleaching) in order to allow thorough wetting of the textile material, emulsification of lipophilic impurities, dispersion of insoluble matter and degradation products.

Non-ionic and anionic surfactants are the compounds more frequently used for this purpose.

Table 2.2: Typical compounds used as detergents/ wetting agents

Class	Examples of products available on the market	Bio-degradability	Bio-eliminability
Non-ionic	Alcohol and fatty alcohols ethoxylates	>90%	80 – 85 %
	Fatty acids ethoxylates	>90 %	80 – 85 %
	Alkylphenol ethoxylates (APEOs)	~60 %	54 – 58 % (toxic metabolites)
	Fatty amines ethoxylates	60 – 80 %	72 – 73 %
Anionic	Alkyl sulphonates	>98 %	
	Alkyl aryl sulphonates	>98 %	
	Alkyl sulphates	>98 %	
	Dialkylsulphosuccinates	>98 %	
	Alkyl carboxylates (e.g. sodium palmitate, -stearate)	>98 %	
	Anionic Sulphated alkanolamides	n.d.	

2.5 AOPs

2.5.1 General Information and Basic Principles

Ozonation and Advanced Oxidation Processes (AOP) have been extensively studied for the removal a wide range of organic pollutants from water and wastewater (Legrini et al., 1993; Alvares et al., 2001; Zhou et al., 2001 and Oppenländer, 2003). AOP are attractive alternatives to conventional chemical oxidation processes using potassium permanganate or chlorine, including a higher oxidation potential (+ 2.8 eV versus SHE) and no production of potentially carcinogenic chlorinated by products. Although AOP have significant advantages over conventional treatment methods since AOP do not result in chemical or biological sludges and almost complete demineralization of organic pollutants is possible, the main disadvantage of AOP is the high cost of chemical agents and (electrical) energy requirements (Galindo et al., 2001). AOP are characterized by a variety of free radical chain reactions that involve combinations of chemical agents (e.g., ozone (O_3), hydrogen peroxide (H_2O_2), transition metals, and metal oxides) and auxiliary energy sources (e.g., ultraviolet-visible (UV-Vis) radiation, electronic current, γ-radiation, and ultrasound). AOP are processes involving in-situ generation of highly reactive species such as the hydroxyl radical ($HO^\bullet$), which is the primary oxidation AOP, while the other free radicals and active oxygen species are superoxide radical anions ($O_2^{\bullet -}$), hydroperoxyl radicals ($HO_2^{\bullet -}$), triplet oxygen ($3O_2$), and organic peroxyl radicals (ROO^-). Unlike many other radicals, $HO^\bullet$ is non-selective and thus readily attacks a large group of organic chemicals to convert them to less complex and less harmful intermediate products. Depending on the AOP, $HO^\bullet$ can be generated by any of one or combination of the following methods: i) chemical oxidation using H_2O_2, O_3, O_3/H_2O_2, Fenton's reagent; ii) radiation methods including UV radiation, γ-radiation, electron-beam and ultrasonic waves; iii) combination of any one of (i) with any of (ii), in particular UV radiation or ultrasonication; and iv) photocatalysis using UV and titanium dioxide (TiO_2) (Ray et al., 2004).

$HO^\bullet$ produced in either way of described above may attack organic pollutants by abstracting a hydrogen atom from the molecule (Clarke and Knowles, 1982). A common pathway for the degradation of organic compounds by $HO^\bullet$ (free radical initiated chain reactions) are given below (Carey, 1990);

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \tag{2.1}$$

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet \tag{2.2}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{2.3}$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \tag{2.4}$$

2.5.2 Types of Photochemicals AOPs

2.5.2.1 H_2O_2/UV-C

UV radiation has been the most widely used radiation method in initiating oxidation processes. The extent of absorption of UV radiation and absorption spectra by any organic compound is related to its molecular/bond (e.g. aromaticity/saturation of bonds) structure and the wavelength of radiation. For direct UV radiation, UV-C (200-280 nm) light irradiation is most commonly used, while UV-A (315-400 nm) is used for photocatalytic processes. UV-based AOPs also transform pollutants in two ways. Some organic chemicals absorb UV light directly, and absorption of this high-energy radiation can cause destruction of chemical bonds and subsequent breakdown of the contaminant. However, some organic species do not degrade very quickly or efficiently by direct UV photolysis. Therefore, addition of H_2O_2 to the UV process creates AOP conditions, often increasing the rate of contaminant degradation significantly. Baxendale and Wilson (1957) first studied the H_2O_2 photocatalytic decomposition in water. The most direct method for generation of $HO^\bullet$ is through the cleavage of H_2O_2. Photolysis of H_2O_2 yields $HO^\bullet$ radicals by a direct process with a yield of two radicals formed per photon absorbed by 254 nm (Baxendale and Wilson, 1957).

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 and Stefan et al., 1996).

$H_2O_2 + h\nu \rightarrow 2HO^\bullet$ **(2.5)**

$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O$ $k=2.7\times10^{7}\ M^{-1}\ s^{-1}$ (Buxton et al., 1988) **(2.6)**

$H_2O_2 + HO_2^\bullet \rightarrow HO^\bullet + H_2O + O_2$ $k=0.5\pm0.09\ M^{-1}\ s^{-1}$ (Buxton et al., 1988) **(2.7)**

$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$ $k=6\times10^{9}\ M^{-1}\ s^{-1}$ (Buxton et al., 1988) **(2.8)**

$2HO_2^\bullet \rightarrow H_2O_2 + O_2$ $k=8.3\times10^{5}\ M^{-1}\ s^{-1}$ (Buxton et al., 1988) **(2.9)**

$2HO^\bullet \rightarrow H_2O_2$ **(2.10)**

$HO^\bullet + M \rightarrow Products$ **(2.11)**

When H_2O_2 solution is exposed to UV irridation, 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 $HO^\bullet$ attacks H_2O_2, leading to the formation of perhydroxyl radical ($HO_2^\bullet$). The $HO_2^\bullet$ 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 $HO^\bullet$ with $HO_2^\bullet$, recombination reactions of $HO_2^{\bullet}$ and $HO^{\bullet}$ to regenerate H_2O_2, as presented in Equations 2.7, 2.8 and 2.9.

A comparative evaluation of Fenton's reaction, O_3 and H_2O_2 treatments coupled with ultraviolet light has shown that the UV/H_2O_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/O_3 system (Alfano et al., 2001). Moreover, UV/ H_2O_2 process forms no vapor emission that can be a significant problem with the treatment of volatile organics in an UV/O_3 system (Bolton and Cater, 1994).

The major drawback to 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).

2.5.2.2 Photo-Fenton Process ($Fe^{2+/3+}$/H_2O_2/UV)

The combination of Fenton reaction with UV light (180-400 nm), the so-called photo-Fenton reaction, had been shown to enhance the efficiency of the Fenton process (Wadley and Waite, 2004; Ruppert et al., 1993 and Sun and Pignatello, 1993).

The reason for the positive effect of irradiation on the degradation rate include the photoreduction of Fe^{3+} to Fe^{2+} ions, which produce new $HO^{\bullet}$ with H_2O_2 (Equation 2.12) according to the following mechanism;

$$Fe^{3+} + H_2O \overset{h\nu}{\rightarrow} Fe^{2+} + HO^{\bullet} + H^+ \qquad \textbf{(2.12)}$$

$$H_2O_2 \overset{h\nu}{\rightarrow} 2HO^{\bullet} \qquad (\lambda<400\text{ nm}) \qquad \textbf{(2.13)}$$

The main compounds absorbing UV light in the Fenton system are ferric ion complexes, e.g. $[Fe^{3+}(OH)^-]^{2+}$ and $[Fe^{3+}(RCO_2)^-]^{2+}$, which produce additional Fe^{+2}

by following (Equation 2.14 and 2.15) photo-induced, ligand-to-metal charge-transfer reactions (Sagawe et al., 2001):

$$[\mathrm{Fe^{3+}(OH)^-}]^{2+} \rightarrow \mathrm{Fe^{2+}} + \mathrm{HO^\bullet} \qquad (< \ ca. 450\, nm) \qquad \textbf{(2.14)}$$

$$[\mathrm{Fe^{3+}(RCO)^-}]^{2+} \rightarrow \mathrm{Fe^{2+}} + \mathrm{CO_2} + \mathrm{R^\bullet} \qquad (< \ ca. 500\, nm) \qquad \textbf{(2.15)}$$

Additionally, Equation 2.14 yields $HO^\bullet$, while Equation 2.14 results in a reduction of the total organic carbon (TOC) content of the system due to the decarboxylation of organic acid intermediates. It is very important to note that both reactions form the ferrous ions required for the Fenton reaction (Equation 2.14). The overall degradation rate of organic compounds is considerably increased in the photo-Fenton process, even at lower concentration of iron salts present in the system (Chen et al., 1997). Although in the photo-Fenton process, the energy requirement is reduced and it is highly effective in the treatment of organic pollutants. As already mentioned in the case of dark-Fenton process, the main disadvantage of the photo-Fenton method is the necessity to work at low pH (normally below 4), because at higher pH ferric ions would begin to precipitate as hydroxide. Furthermore, depending on the iron concentration used, it has to be removed after the treatment in agreement with the regulation established for wastewater discharge (Rodríguez, 2003).

2.5.2.3 Photochemical Ozonation (O_3/UV-C)

The UV photolysis of aqueous O_3 is an indirect method for producing H_2O_2 that in turn reacts with O_3 and also absorbs UV-C light irradiation to initiate a free radical chain reaction leading to $HO^\bullet$ formation (Glaze, 1987);

$$\mathrm{O_3} + \mathrm{H_2O} + h\nu\ (< 310\ \mathrm{nm}) \rightarrow \mathrm{H_2O_2} \qquad \textbf{(2.16)}$$

$$2\mathrm{O_3} + \mathrm{H_2O_2} \rightarrow 2\mathrm{HO^\bullet} + 3\mathrm{O_2} \qquad \textbf{(2.17)}$$

Equation (2.17) presents the net reaction of $HO^\bullet$ production by the $\mathrm{O_3} + \mathrm{H_2O_2}$ process (Hoigné, 1998). In addition, there are several other oxidative degradation mechanisms involved in the O_3+UV and O_3+H_2O_2+UV systems including direct UV-C photolysis, direct ozonation, direct oxidation with H_2O_2 and UV-C photolysis of $\mathrm{H_2O_2}$ (Beltrán, 2003). O_3 strongly absorbs in the UV region with a maximum molar absorption coefficient of 3300 M^{-1} cm^{-1} at 254 nm (Legrini, 1993; Glaze, 1987).The addition of H_2O_2 to the O_3+UV process accelerates O_3 decomposition resulting in an increased rate of $HO^\bullet$ generation. At first sight, process combinations seem to be more efficient, however, the main drawback of the combinative O_3+H_2O_2+UV treatment system is the low efficiency and high running costs associated with continuous O_3 production and UV radiation throughout the process, as well as high capital costs associated with the implementation of O_3 generators and UV photoreactors (Mokrini et al., 1997; CCOT 1995).

2.5.2.4 Heterogeneous Photocatalysis (TiO_2/UV)

Over the last few years, the tendency has been to carry out chemical oxidation in the presence of a catalyst that serves as a generator of $HO^\bullet$, and, therefore, the addition of an oxidizing agent into the reaction medium is not necessary. Heterogeneous photocatalytic processes consist of utilizing near UV radiation to photoexcite a semiconductor catalyst in the presence of molecular oxygen. Under these circumstances oxidizing species, either bound $HO^\bullet$ or free holes (h_{vb}^+), are generated. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near UV fraction of the solar spectrum (irradiation with a wavelength shorter than 380 nm) what transforms it into a economically/technically viable option to be used at large-scale (Malato et al., 2002). Many catalysts have been prepared and testes for their photocatalytic activity, although TiO_2 in the anatase form seems to possess the most interesting features, such as high stability, good treatment performance and low cost (Andreozzi et al., 1999). It presents the disadvantage of catalyst separation from solution, as well as fouling of the catalyst by organic matter.

Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (ca. 3.2 eV for anatase), producing electron-hole (e_{cb}^-, h_{vb}^+) pairs, as written in the Equation (2.18):

$$\mathrm{TiO_2} + hv \rightarrow \mathrm{e_{cb}^-}\,(\mathrm{TiO_2}) + \mathrm{h_{vb}^+}(\mathrm{TiO_2}) \qquad \textbf{(2.18)}$$

Where e_{cb}^- is the conduction band and vb stands for the valence band.

Both reductive and oxidative processes can occur at/or near the surface of the photo excited semiconductor particle. At the external surface, the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion (OH^-), organic compounds, or oxygen. In aerated aqueous suspensions, oxygen is able to scavenge conduction band electrons forming superoxide ions ($O_2^{\bullet-}$) and its protonated form, the hydroperoxyl radical ($HO_2^{\bullet}$) (Augugliaro et al., 2006):

$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad \textbf{(2.19)}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \quad \textbf{(2.20)}$$

In this way, electron/hole recombination can be effectively prevented and lifetime of holes is prolonged. $HO_2^{\bullet}$ can lead to the formation of H_2O_2:

$$HO_2^{\bullet} + e^- \rightarrow HO_2^- \quad \textbf{(2.21)}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad \textbf{(2.22)}$$

The charges can react directly with adsorbed pollutants, but reactions with water are far more likely since the water molecules are far more populous than contaminant molecules. Photogenerated holes can react with adsorbed water molecules (or hydroxide anions) to give hydroxyl radicals (Augugliaro et al., 2006):

$$H_2O + h^+ \rightarrow HO^{\bullet} + H^+ \quad \textbf{(2.23)}$$

2.6 Scavenging Effects in AOP Systems

The efficiency of AOPs depends on the production and utilization of $HO^{\bullet}$ and how effectively it attacks the target compound. A drawback resulting from the high reactivity and non-selectivity of $HO^{\bullet}$ 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 $HO^{\bullet}$ 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 wastewater and natural water, there exist various organic/inorganic substances and background impurities that usually reduce the oxidation efficiency of target pollutants by consuming significant amounts of $HO^{\bullet}$. Humic acids are the most important organic substances that are found in surface and ground water supplies. Of the inorganic impurities, carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) ions are very common. Carbonate and bicarbonate ions frequently found in natural waters, and chloride ion might exist in high concentrations in some effluents such as landfill leachate, bicarbonate species are added into a chemical coagulation unit to adjust or stabilize the solution pH for acquiring treatment performance. (Liao et al., 2001).

2.6.1 Chloride

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

$$HO^\bullet + Cl^- \rightarrow HOCl^{-\bullet} \qquad k = 4.3 \times 10^9\ (M^{-1}\ s^{-1}) \qquad \textbf{(2.24)}$$

2.6.2 Bicarbonate/Carbonate System

Carbonate and bicarbonate ions are known as the strongest hydroxyl radical scavengers; therefore, a high alkalinity wound be expected to adversely affect AOP reatment efficiency. The reaction of $HO^\bullet$ with CO_3^{2-} and HCO_3^- generates carbonate and bicarbonate radicals ($CO_3^{-\bullet}$ and $HCO_3^\bullet$), that exhibit similar reactivities toward other species (Peyton et al., 1998, Liao and Gürol, 1995).

$$CO_3^{2-} + HO^\bullet \rightarrow OH^- + CO_3^{-\bullet} \qquad k = 3.9 \times 10^8\ (M^{-1}\ s^{-1}) \qquad \textbf{(2.25)}$$

$$HCO_3^- + HO^\bullet \rightarrow H_2O + CO_3^{-\bullet} \qquad k = 8.5 \times 10^6\ (M^{-1}\ s^{-1}) \qquad \textbf{(2.26)}$$

The second-order rate of CO_3^{2-} and HCO_3^- with $HO^\bullet$ are 3.9×10^8 and 8.5×10^6 M^{-1} 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 reaction of CO_3^{2-} and HCO_3^- with $HO^\bullet$

radical may generate $HO_2^{\bullet}$ by consuming the H_2O_2 in the surrounding (Buxton et al., 1988) :

$$H_2O_2 + CO_3^{-\bullet} \rightarrow HCO_3^- + HO_2^{\bullet} \qquad k = 4.3 \times 10^5\ M^{-1}\ s^{-1} \qquad \textbf{(2.27)}$$

The $HO_2^{\bullet}$ may also oxidize the target contaminant, but at a much slower rate than $HO^{\bullet}$. Moreover, the $CO_3^{-\bullet}$ itself may act as an oxidant to degrade the target contaminant, however unlike $HO^{\bullet}$, it is highly selective and reacts relatively slowly with organic compounds.

2.6.3 Nitrate

It has been found that NO_3^- irradiation in aqueous solution can yield NO_2^-/HNO_2 directly (Mark et al., 1996).

$$NO_3^- + h\nu + H^+ \rightarrow NO_2^{\bullet} + HO^{\bullet} \qquad \textbf{(2.28)}$$

Nitrite is consumed by either photolysis or reaction with $HO^{\bullet}$ (Fischer and Warneck, 1996)

$$HO^{\bullet} + NO_2^- \rightarrow NO_2^{\bullet} + OH^- \qquad k = 6.0 \times 10^9\ (M^{-1}\ s^{-1}),\ pH = 9.5 \qquad \textbf{(2.29)}$$

$$NO_2^- + h\nu + H^+ \rightarrow NO^{\bullet} + HO^{\bullet} \qquad \textbf{(2.30)}$$

2.6.4 Sulfate

Sulfate radicals ($^{\bullet}SO_4^{2-}$) are strong oxidant species and can be formed by the reaction between sulfate species and $HO^{\bullet}$, (De Laat and Le, 2005).

$$HO^{\bullet} + HSO_4^- \rightarrow {}^{\bullet}SO_4^- + H_2O \qquad k_{HSO4^-} = 3.5 \times 10^5\ M^{-1}\ s^{-1} \qquad \textbf{(2.31)}$$

$^{\bullet}SO_4^-$ reacts with many environmental contaminants involving medium to high second-order reaction rate constants (10^6–10^9 M^{-1} s^{-1}; Neta et al., 1988). $^{\bullet}SO_4^-$ are less reactive but more selective than $HO^{\bullet}$ (10^7–10^{10} M^{-1} s^{-1}; Buxton et al., 1988).

2.6.5 Phosphate

$$HO^{\bullet} + H_3PO_4 \rightarrow H_2O + H_2PO_4^{\bullet} \qquad k = 4.2 \times 10^4\ (L\ mol^{-1}\ s^{-1}),\ T = 293K \qquad \textbf{(2.32)}$$

2.6.6 Humic Acid

At short irradiation times, where humic acids and hydrogen peroxide can be considered the only effective HO• radical scavengers, a steady-state kinetic analysis can be considered on the basis of the following simple reaction scheme (Brezonik and Fulkerson-Brekken, 1998):

$$HO^{\bullet} + \text{humic acid} \rightarrow \text{humic acid radical} + H_2O \qquad k_{HA} = 2.3 \times 10^4 \ (\text{mg of C/l})^{-1} \ s^{-1} \qquad \mathbf{(2.33)}$$

At higher humic acids concentration, it should be noted that the scavenging effect of humic acids may influence the initial rate constant of itself when the concentration of H_2O_2 is low (Liao and Gürol, 1995).

2.7 Studies dealing with the effect of $HO^{\bullet}$ scavengers on AOPs

2.7.1 Chloride

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 dye was possible in the presence of high Cl^- concentrations. They explained that the intermediate radicals that were found in the presence of chloride ions ($Cl_2^{-\bullet}$, $Cl^{\bullet}$, and $HOCl^{\bullet}$) were also responsible for oxidation of dye instead of hydroxyl radicals. They found that the concentration of $Cl^{\bullet}$ and $HOCl^{\bullet}$ were two orders of magnitude lower than the concentration of $Cl_2^{-\bullet}$. On the other hand, the concentration of $HO^{\bullet}$ was found to be three orders of magnitude below the concentration of $Cl_2^{-\bullet}$.The rate constants for the reaction of $HO^{\bullet}$ and $Cl_2^{-\bullet}$ radicals with Orange II were determined by laser kinetic spectroscopy and found as 6×10^9 M^{-1} s^{-1} and $3{,}7 \times 10^9$ M^{-1} s^{-1}, respectively.

2.7.2 Bicarbonate/Carbonate

Neppolian et al. (2002) investigated the influence of carbonate and chloride ions on the potocatalytic degradation of a textile dye, Reactive Blue 4. They found that the degradation of 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 dye solution in the range of 0, 25-2 g /L.

2.8 Advanced Oxidation of Surfactants

There is a wider scope of research on the degradability of surfactants by ozonation and AOP. The aim of following sections was to review and compare published research on the degradability of surfactants. Throughout the review, there are differences in the applied experimental conditions in different studies, which are the principle reason for the variations in final outputs and conclusions. As aforementioned, the following sections covers a brief review of studies conducted on the degradation of surfactants by employing ozonation and different AOP and a comprehensive summary of these studies including experimental conditions employed and eventually identified advanced oxidation intermediates as well as most important findings are presented in Tables.

2.8.1 H_2O_2/UV-C Process

More recently, Adams and Kuzhikannil (2000) investigated the effect of H_2O_2/UV process on the biodegradability of two major classes of QASs namely alkyldimethylbenzyl ammonium chloride (alkyl C12 to C18) and dioctyldimethyl ammonium chloride. The authors found that H_2O_2/UV advanced oxidation pretreatment was highly effective at enhancing the aerobic biodegradability of the alkyldimethylbenzyl ammonium chlorides yet ineffective at enhancing the biodegradability of dioctyldimethyl ammonium chloride.

The potential of H_2O_2/UV advanced photochemical oxidation of a nonionic, alkyl polyethylene ether-based surfactant was studied by Arslan-Alaton and Erdinc (2006) 40 W low-pressure, mercury vapor sterilizatiomp at varying pH (5-12) and H_2O_2 concentrations (10-100 mM) for 120 mins. The study showed that H_2O_2/UV advanced oxidation appeared to be a suitable treatment alternative and 90% COD removal ($COD_0 \approx 500$ mg/L) could be achieved under optimized conditions (H_2O_2 = 1000 mg/L; pH_0= 9).

2.8.2 Photo-Fenton Process ($Fe^{2+/3+}/H_2O_2$/UV)

Lin et al. (1999) studied the abatement of LAS (alkyl C12) and ABS (alkyl C12) by Fenton oxidation. They investigated the effect of pH, Fe(II) and H_2O_2 concentration and temperature on the removal of LAS and ABS. The optimum reaction conditions were found as 90 mg/L Fe(II), 60 mg/L H_2O_2, 50 mins of treatment time and initial pH around 3 for the initial surfactant concentration of 10 mg/L. In their study they concluded that the type of anionic surfactants has no significant effect on Fenton oxidation.

In another study Cuzzola et al. (2002) studied the Fenton-like oxidation of a commercial LAS mixture (alkyl C10 to C15) at pH 2 to 3. The authors found that heterogeneous iron catalysts including FeO(OH), Fe(III)/γ-Al_2O_3, Fe(III)/SiO_2 had very little effect on Fenton-like degradation of 1 g/L LAS in the absence of solar radiation (up to 4% mineralization), but the effect increased in the presence of solar radiation. A silica-based catalyst Fe(III)/SiO_2 (3%) showed comparable, but inferior photo-Fenton activity (27% mineralization) to ferrous sulfate (36% to 62%) without high metal pollution.

Ferrero (2000) investigated the application of Fenton and photo-Fenton oxidations for the degradation of NPEO (average n= 10). It was shown that UV irradiation with a low-pressure mercury lamp (250 W/L) could greatly enhance the TOC removal from the surfactant solution by Fenton process (109 mg/L $FeSO_4$, 1190 mg/L H_2O_2).

2.8.3 Photochemical Ozonation (O_3/UV-C)

Ozonation was examined for the degradation of SDBS by Beltrán et al. (2000). They calculated the kinetic rate constant for the reaction between $HO^{\bullet}$ and SDBS and direct ozone reaction as 1.6×10^{10} $M^{-1}s^{-1}$ and 3.68 $M^{-1}s^{-1}$, respectively.

Rivera-Utrilla et al. (2006) studied the efficacy of the system based on the simultaneous use of ozone and powdered activated carbon (PAC) in removing SDBS from drinking waters and on the influence of operational parameters (PAC dose, ozone dose and presence of radical scavengers) on this process. They found that in the first 5 mins of treatment, the percentage of SDBS removal as 18% and 30% for the O_3 and O_3/H_2O_2 systems, respectively, compared with 70% for the O_3/PAC system. Comparison of the O_3/PAC system with systems based on O_3 and O_3/H_2O_2 showed that the O_3/PAC system was more effective in the removal of SDBS. They concluded that the system based on the combined use of O_3/PAC represents an alternative to the oxidation systems commonly used in the treatment of drinking water (O_3, O_3/H_2O_2).

In another study, Mendez-Diaz et al. (2009) inspected SDBS aqueous solutions was subjected to O_3 and O_3/H_2O_2 and O_3/activated carbon systems. In their study they found ozone direct reaction rate with SDBS as 3.68 $M^{-1}s^{-1}$ and they concluded that O_3/H_2O_2 and O_3/activated carbon treatment processes, which generate $HO^{\bullet}$ radical, as promising AOPs to remove SDBS from water.

2.8.4 Heterogeneous Photocatalysis (TiO_2/UV)

Ike et al. (2002) studied the ozonation and TiO_2/UV treatment of the biodegradation products of NPEO, including nonylphenol and nonylphenol monoethoxylate, and nonylphenol carboxylic acid. The authors found that the effectiveness of ozonation (17 mg/L applied) for the degradation of these compounds was on the order of nonylphenol carboxylic acid >> nonylphenol > nonylphenol monoethoxylate, which was different from that achieved by TiO_2/UV oxidation: nonylphenol > nonylphenol monoethoxylate > nonylphenol carboxylic acid. This result suggests that the degradation mechanisms of these compounds by the two oxidation processes are substantially different.

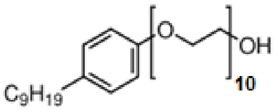
3. MATERIALS AND METHOD

3.1 Materials

3.1.1 Nonyl Phenol Ethoxylate (NP-10)

The selected model pollutant NPEO is a nonionic textile surfactant with 10 ethoxylated chains. This commercially important product is called NP-10 and is usually applied as an aqueous solution in the concentration range of 0.5-1.0 g/L at pH 10-11. It is frequently employed as a wetting agent in the textile fabric preparation stage. Its organic carbon contribution to the ultimate, combined textile effluent is around 400-500 mg/L in terms of COD (Zollinger, 2003). NP-10 was obtained from a local textile chemicals manufacturing plant (purity > 99%) and used as received. For all experimental runs, aqueous NPEO solutions were prepared at an initial COD of 450 mg/L to mimic their typical concentration in textile preparation effluent. The molecular structure and physicochemical properties of NPEO are shown in Table 3.1.

Table 3.1: Molecular structure and physicochemical properties of NPEO

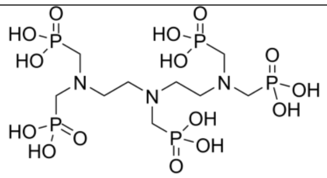
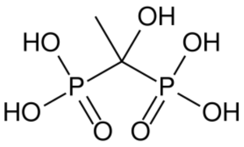
	NPEO
Molecular Structure	
Molecular Formula	$C_9H_{19}\text{-}C_6H_6\text{-}(CH_2\text{-}CH_2O)_{10}OH$
Molecular Mass (g/mol)	666
g NPEO / g COD	2.14
g NPEO / g TOC	0.69

*Obtained from the calibration curves established for COD and TOC values of aqueous NPEO

3.1.2 Phosphonic Acid Based Sequestering Agents

The effect of organic sequestering agents on the photochemical removal of NPEO was investigated by applying varying concentrations of two different phosphonic acid-based compounds. The selected sequestering agents were diethylene triamine penta-methylene phosphonic acid (DTPMP) and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) which are frequently being used in textile preparation stage. The molecular structures and physicochemical properties of DTPMP and HEDP are presented in Table 3.2.

Table 3.2: Molecular structure and physicochemical properties of selected sequestering agents

	DTPMP	HEDP
Molecular Structure		
Molecular Formula	$C_9H_{28}N_3O_{15}P_5$	$C_2H_8O_7P_2$
Molecular Mass (g/mol)	573	206
g Sequestering agent / g COD	0.71	0.47
g Sequestering agent / g TOC	0.18	0.12

3.1.3 Other Chemicals

35% w/w H_2O_2 (Fluka) was used as received without any dilution. HPLC-grade acetonitrile (Merck, Germany), sodium carbonate (Merck), sodium chloride (Merck) and all other chemicals were of analytical grade and used as received. Aqueous solutions were prepared with deionized water (Sartorius Stedim Biotech. S.A., France). Ultrapure water used in HPLC analyses was prepared using an Arium 611 UV water purification system (Sartorius Stedim Biotech. S.A., France). The pH of the reaction solutions was adjusted using concentrated (6 N) or diluted (1 N) H_2SO_4 and NaOH solutions. Catalase enzyme (*Micrococcus lysodeikticus*; 100181 AU/mL) was purchased from Fluka.

3.2 UV-C Photoreactor and Light Source

In the H_2O_2/UV-C oxidation experiments aqueous NPEO solutions and synthetic textile preparation samples under the experimental conditions given in Table 3.3 for a photochemical reaction time of 120 min. The pH and ionic strength of the synthetic solutions were not controlled throughout the experiments. H_2O_2/UV-C oxidation experiments were carried out using a 3250 mL-capacity batch stainless steel photoreactor (length=95 cm; width=6 cm) bearing a 40W low-pressure, mercury vapor sterilization lamp that was located at the center of the reactor in a quartz glass envelope (Figure 3.1). The incident light flux of the UV lamp at 253.7 nm and effective UV-C light path length were determined with H_2O_2 actinometry (Nicole et al., 1990) as 1.44 x 10^{-5} Einstein L^{-1} s^{-1} and 5.67 cm, respectively. During a typical run, 3250 mL reaction mixture was continuously circulated through the reactor at a rate of 360 mL/min using a peristaltic pump (Aripa). A typical experiment was run as follows; H_2O_2 (30 mM) was added from the stock solution to aqueous NPEO and desired amounts of textile preparation additives. Thereafter, the reaction mixture was fed to the UV-C photoreactor and a sample t = 0 was taken. At this point, the reaction was initiated by turning on the UV-C lamp. Samples were taken at regular time intervals for up to 120 min and analyzed for NPEO, COD and TOC, pH and residual H_2O_2. Residual (unreacted) H_2O_2 was determined iodometrically during the course of the reaction. After that, the remaining H_2O_2 was immediately destroyed with enzyme catalase to prevent any positive interferences with the COD measurements.

Energy per volume treatd: Pt/V=40w×1.2h/3.2L=15J/L.

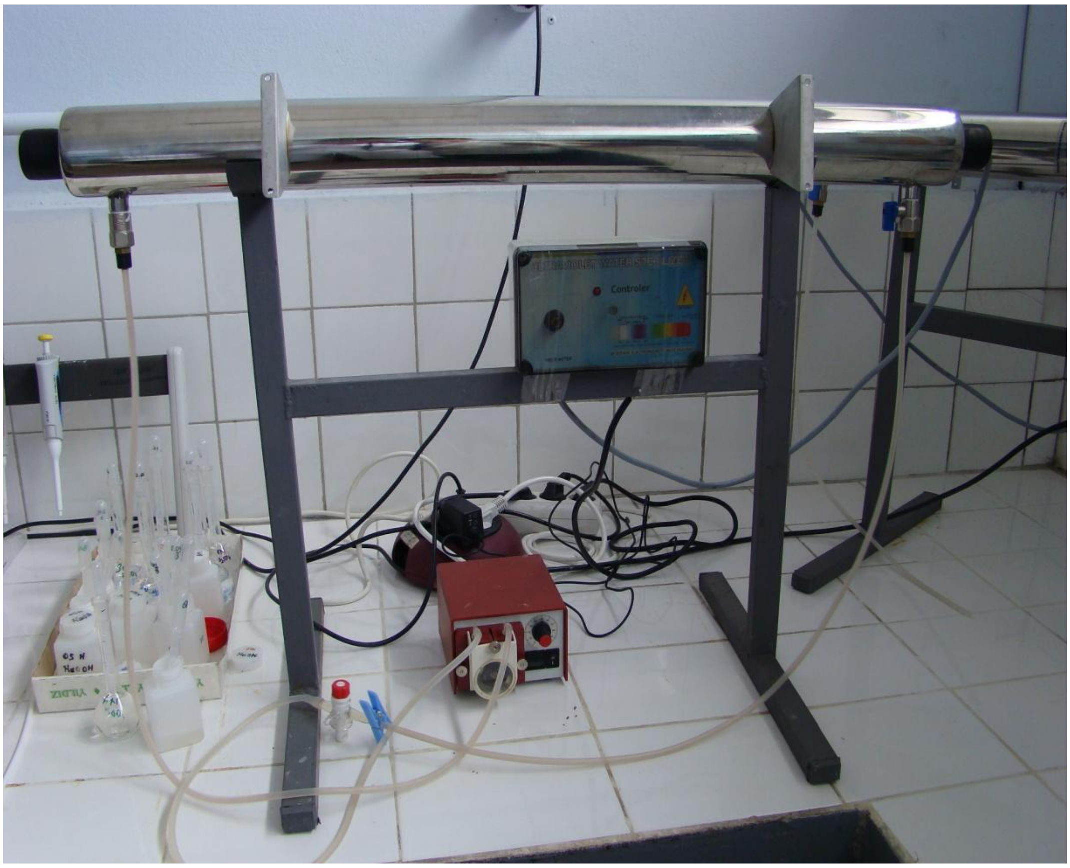


Figure 3.1 : Experimental set-up of the H_2O_2/UV-C photoreactor and light source

3.3 Experimental Procedures

In the first part of the study, H_2O_2/UV-C treatment of aqueous NPEO solution was investigated at an initial H_2O_2 concentration of 30 mM and a reaction pH of 10.5 in order to assess the degradation characteristics of the nonionic textile surfactant. For this purpose, aqueous NPEO solutions were prepared in deionized water at an initial COD of 450 mg/L since a typical textile dye manufacturing wastewater exerts a COD in the range of 400-500 mg/L (IPPC, 1998). The selected initial reaction pH is also typical for textile preparation effluent (IPPC, 1998). The experiment conducted at the above-mentioned conditions was called “Plain Experiment” herein.

Textile preparation processes involve the use of different textile auxiliaries such as soda-ash (Na_2CO_3), sodium hydroxide (NaOH), sodium chloride (NaCl) and organic sequestering agents (IPPC, 1998). In the second part of the study, the individual effects of these auxiliaries on NPEO oxidation were studied at varying typical concentrations of these auxiliaries. For this purpose H_2O_2/UV-C photochemical oxidation of aqueous NPEO and textile auxiliaries was carried out at the same conditions used for the plain experiment (H_2O_2 = 30 mM; pH = 10.5). The influence of NaCl was investigated at two different pH values (3.0 and 10.5) to examine the inhibitory effect of Cl^- to the system performance at acidic and alkaline pH conditions.

In the last part of the experimental study, the effect of textile preparation chemicals on aqueous NPEO removal was examined in order to mimic real textile preparation effluents. The experimental conditions of the selected H_2O_2/UV-C treatment combinations are listed in Table 3.1. As can be seen from Table 3.1, the aqueous solutions of the Textile Preparation Effluent No III and IV were prepared by using NaOH instead of soda-ash and the type and concentration of organic sequestering agent (DTPMP, HEDP) was also changed.

Table 3.3: Experimental conditions of the H_2O_2/UV-C oxidation studies for NPEO removal by each effect of the textile preparation auxiliaries

Studied Effect	Experimental Conditions
Chloride	pH_o = 10.5 and 3.5; H_2O_{2o}=30 mM; Cl^- = 3.0g/L; $NPEO_o$ = 210 mg/L; COD_o = 450 mg/L ; TOC_o = 145 mg/L
Bicarbonate/ Carbonate	pH_o = 10.5; H_2O_{2o}=30 mM; CO_3^{2-} = 1, 2,3, 4 and 5.0 g/L $NPEO_o$=210 mg/L; COD_o = 450 mg/L; TOC_o = 145 mg/L
Bicarbonate/Carbonate and Chloride	pH_o = 10.5; H_2O_{2o}=30 mM; CO_3^{2-} = 1.0 g/L; Cl^- = 3.0 g/L $NPEO_o$=210 mg/L; COD_o=450 mg/L; TOC_o = 145 mg/L
Organic Sequestering Agents (DTPMP and HEDP)	pH_o = 10.5; H_2O_{2o}=30 mM $NPEO_o$=210 mg/L; COD_o=550-1350 mg/L; TOC_o = 205-390 mg/L; DTPMP = 0.5, 1.0, 1.5, 2.0, 2.5 g/L; HEDP = 0.5, 1.0, 1.5 g/L
Textile Preparation Effluent I	pH_o = 10.5; H_2O_{2o}=30 mM CO_3^{2-} = 3.0 g/L; Cl^- = 3.0g/L; DTPMP = 1.5 g/L $NPEO_o$=210 mg/L; COD_o=940 mg/L; TOC_o = 350 mg/L;
Textile Preparation Effluent II	pH_o = 10.5; H_2O_{2o}=30 mM CO_3^{2-} = 3.0 g/L; Cl^- = 3.0g/L; HEDP = 1.5 g/L $NPEO_o$=210 mg/L; COD_o=1000 mg/L; TOC_o = 270 mg/L
Textile Preparation Effluent III	pH_o = 11.5; H_2O_{2o}=30 mM Cl^- = 3.0 g/L; NaOH = 1.5 g/L; DTPMP = 1.0 g/L $NPEO_o$=210 mg/L; COD_o=800 mg/L; TOC_o = 270 mg/L
Textile Preparation Effluent IV	pH_o = 11.5; H_2O_{2o}=30 mM Cl^- = 3.0 g/L; NaOH = 1.5 g/L; HEDP = 1.0 g/L $NPEO_o$=210 mg/L; COD_o=650 mg/L; TOC_o = 225 mg/L

3.4 Analytical procedures

The amount of NPEO was measured via high-performance liquid chromatography (HPLC, Agilent 1100 Series, USA) equipped with a Diode-Array Detector (DAD, G1315A, Agilent Series) and Nova-pack reverse phase C18 column (3.9 × 150 mm, 5 µm, Waters). The detector was adjusted to a wavelength of 280 nm. Methanol-water solution (80:20, v/v) was used as mobile phase at a flow rate of 1.1 mL/min. The column temperature was fixed at 25°C during the measurements. The injection volume was selected as 50 µL. Under the conditions described above, the NPEO detection limit was 5 mg/L.

COD measurements were done by the close reflux titrimetric method according to ISO 6060 (1986). Prior to analyses, residual H_2O_2 was destroyed with catalase to prevent its positive interference with COD measurements. A Shimadzu V_{CPN} model carbon analyzer (combustion method) equipped with an autosampler was used for monitoring the TOC.

Residual (unreacted) H_2O_2 was determined by employing the molibdate-catalyzed iodometric method (Official Methods of Analysis, 1980).

The changes in pHs of the reaction solutions was measured with a Thermo Orion model 520 pH-meter.

3.5 UV absorbance measurements

In order to measure the UV absorbance of aqueous DTPMP, NPEO and HEDP solutions individually and in combination as well as that of aqueous H_2O_2, spectrophotometric measurements were conducted. The obtained UV absorbance measurements were used to explain the competition of the organic sequestering agents with NPEO for UV-C light absorption at 254 nm, where the light source used in the present study has is maximum light emission. The results of the measurements as well as the conditions are given in Table 3.4. For the UV spectrophotometric measurements a Perkin-Elmer Lambda 25 model spectrophotometer was used. Absorbance measurements were carried out at 254 nm and an optical cell path length of 1 cm.

Table 3.4: Absorbance of aqueous NPEO, DTPMP and HEDP at 254 nm

Solution	**UV absorbance (cm^{-1})**
NPEO =210 mg/L, pH = 10.5	0.0920
HEDP = 1.5 g/L, pH = 10.5	0.0151
DTPMP = 1.5 g/L, pH = 10.5	0.0588
NPEO (210 mg/L) + HEDP (1.5 g/L), pH = 10.5	0.1069
NPEO (210 mg/L) +DTPMP (1.5 g/L), pH=10.5	0.1162

4. RESULTS AND DISCUSSION

The main objective of the present study was to evaluate and discuss the experimental results which were divided into two sections. In the first part, it was primarily focus on investigating the individual effects of common salts which are chloride (3 g/L) and soda ash (carbonate – bicarbonate; 1-5 g/L) and two commercially important organic sequestering agents which are DTPMP (0.5-2.5 g/L) and HEDP (0.5-1.5 g/L). In the second part, four different textile preparation effluents were simulated in order to choose the ideal textile preparation recipe, which can supply the best performance during the H_2O_2/UV-C oxidation process.

4.1 Plain Experiment

4.1.1 Rate of NPEO, COD and TOC degradation

NPEO degradation was found to follow pseudo-first order kinetics as represented by Equation 4.1.

$$dc/dt=k'C \qquad \textbf{(4.1)}$$

Where, C is the concentration of the NPEO (mg/L) and k' is the pseudo-first-order reaction rate constant ($time^{-1}$). Upon integration of Equation 4.1, the following equation was obtained,

$$\ln(C_t/C_0)=-k't \qquad \textbf{(4.2)}$$

Where, t is the irradiation time (min), C_0 and C_t are the concentration of NPEO (in mg/L) at time zero and time t, respectively.

In addition, degradation of COD and TOC as well as H_2O_2 consumption also followed the pseudo-first order kinetics, calculations of pseudo-first-order reaction rate constants are same with NPEO's.

4.1.2 Degradation of NPEO, COD, TOC

The plain experiment was run without any textile preparation auxiliary introduction, only in the presence of the target compound NPEO (210 mg/L) with 30 mM H_2O_2 at pH_0=10.5, for a 120 mins photochemical treatment time.

The NPEO, COD and TOC results of the plain experiment were illustrated in Figure 4.1. The degradation of all studied NPEO via H_2O_2/UV-C process followed pseudo-first order kinetics with respect to NPEO, COD and TOC exerting high correlation coefficients ($R^2 > 0.99$) for the treatment period 0–120 mins. The pseudo-first order of NPEO, COD and TOC degradation rate constants (k) were determined by Equation (4.2), and k values displayed in the Table 4.1.

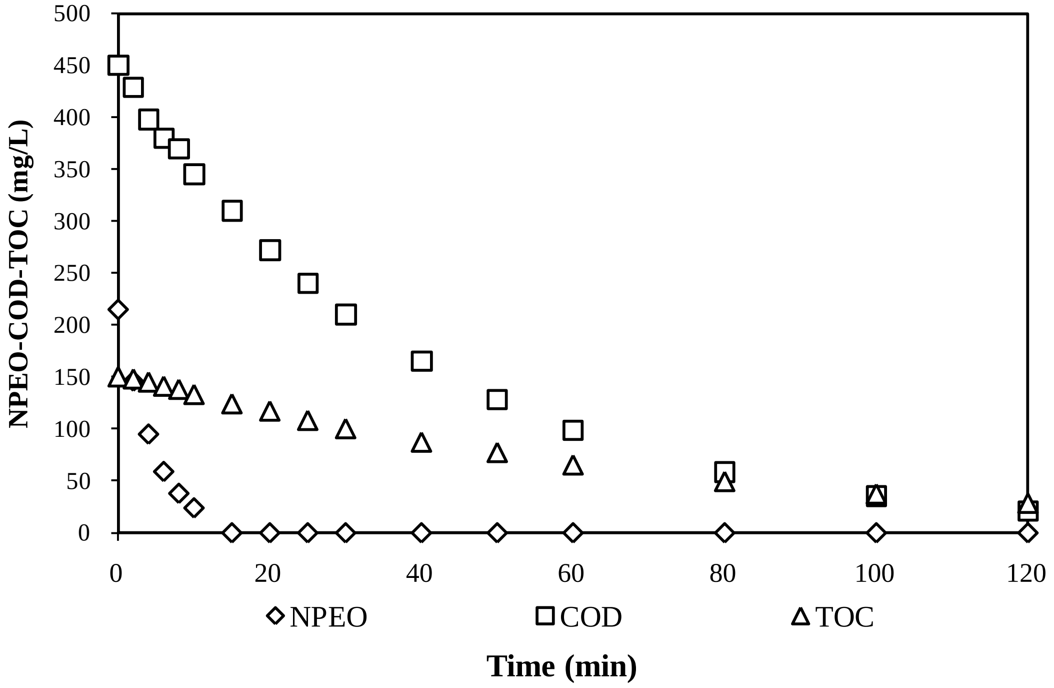


Figure 4.1 : Degradation of NPEO, COD and TOC by H_2O_2/UV-C process in 120 mins.

As is evident in Figure 4.1 depicting NPEO, COD and TOC abatement versus treatment time, at the end of the reaction period, complete COD and TOC degradation was obtained and complete NPEO removal could be achieved after only 15 mins photochemical oxidation by H_2O_2/UV-C. Hereby, it is comprehended that the fastest degradation rate was NPEO and slowest one was TOC.

NPEO disappeared in 15 mins showed that all NPEO converted to the photochemical degradation products but not the final one CO_2. The abatement of advanced oxidation intermediates were collectively presented by the environmental sum parameter COD. Information about the speed and degree of ultimate oxidation can be derived from the TOC data, representing mineralization of the NPEO and its photodegradation products to oxidation end products- CO_2.

COD and TOC should be used together to present the state of the photochemical degradation, although COD is regarded as an appropriate indicator for the degree of oxidation, a complex molecule cannot be completely destroyed during the standard digestion procedure of the COD test (APHA, 1998). Furthermore, oxidative attack of amino groups cannot be observed by COD measurements only (Shiyun et al., 2002). Hence, it is important to follow TOC together with COD removal during photochemical treatment.

Degradation rates had established in the following decreasing order: NPEO > COD > TOC (Table 4.1). As generally being expected for photochemical advanced oxidation processes, the degradation of the NPEO is fastest, followed by COD and TOC abatements that occurred at significantly slow rates (Oppenlander, 2003).

The effect of pH on NPEO degradation with H_2O_2/UV-C treatment process: The effect of initial pH on NPEO degradation was also examined in separate experiments (COD_0 = 450 mg/L; 30 mM H_2O_2, treatment time = 120 mins) conducted at varying pHs (3, 7, 10.5, extremely high pH; 11.8). Experimental results have shown that there was no noticeable difference between NPEO degradation rates and efficiencies in the pH range of 3-10.5; however, inhibition of oxidation kinetics was observed at an initial pH of 11.8 (data not shown), because of the accelerating effect of increasing pH on H_2O_2 ionization at pH > 11 (pKa = 11.6).

In addition, control experiments with aqueous NPEO solution (450 mg/L COD; pH = 10.5) were carried out to observe the effects of direct UV-C photolysis and direct H_2O_2 oxidation on NPEO degradation. Experimental results have demonstrated that NPEO degradation due to UV-C treatment only and due to direct H_2O_2 oxidation in the absence of UV-C light irradiation was negligible); less than 15% (data not shown).

4.1.3 H_2O_2

The result of H_2O_2's consumption during NPEO photochemical advanced oxidation was illustrated in Figure 4.2. The initial H_2O_2 concentration was 30 mM.

As is seen from Figure 4.2, H_2O_2 has a downtrend which was mainly attribute to the reaction which is the photolysis of H_2O_2 under the UV light into two hydroxyl radicals ($HO^•$) (Baxendale and Wilson, 1956).

$$H_2O_2 + h\nu \rightarrow 2\ HO^• \qquad \textbf{(4.3)}$$

The degradation of the NPEO is due to the generation of hydroxyl radicals through the H_2O_2 photolysis upon irradiation by UV light (Equation 4.3).

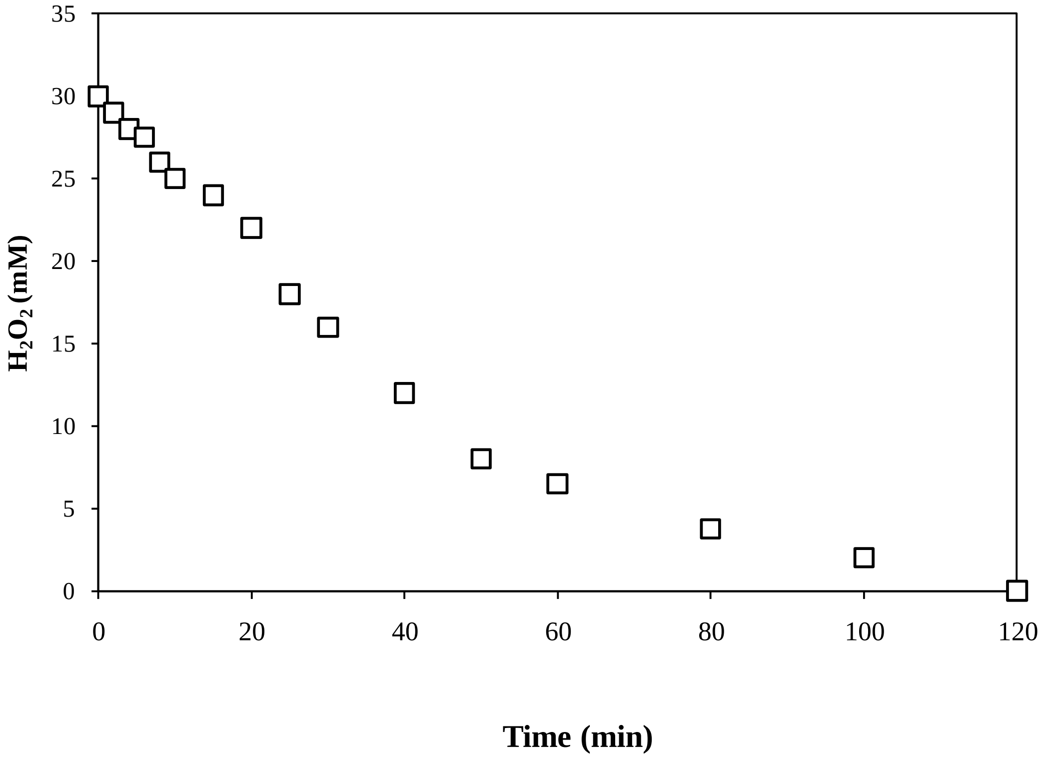


Figure 4.2 : Consumption of H_2O_2 (30 mM) during NPEO degradation by H_2O_2/UV-C process in 120 mins.

In all H_2O_2/UV-C experiments, residual H_2O_2 remained in the reaction solution (>30 mg/L) indicating that it was provided in excess and exerted no rate limiting effect on the oxidation reaction (Arslan-Alaton et al., 2001). Throughout all H_2O_2/UV-C of different water quality conditions, the H_2O_2 decomposition rate remains unchanged (Liao et al., 2000).

Table 4.1: Pseudo-first order rate constants for NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k value (min^{-1})			
Experiment	NPEO	COD	TOC	H_2O_2
Plain (NPEO only)	0.2211	0.0255	0.0142	0.0270

4.1.4 pH

The changes in pH (pH_0=10.5) value during NPEO photochemical advanced oxidation was illustrated in Figure 4.3.

As it shown in Figure 4.3, pH value declined as the oxidation reaction occurs, at the 50 mins solution became to most acidic, pH value around 3.8, after that pH value slightly increased.

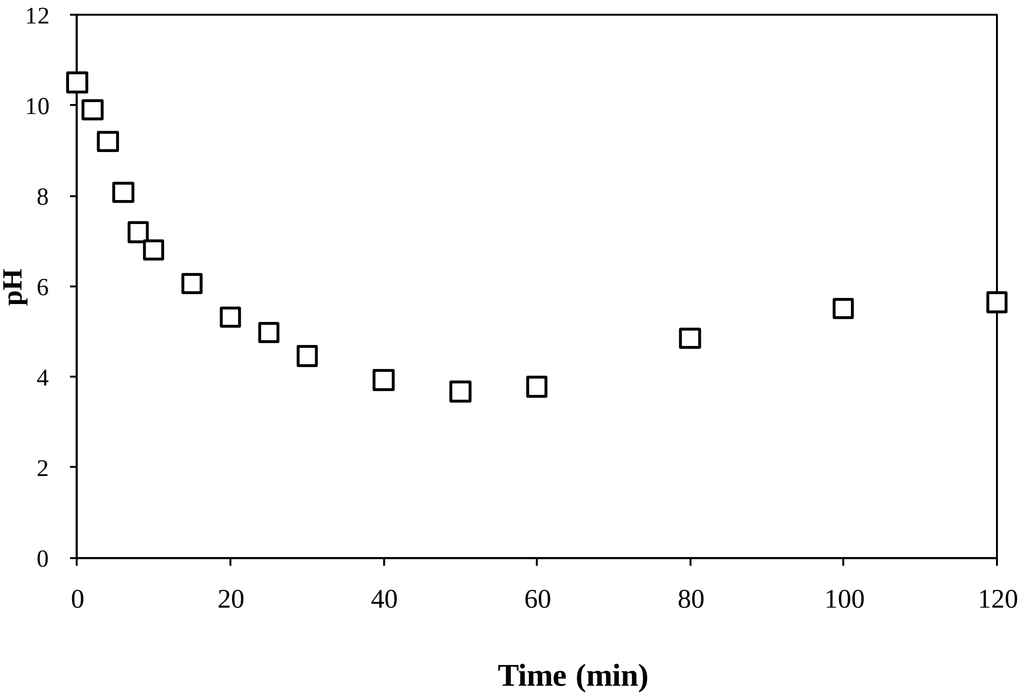


Figure 4.3 : pH value (pH_0=10.5) during NPEO degradation by H_2O_2/UV-C process in 120 mins.

Such trend of pH value changing appears in any kind of the oxidation reaction, that is continuously converted to photochemical degradation products, which are acidic intermediates, leaded to decline of pH value during treatment. Those acidic intermediates were continuously oxidized into the final products, such as CO_2 which resulted in the pH slightly move up to around 6.0. Such changing trend can be seen as evidence for proving the oxidation occurs or not in the following study. Gültekin (2002) also reported similar trend of the pH effect.

Due to the fact that H_2O_2 is a weak acid (pK_a= 11.6), at pH_0=10.5 only 7.2% H_2O_2 ionized, pH effect is negligible.

4.2 Effect of Chloride

In these experiments, Cl^- (3 g/L) was introduced to the H_2O_2/UV-C system at two different pH values in order to investigate effect of chloride on the degradation of NPEO by H_2O_2/UV-C treatment at different pH (acidic and alkaline).

4.2.1 NPEO

The changes in the concentration of NPEO during photochemical advanced oxidation in the presence of chloride were illustrated in Figure 4.4. The pseudo-first order of NPEO, COD and TOC degradation as well as H_2O_2 consumption rate constants of chloride effect had determined by Equation (4.2), k values displayed in the Table 4.2.

The effect of Cl^- on the degradation of NPEO by the H_2O_2/UV-C process was examined with the initial chloride concentration of 3 g/L at pH_0=10.5 and pH_0=3.5.

As is shown in the Figure 4.4, 3 g/L chloride at pH_0=10.5 the NPEO concentration changing trend is similar with the plain experiment's which means chloride has no negative effect on the process at pH_0=10.5. The rate coefficient of NPEO abatement in the presence with chloride at pH_0=10.5 is 0.1995 min^{-1} very close to plain experiment which is 0.2211 min^{-1} whereas 3 g/L chloride at pH_0=3.5 NPEO concentration changing trend showed a pronounceable difference with the plain experiment's at pH_0=10.5 which means slight inhibitory effect observed. The rate coefficient of NPEO abatement in the presence with chloride at pH_0=3.5 is 0.1496 min^{-1} which is smaller than plain experiment's 0.2211 min^{-1} (Table 4.2).

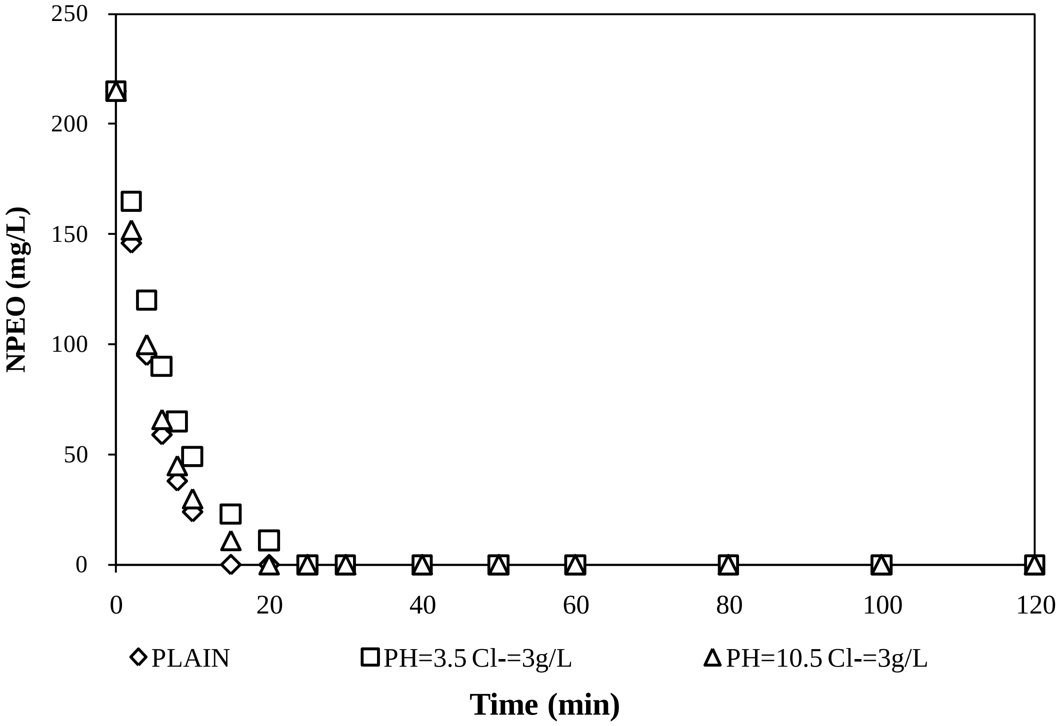


Figure 4.4 : Degradation of NPEO in the presence of Cl^-(3 g/L) by H_2O_2/UV-C process at different pH (pH_0=10.5 and pH_0=3.5).

This is to say that neutral or alkaline condition is desired to achieve a better oxidation efficiency of a target contaminant in presence of chloride ions (Jayson and Parsons, 1973). Under the same chloride concentration, increasing the pH will counteract the effect of chloride concentration increase on $HO^•$ scavenging as depicted in Reaction (4.4) and (4.5) (Liao et al., 2000).

$HO^•+Cl^-\rightarrow HOCl^{-•}$ $k = 4.3 \times 10^9$ M^{-1} s^{-1} **(4.4)**

$HOCl^{-•}+H^+\rightarrow Cl^•+H_2O$ $pK_a=7.2$ **(4.5)**

As reported, the $HO^•$ was formed first through H_2O_2 photolysis (Baxendale and Wilson, 1956). Then, the $HO^•$ scavenged by Cl^- at a bimolecular rate constant being $(4.3 \pm 0.4) \times 10^9$ M^{-1} s^{-1} (Jayson and Parsons, 1973), according to Reaction (4.4). The $HOCl^{-•}$ initially formed in Reaction (4.4) can further dissociate back to $HO^•$ and Cl^- with a dissociation rate constant of $(6.1 \pm 0.8) \times 10^9$ s^{-1} (Jayson and Parsons, 1973), which was slightly larger than the $HO^•$ scavenging reaction rate constant. On the other hand, the $HOCl^{-•}$ can also be converted to form chlorine atoms rapidly through the protonation reaction, as shown in Reaction (4.5), with the rate constant being $(2.1 \pm 0.7) \times 10^{10}$ M^{-1} s^{-1} (Jayson and Parsons, 1973). The reverse reaction rate constant of Reaction (4.5) (1.3×10^3 s^{-1}; Jayson and Parsons, 1973) is relatively small when compared to the forward reaction rate constant. Note that the pK value for deprotonation reaction (i.e., reverse reaction) in Reaction (4.5) is 7.2, which is a critical value in affecting the $HO^{\bullet}$ concentration. As the pH value is greater than 7.2, the $HOCl^{-\bullet}$ becomes the dominant species, and conversely the $Cl^{\bullet}$ becomes the dominant one at pH < 7.2. Hence, the raise of pH can lead to more amount of $HO^{\bullet}$ formation through $HOCl^{-\bullet}$ dissociation reaction, as depicted in Reaction (4.5).

4.2.2 COD

The COD abatement during NPEO photochemical advanced oxidation in the presence of chloride at pH_0=10.5 and pH_0=3.5 were illustrated in Figure 4.5.

As is shown in the Figure 4.5, 3 g/L chloride at pH_0=10.5 the COD abatement changing trend is similar with the plain experiment's. The rate coefficient of COD abatement in the presence with chloride at pH_0=10.5 is 0.0201 min^{-1} very close to plain experiment which is 0.0255 min^{-1} whereas 3 g/L chloride at pH_0=3.5 COD abatement trend showed a pronounceable difference with the plain experiment's at pH_0=10.5 which means slight inhibitory effect observed. The rate coefficient of COD abatement in the presence with chloride at pH_0=3.5 is 0.0156 min^{-1} which is smaller than plain experiment's 0.0255 min^{-1} (Table 4.2).

Upon comparison with plain experiment, it can be concluded that COD abatement of the plain experiment is faster, the effect of chloride is more pronounced at acidic pH (pH_0 =3.5).

The possible reason may be due to the Cl^-'s scavenger effect at acidic pH, the oxidation reaction rate retarded.

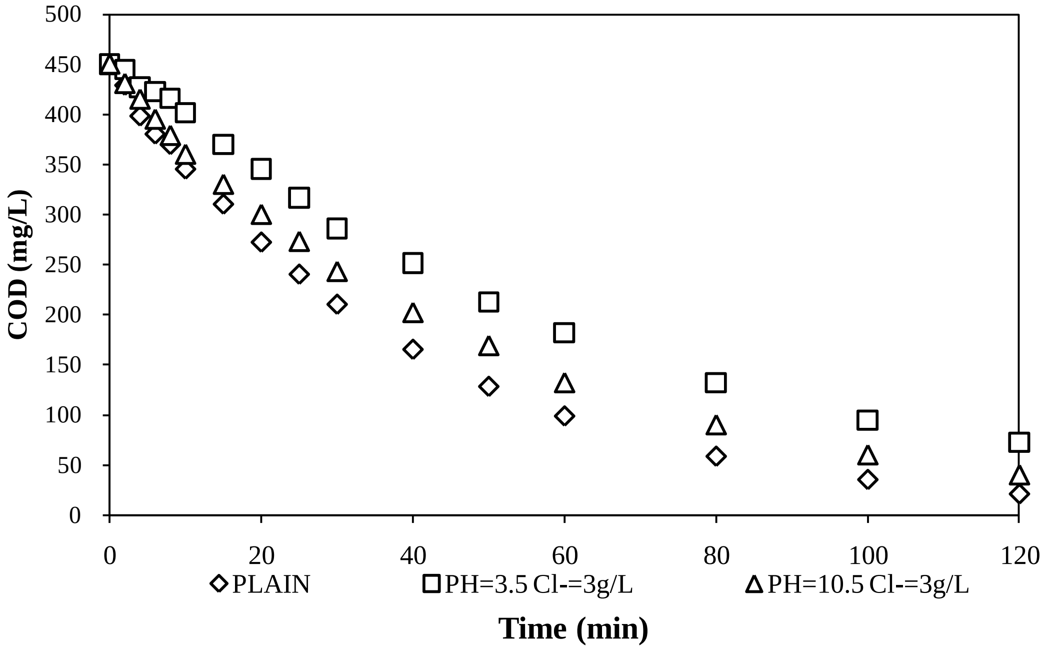


Figure 4.5 : COD abatement in the presence of 3 g/L Cl^- during NPEO degradation by H_2O_2/UV-C process at different pH (pH_0=10.5 and pH_0=3.5).

4.2.3 TOC

The TOC abatement during NPEO photochemical advanced oxidation in the presence of chloride at pH_0=10.5 and pH_0=3.5 were illustrated in Figure 4.6.

Figure 4.6 showed the same situation as the COD, which is TOC abatement changing trend in the presence of 3 g/L chloride at pH_0=10.5 is similar with the plain experiment's TOC changing trend. The rate coefficient of TOC abatement is 0.0145 min^{-1} in the presence with chloride and 0.0142 min^{-1} in the absence with chloride at pH_0=10.5, respectively.

At pH_0=3.5 TOC abatement trend showed a pronounceable difference with the plain experiment at pH_0=10.5 which means slight inhibitory effect obtained. The rate coefficient of TOC abatement in the presence with chloride at pH_0=3.5 is 0.0129 min^{-1} (Table 4.2).

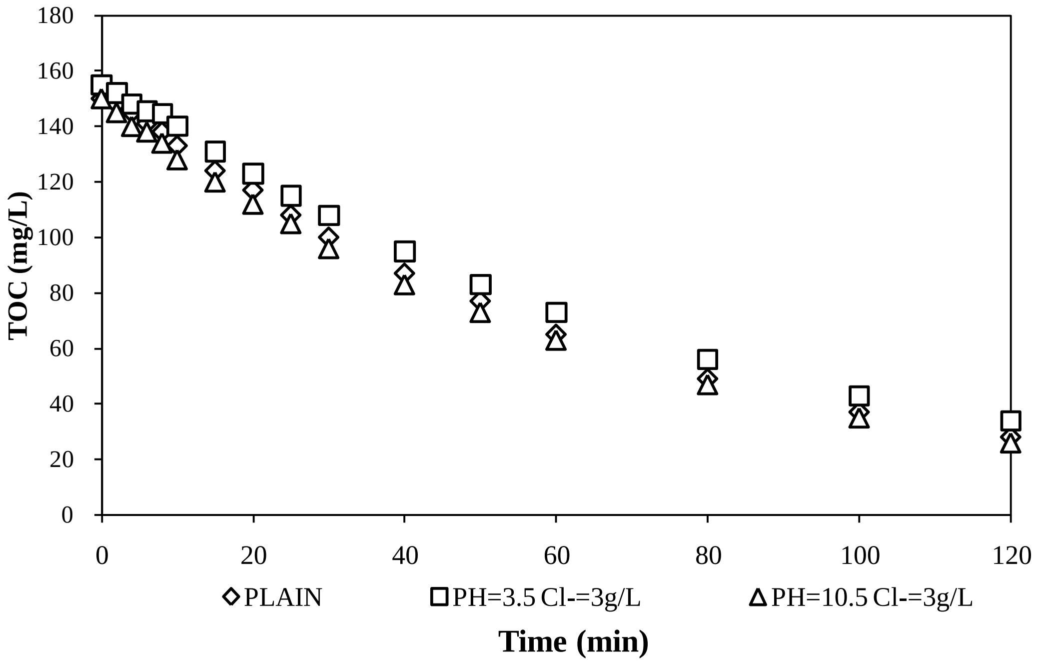


Figure 4.6 : TOC abatement in the presence of Cl^- during NPEO degradation by H_2O_2/UV-C process at different pH (pH_0=10.5 and pH_0=3.5).

The retardation can be explained by the fact that Cl^- is a scavenger which consumed the $HO^•$, as Liao et al (2000) reported that in the presence of Cl^- only showed the significant retardation at the acidic pH.

Upon comparison with plain experiment, it can be concluded that TOC abatement of the plain experiment is faster, the effect of chloride is more pronounced at acidic pH (pH_0 =3.5).

4.2.4 H_2O_2

The result of H_2O_2 consumption during NPEO photochemical advanced oxidation in the presence of Cl^- at pH_0=10.5 and pH_0=3.5 were illustrated in Figure 4.7. The initial H_2O_2 concentration was 30 mM.

As is shown in the Figure 4.7, H_2O_2 totally be consumed in 120 mins, the rate of H_2O_2 consumption had no evident differences between plain and in the presence of chloride at pH=3.5 and 10.5. According to the related literature, the presence of Cl^- at pH(<11) had no effect on H_2O_2 consumption via UV-C photolysis (Liao et al., 2001).

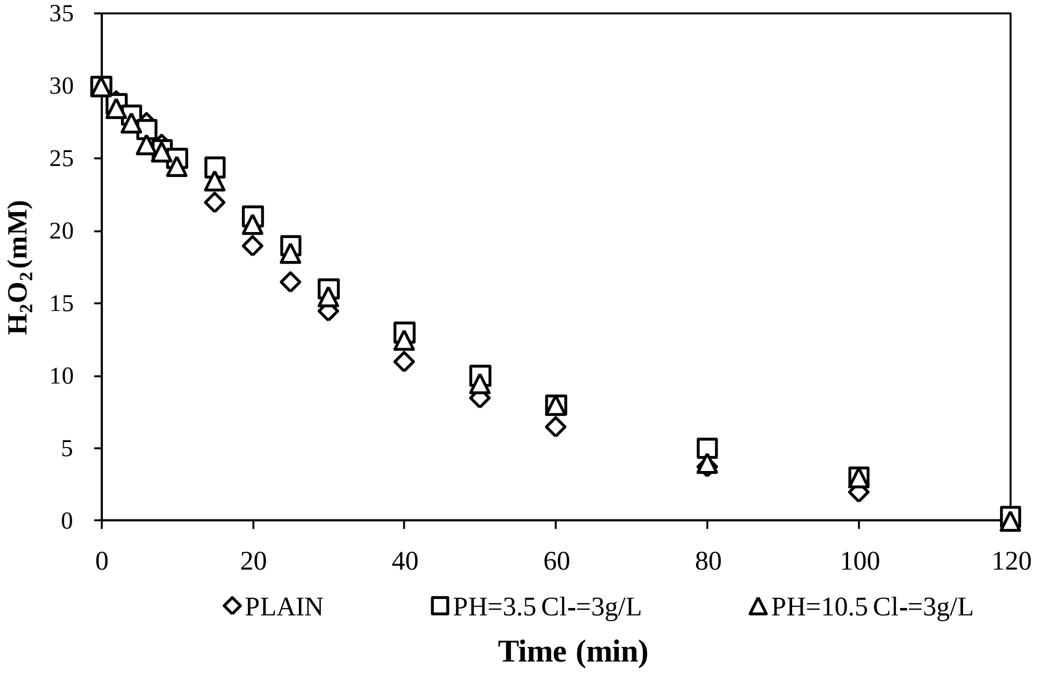


Figure 4.7 : H_2O_2 consumption in the presence of 3 g/L Cl^- during NPEO degradation by H_2O_2/UV-C process at different pH (pH_0=10.5 and pH_0=3.5).

Table 4.2: Pseudo-first order rate constants in the presence of chloride for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k value (min^{-1})			
Experimental conditions	NPEO	COD	TOC	H_2O_2
Plain (NPEO only)	0.2211	0.0255	0.0142	0.0270
pH=3.5 Cl^-=3g/L	0.1496	0.0156	0.0129	0.0230
pH=10.5 Cl^-=3g/L	0.1995	0.0201	0.0145	0.0231

4.2.5 pH

The changes in pH (pH_0=10.5) value during NPEO photochemical advanced oxidation in the presence of Cl^- at pH_0=10.5 and pH_0=3.5 were illustrated in Figure 4.8.

As is shown in the Figure 4.8, Cl^- at pH_0=10.5 has a similar changing trend with plain experiment which can prove and confirm oxidation indeed occurred. Similar pH change trend also reported in other scientific literature (Gültekin, 2002), since the pH_0=3.5 which is already acidic, so the pH didn’t decline as plain experiment did, but after reach the most acidic point, the trend slightly moved up which also proved that at pH_0=3.5 the oxidation occurred.

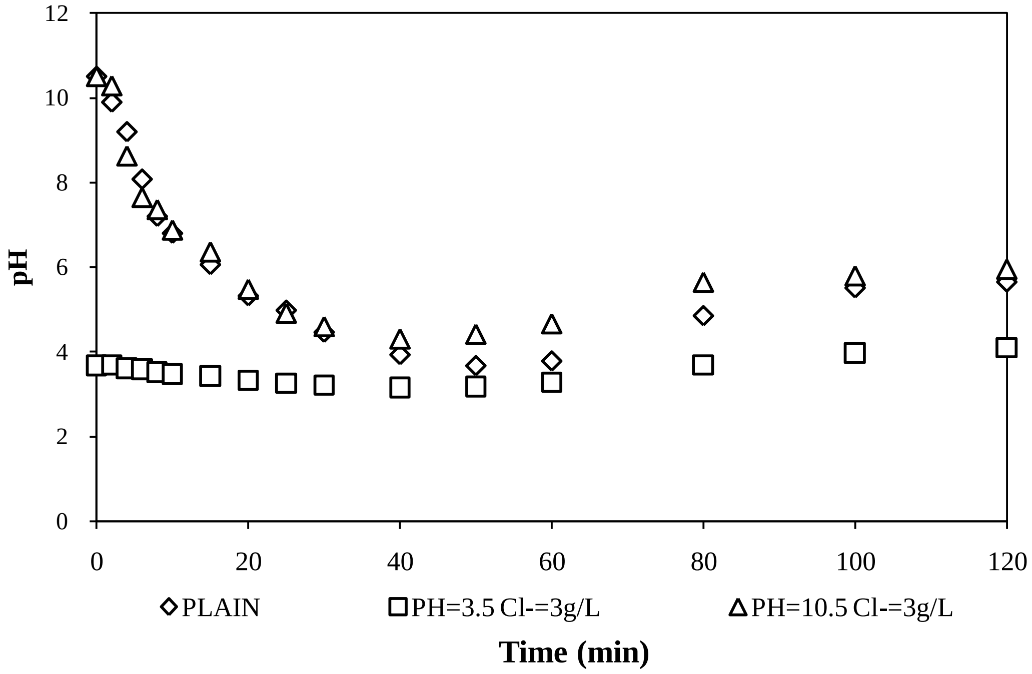


Figure 4.8 : pH value in the presence of 3 g/L Cl^- during NPEO degradation by H_2O_2/UV-C process at different pH (pH_0=10.5 and pH_0=3.5).

4.3 Effect of HCO_3^-/CO_3^{2-}

In this section, the CO_3^{2-} (1-5 g/L) introduced to the H_2O_2/UV-C at pH_0=10.5 in order to study the effect of HCO_3^-/CO_3^{2-} by evaluated in terms of parent pollutant NPEO, COD and TOC abatement as well as H_2O_2 consumption.

The pseudo-first order of NPEO, COD and TOC degradation as well as H_2O_2 consumption rate constants of carbonate effect had determined by Equation (4.2), k values displayed in the pseudo-first order constant rate presented in Table 4.3.

4.3.1 NPEO

The effect of various initial carbonate concentrations during the NPEO photochemical degradation had been investigated from 1-5 g/L at pH_0=10.5, the changes in the concentration of NPEO during photochemical advanced oxidation in the presence of carbonate were illustrated in Figure 4.9.

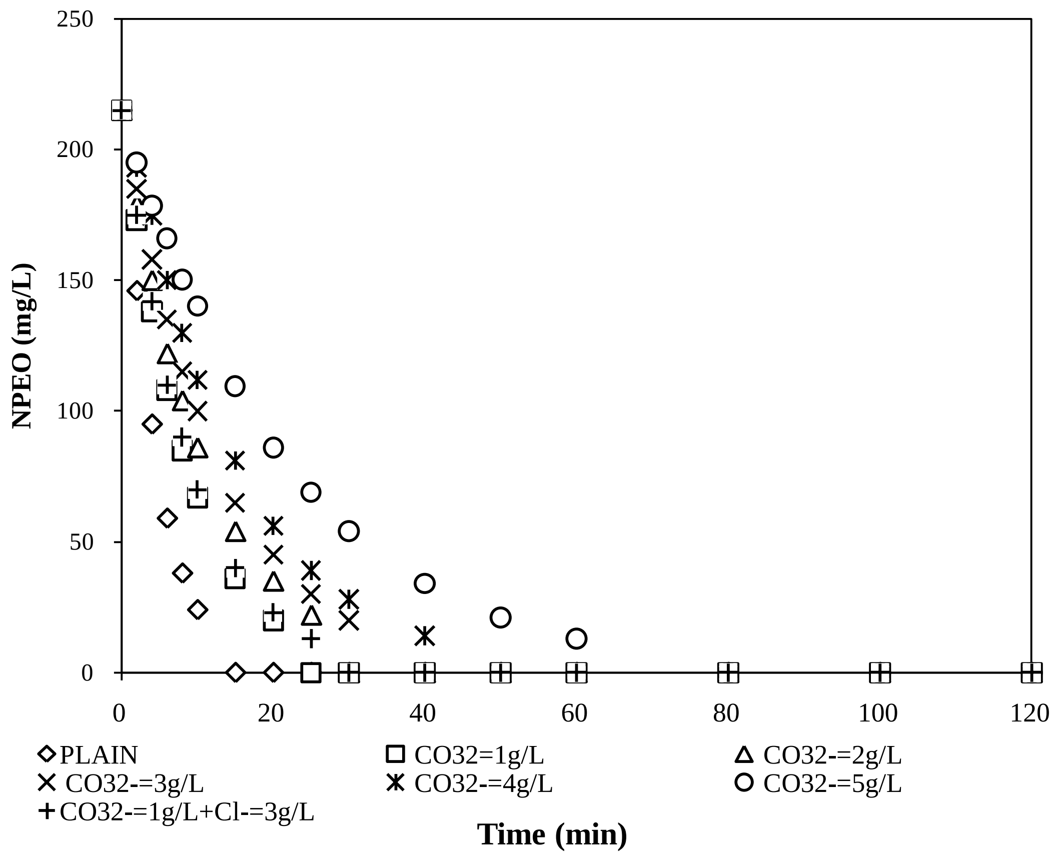


Figure 4.9 : Degradation of NPEO in the presence of CO_3^{2-} (1-5 g/L) by H_2O_2/UV-C process.

The significant inhibitory effect of carbonate displayed in Figure 4.9, which is unsurprising, as the concentration increased the effect had enhanced. The k_{NPEO}=0.0467 min^{-1} in the presence of the 5 g/L carbonate which is five times decreased than the plain experiment (k_{NPEO}=0.2211 min^{-1}). Normally 89% NPEO would be degraded after 10 mins, but only 35% NPEO was be observed in the presence of CO_3^{2-} (5 g/L).

The possible reasons of the strong retardation effect can be contributed to the $HO^{\bullet}$ radical scavenging effect by carbonate and bicarbonate ions. These results could be explained by the following reaction Equation (4.6) that has a higher reaction rate constant k value comparing with reaction Equation (4.7) that has a lower one. Therefore, upon the comparison with these two reaction constant rates, it can be concluded that carbonate is stronger scavenger than bicarbonate (Buxton et al., 1988).

$$CO_3^{2-} + HO^{\bullet} \rightarrow OH^{-} + CO_3^{-\bullet} \qquad k = 3.9 \times 10^{8}\ M^{-1}\ s^{-1} \qquad \mathbf{(4.6)}$$

$HCO_3^- + HO^\bullet \rightarrow H_2O + CO_3^{-\bullet}$ $k = 8.5 \times 10^6\ M^{-1}\ s^{-1}$ **(4.7)**

As reported that higher pH leads to lower $HO^\bullet$ concentration in the presence of bicarbonate species alone (Liao et al., 1995). At higher pH value, the equilibrium between bicarbonate and carbonate species shifts towards carbonate ion, which has higher reactivity towards $HO^\bullet$ than the bicarbonate ion. The rate constant of reaction between $HO^\bullet$ and the bicarbonate ion is $8.5 \times 10^6\ M^{-1}\ s^{-1}$ and the carbonate ion $3.9 \times 10^8\ M^{-1}\ s^{-1}$ (Buxton et al., 1988).

$HCO_3^- \rightarrow CO_3^{2-} + H^+$ $pKa_2 = 10.33$ **(4.8)**

The reaction (4.8) shows the bicarbonate and carbonate equation that bicarbonate can convert into carbonate with $pKa_2=10.33$, in this case, at pH=10.5 11.27 mM (67%) bicarbonate was formed when the carbonate concentration is 16.67 mM (1 g/L).

Furthermore, when the carbonate 1 g/L combined with 3 g/L chloride the results showed that similar with the 1 g/L carbonate alone (Table 4.3) which reconfirmed the conclusion which is the chloride caused a negative effect on the process only at an acidic pH. Therefore, when the carbonate ions were introduced into the solution, which kept a constant high pH chloride, did not show its inhibitory effect.

Upon comparison with the plain experiment, it can be concluded that NPEO abatement of plain experiment is faster, effect of carbonate is significant.

4.3.2 COD

The COD abatement during NPEO photochemical advanced oxidation in the presence of carbonate (1-5 g/L) at $pH_0=10.5$ were illustrated in Figure 4.10.

As is shown in the Figure 4.10, COD abatement changing trend in the presence of carbonate has significant difference when compare with the plain experiment's. The rate coefficient of COD abatement in the presence with 5 g/L carbonate at $pH_0=10.5$ is $0.0028\ min^{-1}$. The COD abatement of 1 g/L carbonate combine with 3 g/L chloride has a similar changing trend with 1g/L carbonate also observed.

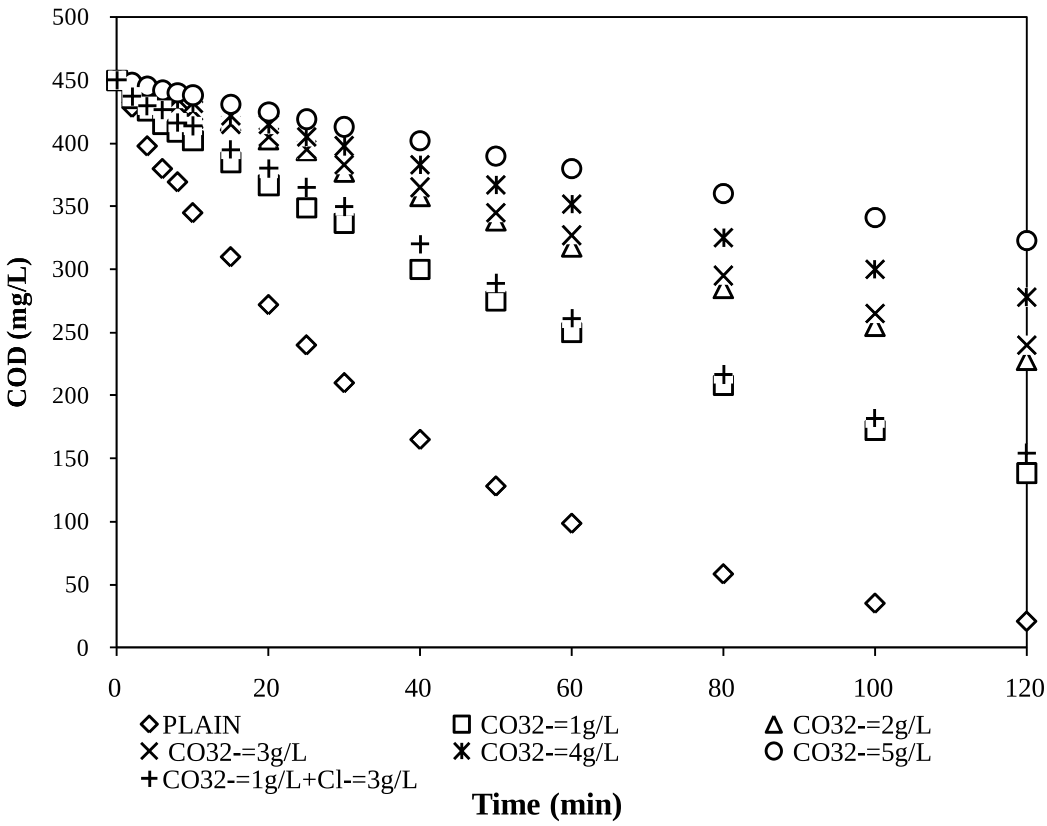


Figure 4.10 : COD abatement during NPEO degradation in the presence of CO_3^{2-} (1-5 g/L) by H_2O_2/UV-C process.

The possible reason might be explained by the reaction Equation (4.6) and (4.7), the same reason caused the retardation of NPEO degradation, which is carbonate scavenger effect that consumed the $HO^{\bullet}$ and retarded the reaction rate.

4.3.3 TOC

The TOC abatement during NPEO photochemical advanced oxidation in the presence of carbonate (1-5 g/L) at pH_0=10.5 were illustrated in Figure 4.11.

As is shown in the Figure 4.11, TOC abatement changing trend in the presence of carbonate has significant difference when compare with the plain experiment's. The rate coefficient of TOC abatement in the presence with 5 g/L carbonate at pH_0=10.5 is 0.0020 min^{-1} almost come to zero. The TOC abatement of 1 g/L carbonate combine with 3 g/L chloride has a similar changing trend with 1 g/L carbonate also observed.

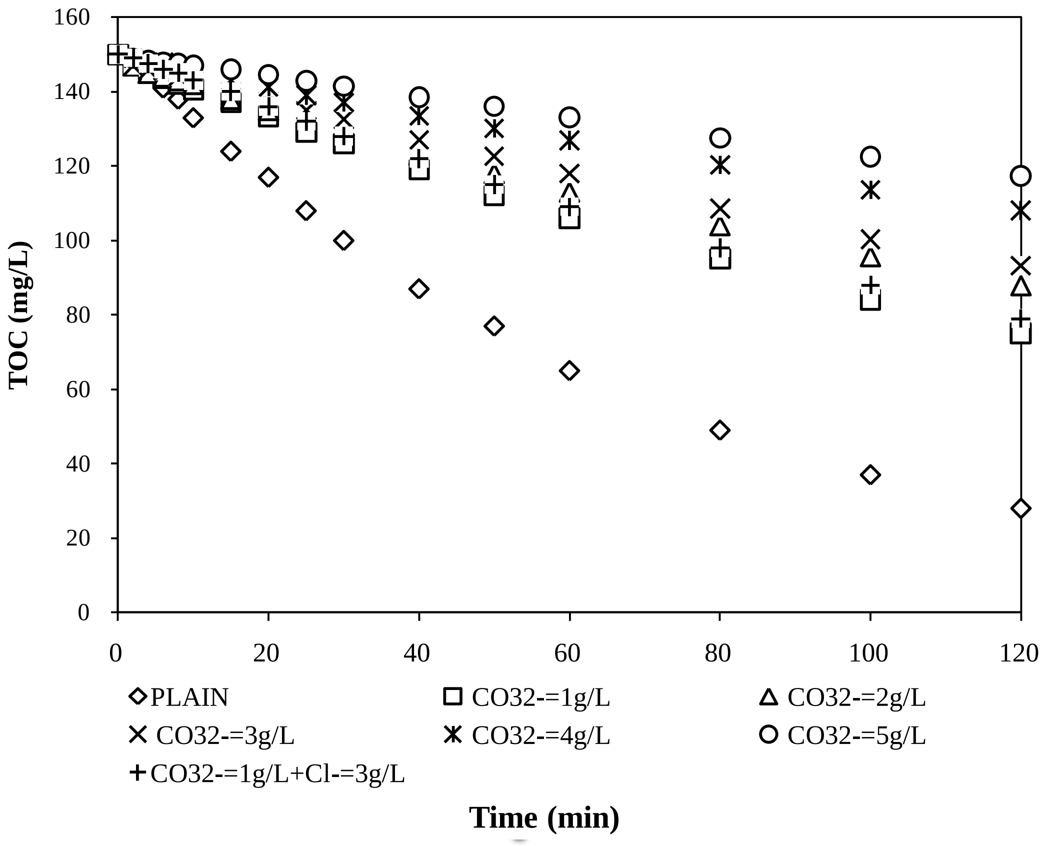


Figure 4.11 : TOC abatement during NPEO degradation in the presence of CO_3^{2-} (1-5 g/L) by H_2O_2/UV-C process.

As aforementioned CO_3^- and HCO_3^- may cause retardation of NPEO oxidation and degradation rate, which is the same situation had also observed on the abatement of COD and TOC (Figure 4.10 and 4.11). The possible reason might be explained by the reaction Equation (4.6 and 4.7) which is the same reason caused the retardation of NPEO degradation.

4.3.4 H_2O_2

The H_2O_2 consumption in the presence of carbonate (1-5 g/L) at pH_0=10.5 was illustrated in Figure 4.12.

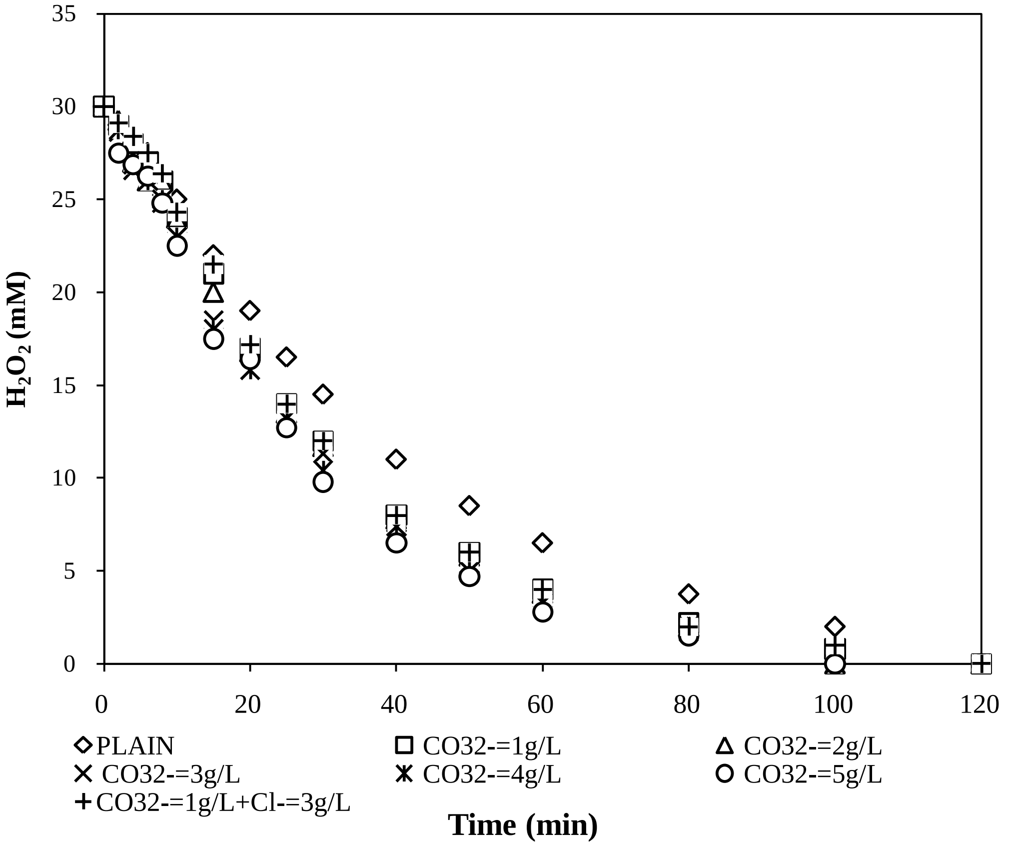


Figure 4.12 : H_2O_2 consumption in the presence of CO_3^{2-} (1-5 g/L) by H_2O_2/UV-C process.

As is evident in Figure 4.12, slightly higher H_2O_2 consumption was observed, but not that much significant difference. The possible reason might be the change of pH value, the ionization of H_2O_2 was effected. As reported that H_2O_2 consumption rate is not affected by inorganic ions present in the reaction solution (Liao et al., 2000).

Table 4.3: Pseudo-first order rate constants in the presence of carbonate for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k value (min^{-1})			
CO_3^{2-} (g/L)	NPEO	COD	TOC	H_2O_2
0 (Plain)	0.2211	0.0255	0.0142	0.0270
1	0.1197	0.0096	0.0057	0.0362
2	0.0911	0.0056	0.0044	0.0364
3	0.0792	0.0052	0.0039	0.0367
4	0.0693	0.0040	0.0027	0.0370
5	0.0467	0.0028	0.0020	0.0388
1 g/L CO_3^{2-}+3 g/L Cl^-	0.1128	0.0090	0.0142	0.0361

4.3.5 pH

The changes in pH values in the presence of carbonate were illustrated in Figure 4.13.

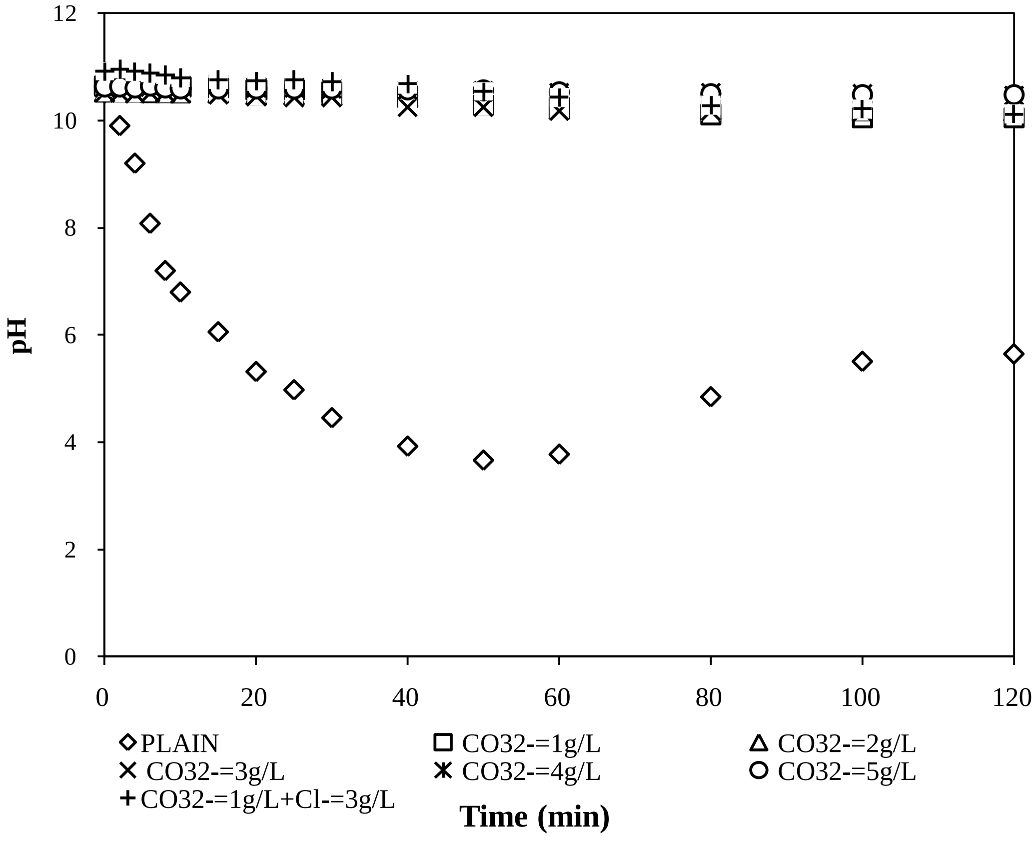


Figure 4.13 : pH value in the presence of CO_3^{2-} (1-5 g/L) during NPEO degradation by H_2O_2/UV-C process.

It is obtained from Figure 4.13, carbonate is a good pH buffer, and the pH remained constant around 10.5 in the presence of carbonate. The curve trend came to the straight line. It can be explained by the fact that carbonate is good pH buffer, another reason might be oxidation reaction got retarded by carbonate $HO^{\bullet}$ scavenging effect so the pH changing trend stayed in still.

According to the literature, the $HO^{\bullet}$ concentration in the H_2O_2/UV-C process is affected significantly due to pH change (2–10) in the presence of bicarbonate species alone (Liao et al., 1995). Many other researchers have also reported the effect of pH on the performance of $HO^{\bullet}$ formation when the bicarbonate species is present in the target water sample.

4.4 Effect of DTPMP

In this section, the organic sequestering agent DTPMP (0.5-1.5 g/L) introduced to the H_2O_2/UV-C system, in order to investigate sequestering agent affect due to evaluated in terms of parent pollutant (NPEO), COD and TOC abatement as well as H_2O_2 consumption kinetics. Pseudo-first order constant rate k values are presented in Table 4.4.

4.4.1 NPEO

The effect of various initial DTPMP concentrations on the NPEO photochemical degradation had investigated from 0.5-2.5 g/L. The changes in NPEO concentration was illustrated in Figure 4.14.

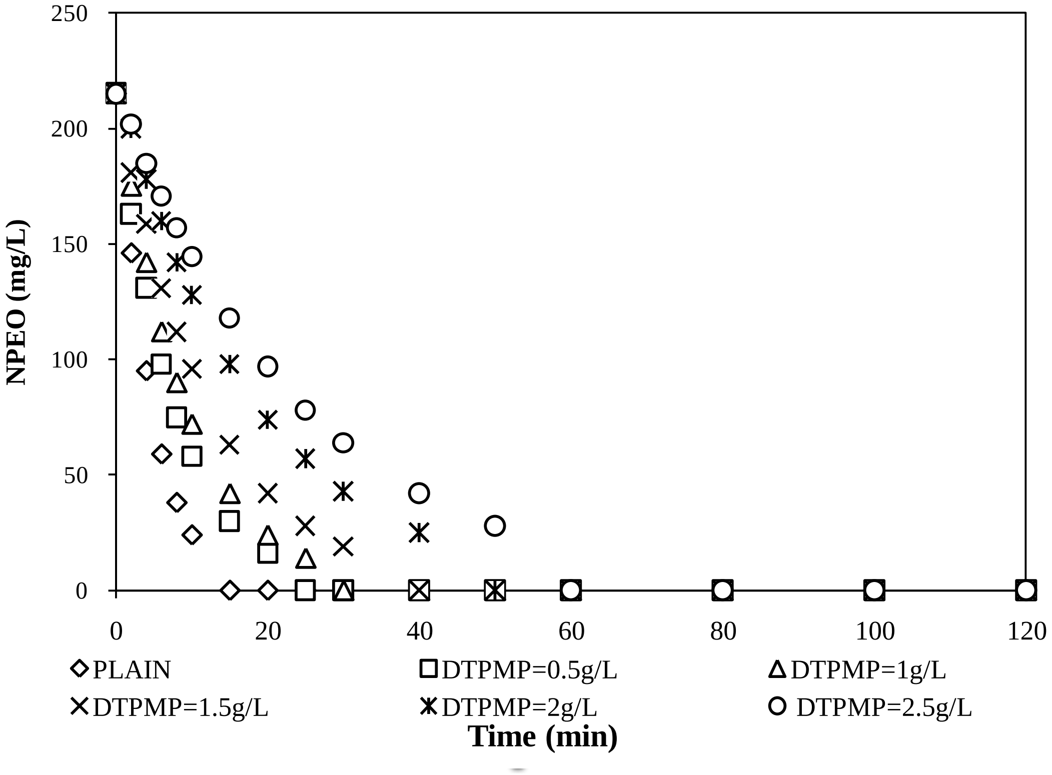


Figure 4.14 : Degradation of NPEO in the presence of DTPMP (0.5-2.5 g/L) by H_2O_2/UV-C.

A significant negative effect was observed in the Figure 4.14, which was enhanced as the DTPMP concentration increased where more than 89% NPEO would normally be degraded, the degradation rate of NPEO reduced to only 33% at 10 mins in the presence of DTPMP. The possible reason can be explained by the fact that DTPMP (1.5 g/L at pH=10.5) in solution interfere with UV light, absorbs UV light at 254 nm is 0.0558 cm^{-1} with DTPMP alone; 210 mg/L NPEO at pH=10.5 is 0.0920 cm^{-1}; combine DTPMP with NPEO is 0.1162 cm^{-1} (1.5 g/L DTPMP+0.21 g/L NPEO at pH=10.5). Consequently, In the presence of both DTPMP and NPEO leaded to the worst UV absorbance situation which directly caused reduction of $HO^{\bullet}$ generation in the solution, as a result NPEO degradation rate (2.5 g/L DTPMP) k_{NPEO}=0.0410 min^{-1} which is five times smaller than the plain one (k_{NPEO}=0.2127 min^{-1}). The strong retardation is not only due to the sequestering agents hinders but also consumes the H_2O_2.

4.4.2 COD

The COD abatement during NPEO photochemical advanced oxidation in the presence DTPMP at pH_0=10.5 were illustrated in Figure 4.15.

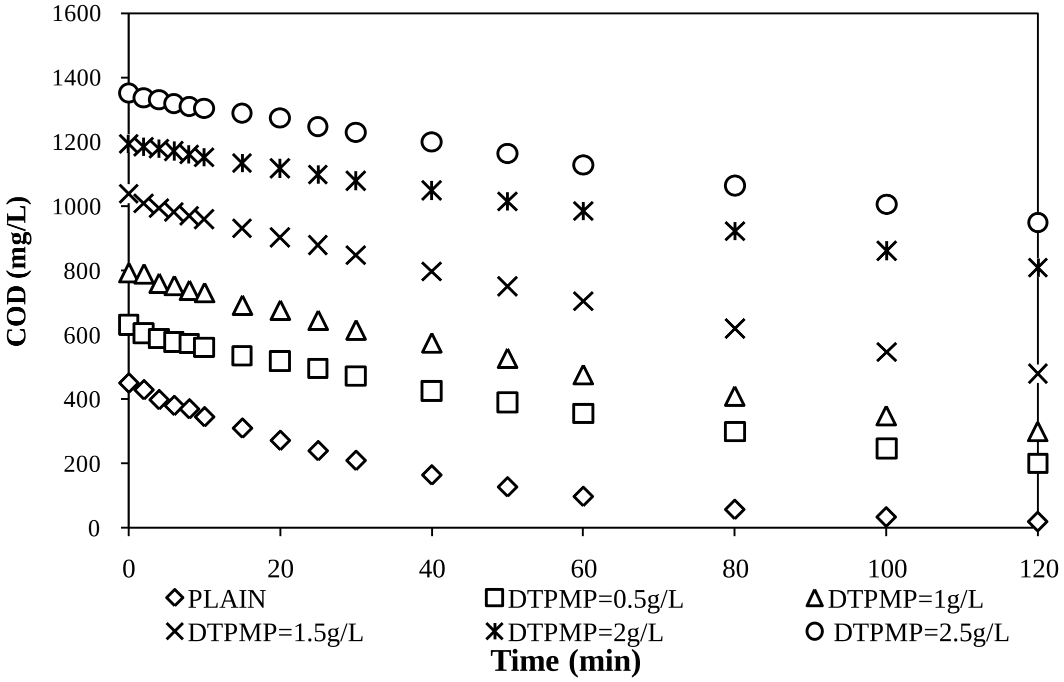


Figure 4.15 : COD abatement during NPEO degradation in the presence of DTPMP (0.5-2.5 g/L) by H_2O_2/UV-C process.

As is shown in the Figure 4.15, in the presence of DTPMP at pH_0=10.5 the initial COD values are very high as DTPMP concentration increase, that DTPMP is an organic sequestering agent. Serious inhibition was observed, the rate coefficient of COD abatement in the presence with DTPMP at pH_0=10.5 was 0.0029 min^{-1} almost came to zero.

The inhibition due to two possible reasons, first is the fact that DTPMP interfered the UV-C lights and consumed the $HO^{\bullet}$ leaded to the oxidation rate retardation as well. Another possible reason could be the fact that DTPMP is an organic sequestering agent who coursed the high initial COD, but the H_2O_2 concentration did not increase as the initial COD. Due to these two possible reasons, the COD abatement rate coefficient came to zero.

4.4.3 TOC

The TOC abatement during NPEO photochemical advanced oxidation in the presence DTPMP (0.5-2.5 g/L) at pH_0=10.5 were illustrated in Figure 4.16.

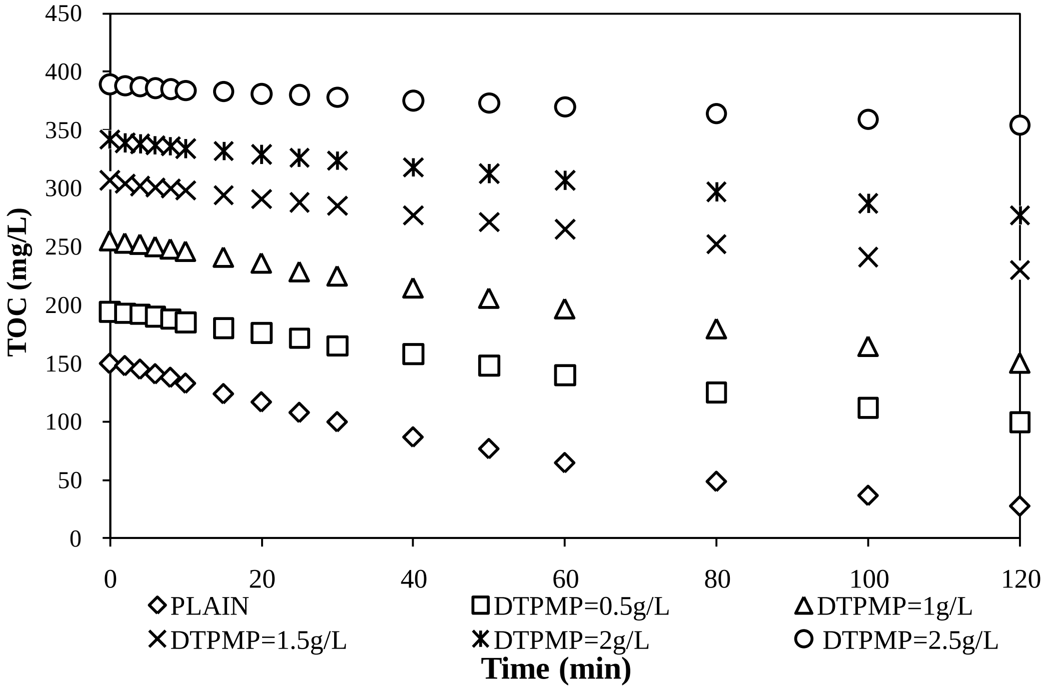


Figure 4.16 : TOC abatement during NPEO degradation in the presence of DTPMP (0.5-2.5 g/L) by H_2O_2/UV-C process.

Same retardation showed on TOC abatement in the 4.16. The high initial value of TOC was observed which can attributed to DTPMP is organic compound, considering that H_2O_2 (30 mM) concentration is restricted, accordingly high initial TOC resulted in the low oxidation rate.

Another reason might be that DTPMP competed with NPEO for $HO^{\bullet}$ meanwhile compete with H_2O_2 for UV light.

Upon the discussions, it can be concluded that two reasons caused the low rate of TOC abatement which are DTPMP consumed the $HO^{\bullet}$ and absorbed the UV light and DTPMP is organic compound which cause the high initial TOC value.

4.4.4 H_2O_2

The H_2O_2 consumption in the presence of DTPMP (0.5-2.5 g/L) at pH_0=10.5 was illustrated in Figure 4.17.

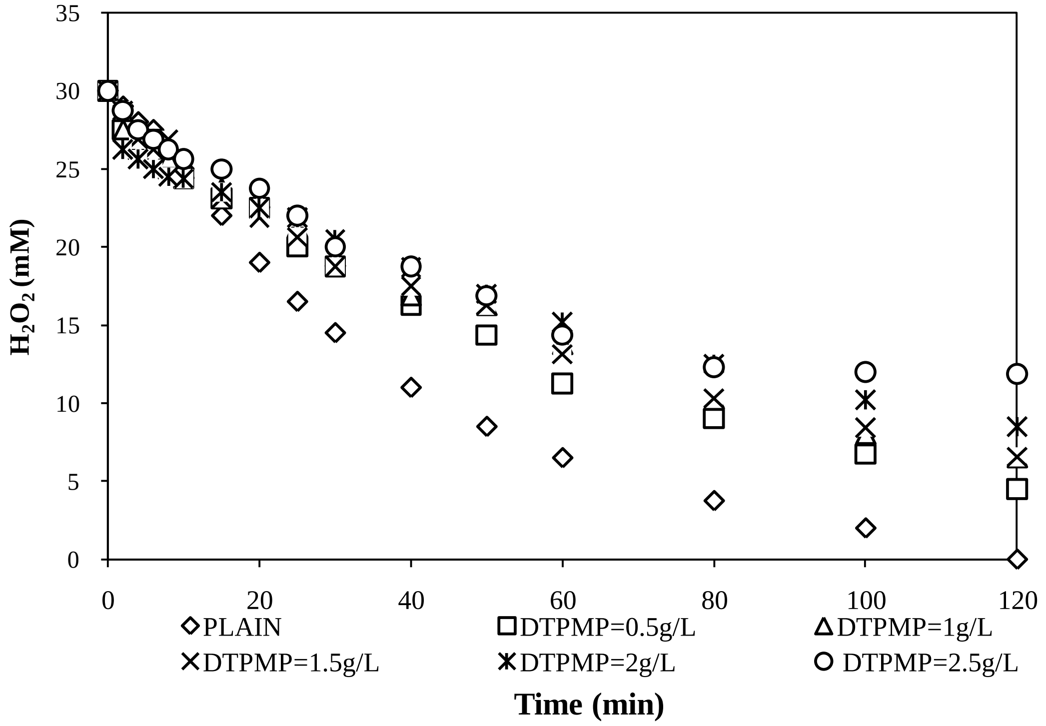


Figure 4.17 : H_2O_2 consumption in the presence of DTPMP (0.5-2.5 g/L) during NPEO degradation by H_2O_2/UV-C process.

Figure 4.17 showed the changes in the H_2O_2 consumption at the different concentration of DTPMP, H_2O_2 consumption of 2.5 g/L DTPMP at 60 mins is 52% and plain experiment (DTPMP free) is 78%. The possible reason might be that DTPMP interferes with absorption directly affect the rate of H_2O_2 photolysis. Introducing DTPMP to NPEO solution means that bring the UV lights competition between H_2O_2 and DTPMP. DTPMP absorbed the UV lights which results in H_2O_2 cannot get enough UV light to decompose to $HO^{\bullet}$ which will oxidatively attack the target pollutant (NPEO). Consequently, as the figure 4.17 shown that H_2O_2 consumption rate decreased.

Table 4.4: Pseudo-first order rate constants in the presence of DTPMP for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k value (min^{-1})			
DTPMP (g/L)	NPEO	COD	TOC	H_2O_2
0 (Plain)	0.2211	0.0255	0.0142	0.0273
0.5	0.1304	0.0092	0.0056	0.0151
1.0	0.1098	0.0082	0.0044	0.0125
1.5	0.0812	0.0063	0.0024	0.0123
2.0	0.0543	0.0032	0.0017	0.0113
2.5	0.0410	0.0029	0.0008	0.0098

4.4.5 pH

The changes in pH values in the presence of carbonate were illustrated in Figure 4.18.

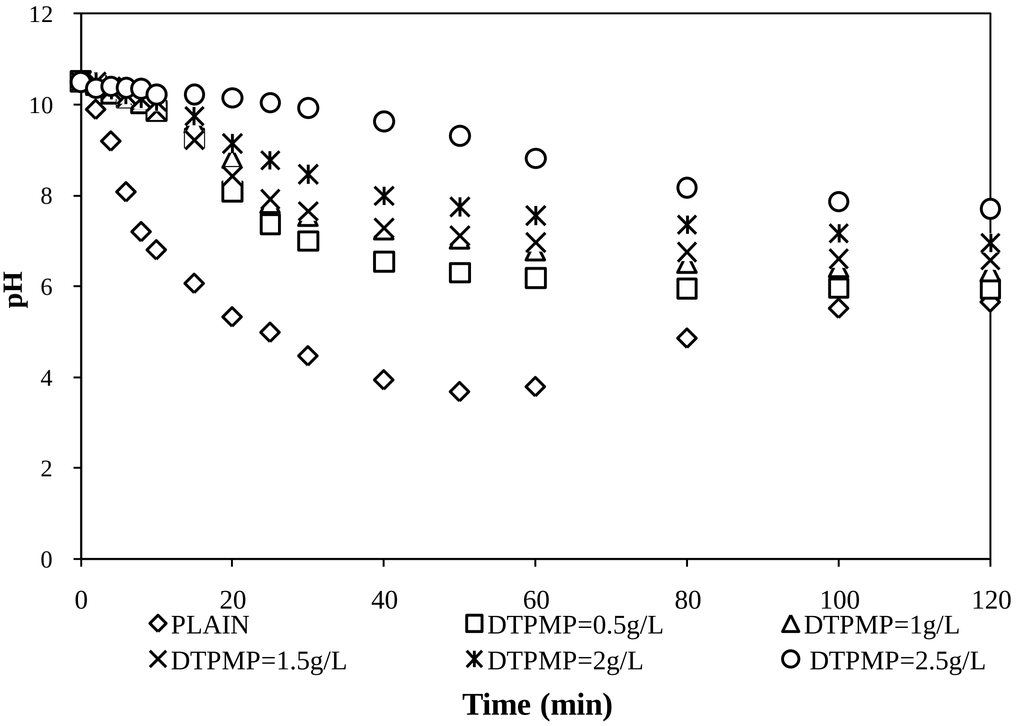


Figure 4.18 : pH value in the presence of DTPMP (0.5-2.5 g/L) NPEO degradation by H_2O_2/UV-C process.

As presented in Figure 4.18 that changed slowly at DTPMP=2.5 g/L which reflected the extendibility of oxidation by generation of the acidic oxidation products. As previous section study, that pH-changing trend can be evidence for proving oxidation reaction occurs inside the reactor. In contrast, likely to the straight line reflect that the reaction has been limited. According to this theory and the Figure 4.18 showed that the DTPMP strongly retarded the reaction, such inhibition also reflected on the abatement of NPEO, COD and TOC.

4.5 Comparison of DTPMP and HEDP

In order to investigate the effect of sequestering agents on oxidation rate and gathering data for supporting the alternative of textile preparation auxiliaries and supply a best available recipe for the H_2O_2/UV-C treatment another common commercial sequestering agent-HEDP introduced into the system, study will through checking collective environmental parameters NPEO, COD and TOC as well as consumption of H_2O_2.

4.5.1 NPEO

In order to get the more preferable data, the way to compare these two sequestering agents divide into two different concentration units which are 1.0 and 1.5 g/L HEDP compare with same amount DTPMP and 0.0026 mol/L (equal to 1.5g/L DTPMP) HEDP compare with 2.6 mM DTPMP. The results are showing in the Figure 4.18 and 4.19.

4.5.1.1 NPEO (DTPMP and HEDP comparison on mass basis)

The changes in NPEO concentration was illustrated in Figure 4.19.

Figure 4.19 showed changes in NPEO concentration of DTPMP and HEDP at same concentration on mass basis. Comparing HEDP with DTPMP in the Figure 4.19 at concentration 1.0 g/L revealed that DTPMP has a stronger and more pronounced negative effect on NPEO degradation. The same effect also revealed at concentration 1.5 g/L. This can be explained by the fact that DTPMP interferes with UV light more than HEDP. DTPMP (1.5 g/L) absorbs UV light at 254 nm is 0.0558 $cm^{-1,}$ combined DTPMP (1.5 g/L) with NPEO (210 mg/L) absorbs UV light at 254 nm is 0.1162 cm^{-1}. HEDP (1.5 g/L) absorbs UV lights at 254 nm is 0.0151cm^{-1} which is smaller compare with the previous one, combined HEDP (1.5 g/L) with NPEO (210 mg/L) absorbs UV light at 254 nm is 0.1069 cm^{-1} which is smaller than DTPMP combine with NPEO’s.

Upon the all comparison it can be concluded that DTPMP has a stronger UV light absorbance than HEDP at 254 nm, DTPMP is more competitive than HEDP on interfere with UV lights. Hence, DTPMP caused a more seriously competition with H_2O_2 for the UV-C light at 254 nm.

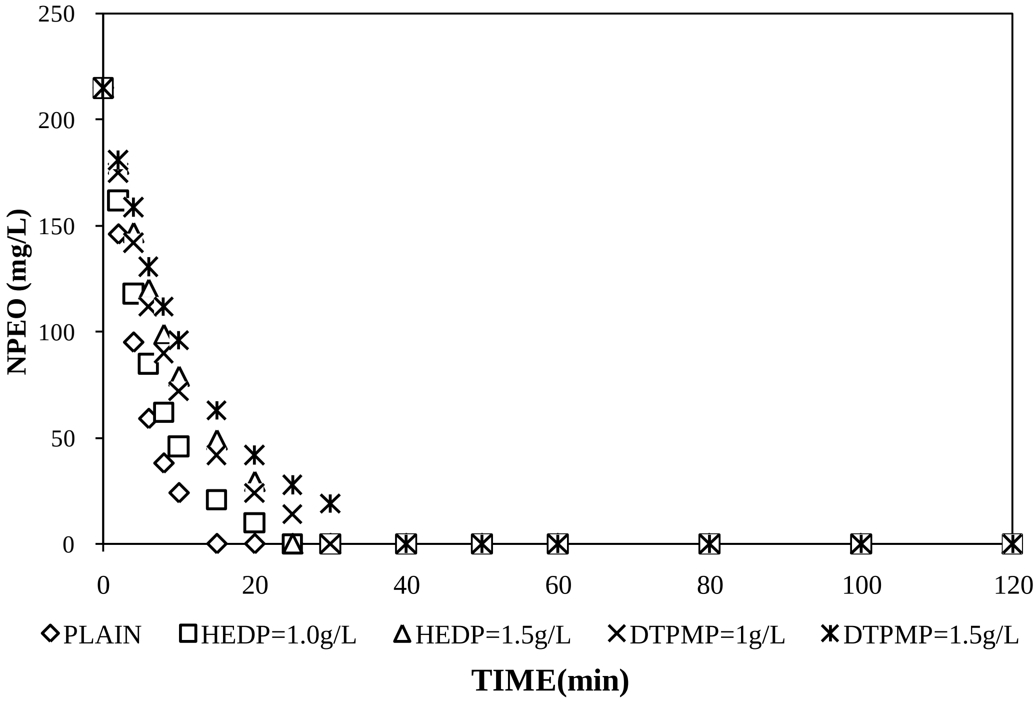


Figure 4.19 : Comparison the effect of DTPMP and HEDP (1-1.5 g/L) effect on mass basis for NPEO degradation by H_2O_2/UV-C treatment process.

4.5.1.2 NPEO (DTPMP and HEDP comparison on molar basis)

Figure 4.20 showed changes in NPEO concentration of DTPMP and HEDP at 2.6 mM. Molecular unit shows same inhibitory effect with the g/L unit, which DTPMP shows the significant negative effect during the treatment. The possible reason might be these two sequestering agents have different molecular structures, which the DTPMP has a more complicated and long-chain molecular structure than HEDP’s.

4.5.2 COD

4.5.2.1 COD (DTPMP and HEDP comparison on mass basis)

The changes in COD in the presence of DTPMP and HEDP on mass basis were illustrated in Figure 4.21.

As Figure 4.21 shown that DTPMP coursed the higher initial COD value than HEDP when these two sequestering agents at the same concentration. In the presence of DTPMP leaded to the more serious inhibition than HEDP also observed.

The possible reason might be that DTPMP has a more complicate molecular structure than HEDP's, so DTPMP coursed the higher initial COD. Another reason could be DTPMP has a stronger absorptive capacity, which coursed the more serious competition with H_2O_2 for the UV-C lights than HEDP. The results of UV-C absorbance measurement at 254 nm (Table 3.4) verified that DTPMP interferes with the UV-C lights is more serious than HEDP.

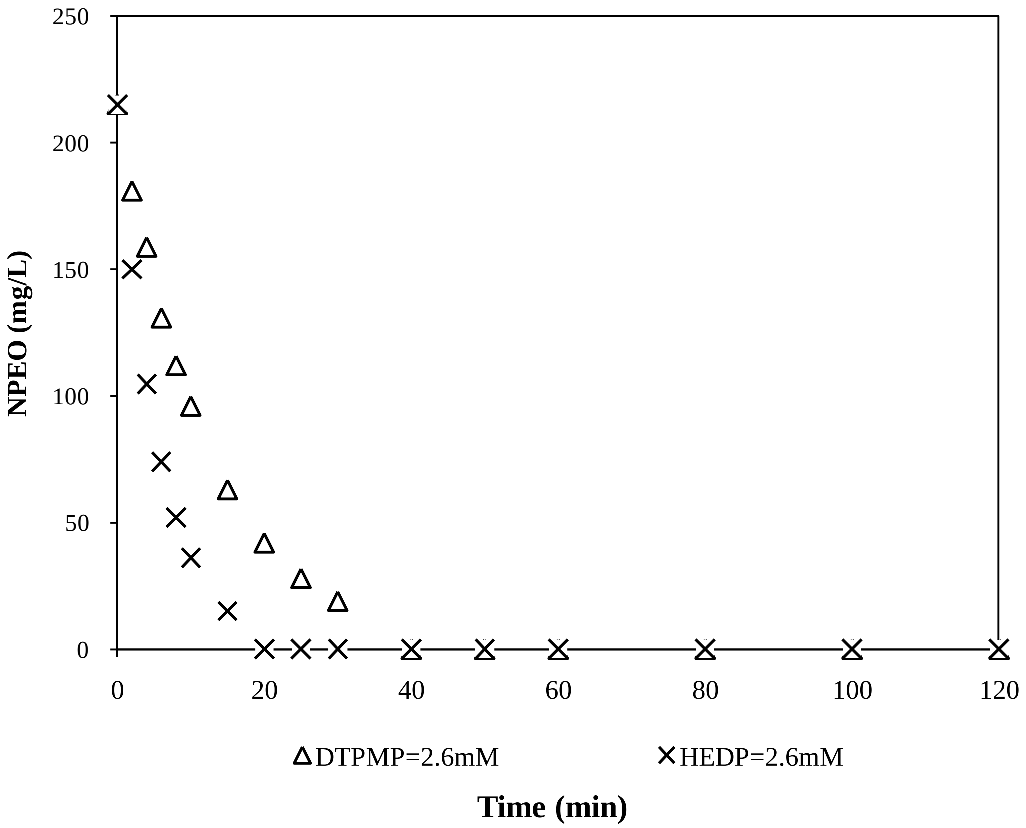


Figure 4.20 : Comparison the effect of DTPMP and HEDP (2.6 mM) effect on molar basis for NPEO degradation by H_2O_2/UV-C treatment process.

4.5.2.2 COD (DTPMP and HEDP on molar basis)

The COD abatement during NPEO photochemical advanced oxidation in the presence of DTPMP and HEDP on molar basis was illustrated in Figure 4.22.

The same situation showed here which DTPMP coursed the higher initial COD value than HEDP when these two sequestering agents at the same concentration. In the presence of DTPMP leaded to the more serious inhibition than HEDP also observed.

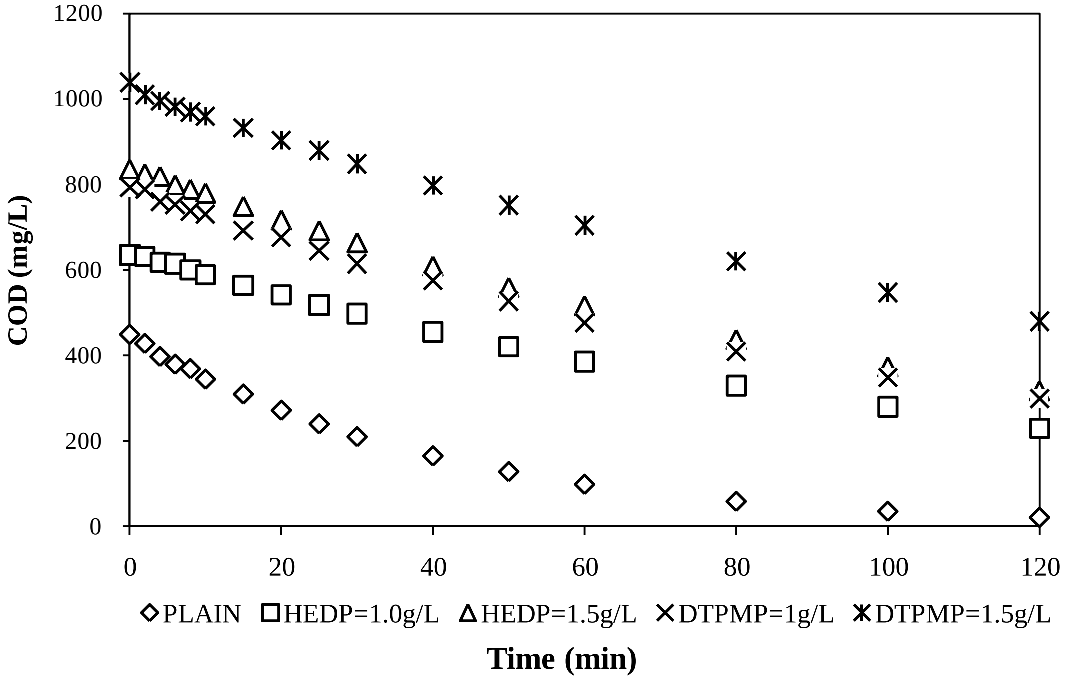


Figure 4.21 : Comparison the effect of DTPMP and HEDP (1-1.5 g/L) effect on mass basis for COD degradation by H_2O_2/UV-C treatment process.

4.5.3 TOC

4.5.3.1 TOC (DTPMP and HEDP comparison on mass basis)

The TOC abatement during NPEO photochemical advanced oxidation in the presence of DTPMP and HEDP on the mass basis was illustrated in Figure 4.23.

As is shown in the Figure 4.23, DTPMP coursed the higher initial TOC value than HEDP when these two sequestering agents at the same concentration, this also can explain why the DTPMP coursed very low TOC abatement rate, high initial TOC and limited H_2O_2. In the presence of DTPMP leaded to the more serious inhibition than HEDP also observed.

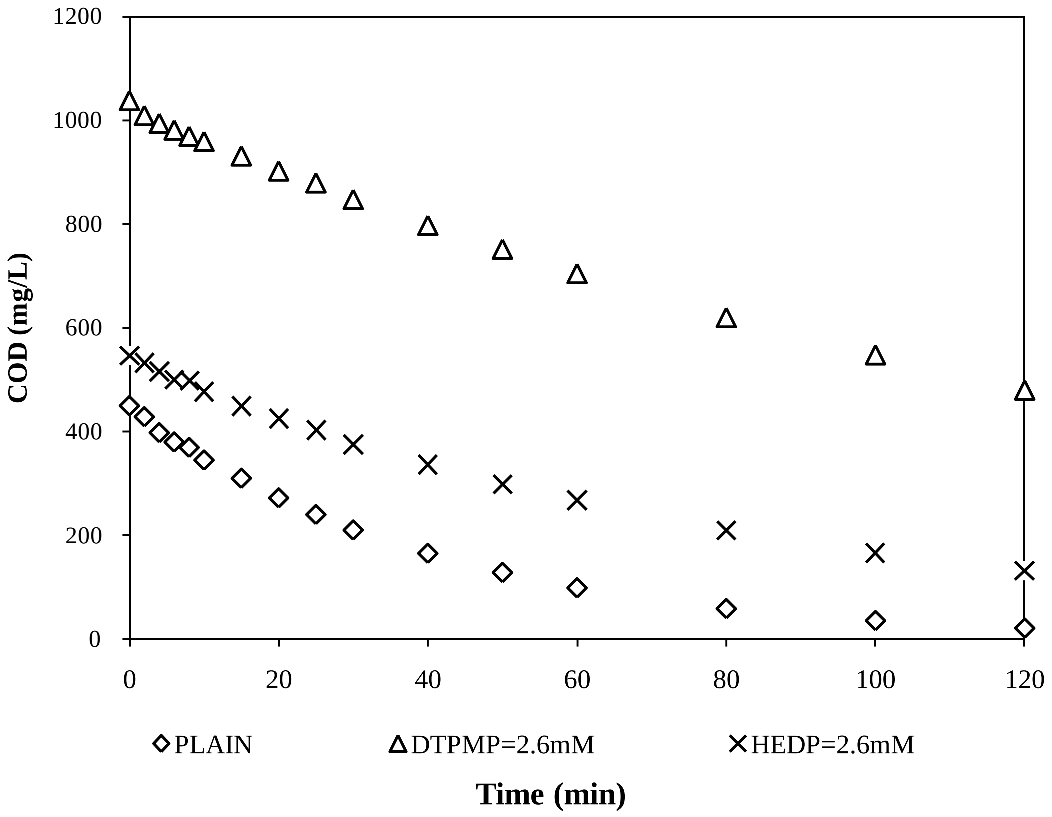


Figure 4.22 : Comparison the effect of DTPMP and HEDP (2.6 mM) effect on molar basis for COD degradation by H_2O_2/UV-C treatment process.

The possible reason might be that DTPMP has more complicated molecular structure than HEDP's, so DTPMP coursed the higher initial TOC. Another reason could be DTPMP has a stronger absorptive capacity, which coursed the more serious competition with H_2O_2 for the UV-C lights than HEDP.

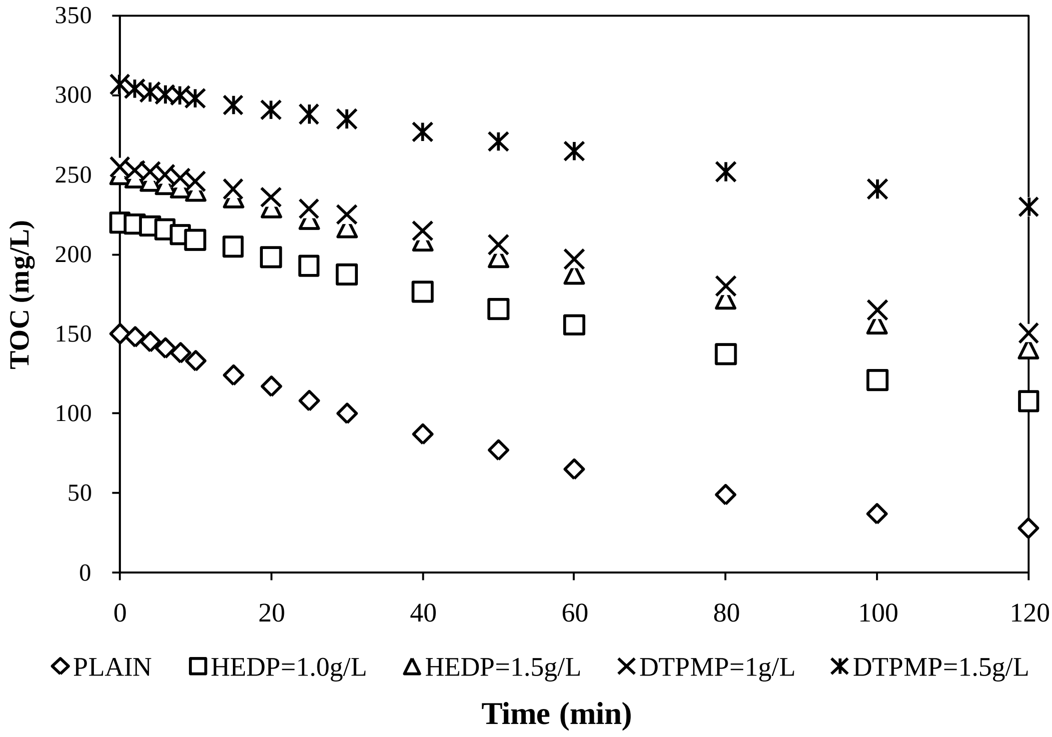


Figure 4.23 : Comparison the effect of DTPMP and HEDP (1-1.5 g/L) effect on mass basis for TOC degradation by H_2O_2/UV-C treatment process.

4.5.3.2 TOC (DTPMP and HEDP on molar basis)

The TOC abatement during NPEO photochemical advanced oxidation in the presence of DTPMP and HEDP on the molar basis was illustrated in Figure 4.24.

The same situation showed here which DTPMP coursed the higher initial TOC value than HEDP when these two sequestering agents at the same concentration. In the presence of DTPMP leaded to the more serious inhibition than HEDP also observed.

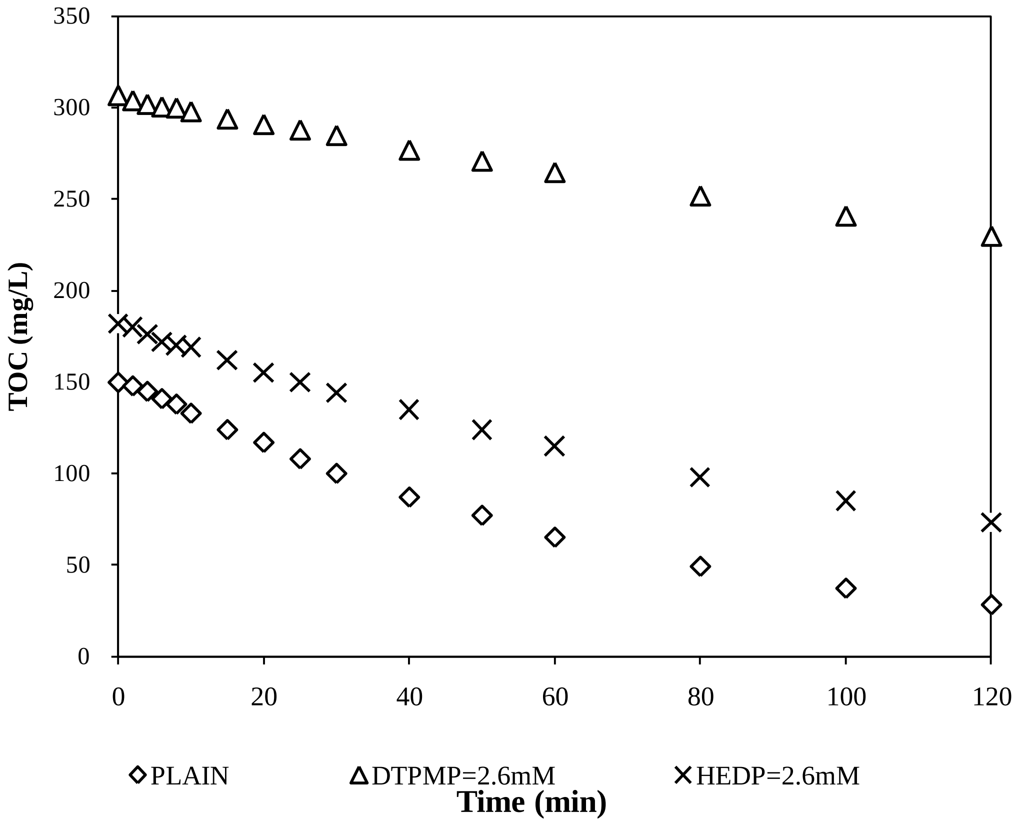


Figure 4.24 : Comparison the effect of DTPMP and HEDP (2.6 mM) effect on molar basis for TOC degradation by H_2O_2/UV-C treatment process.

4.5.4 H_2O_2

4.5.4.1 H_2O_2 (DTPMP and HEDP in g/L)

The H_2O_2 consumption during NPEO photochemical advanced oxidation in the presence of DTPMP and HEDP on the mass basis was illustrated in Figure 4.25.

Figure 4.25 displayed the changes of H_2O_2 consumption during H_2O_2/UV-C treatment with the HEDP and DTPMP, the data obtained that DTPMP has the stronger hinder effect on H_2O_2 decomposition which directly influence the rate of oxidation rate due to H_2O_2 is the only source of $HO^•$ in the solution.

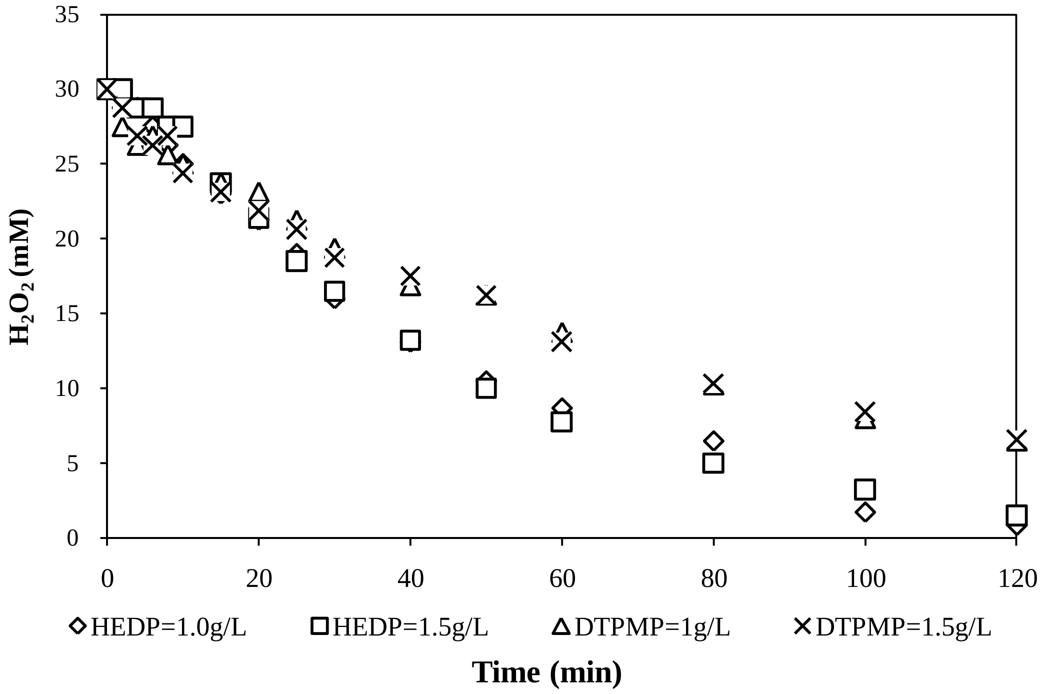


Figure 4.25 : Comparison of effect of DTPMP and HEDP (1-1.5 g/L) on mass basis for H_2O_2 consumption during by H_2O_2/UV-C treatment process.

4.5.4.2 H_2O_2 (DTPMP and HEDP on molar basis)

The H_2O_2 consumption during NPEO photochemical advanced oxidation in the presence of DTPMP and HEDP on the molar basis was illustrated in Figure 4.26.

Figure 4.26 displayed the same situation with the Figure 4.25.

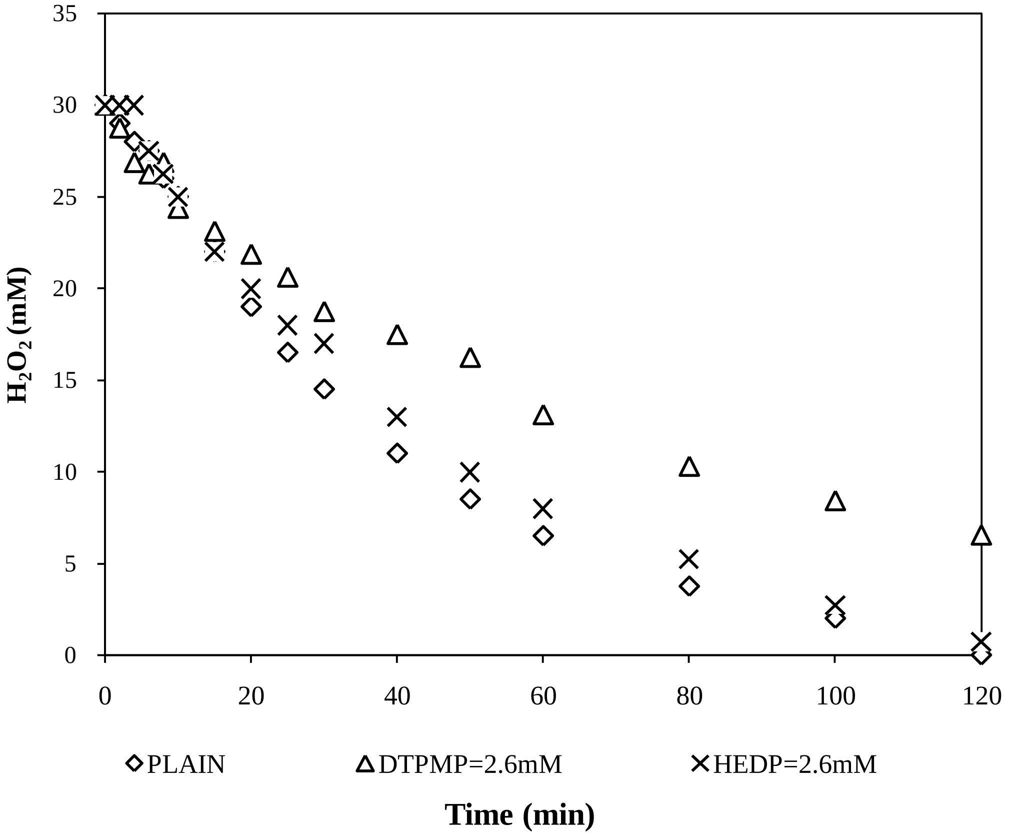


Figure 4.26 : Comparison of effect of DTPMP and HEDP (2.6 mM) on malor basis for H_2O_2 consumption during by H_2O_2/UV-C treatment process.

Table 4.5: Comparison of pseudo-first order rate constants for the effect of DTPMP and HEDP on NPEO degradation by H_2O_2/UV-C treatment process

	k value (min^{-1})			
Experimental conditions	NPEO	COD	TOC	H_2O_2
Plain (Sequestering agents free)	0.2211	0.0255	0.0142	0.0270
HEDP=1 g/L	0.1546	0.0840	0.0060	0.0203
DTPMP =1 g/L	0.1098	0.0082	0.0044	0.0125
HEDP =1.5 g/L	0.0998	0.0081	0.0048	0.0244
DTPMP =1.5 g/L	0.0812	0.0063	0.0024	0.0123
HEDP=2.6 mM	0.1775	0.0118	0.0076	0.0235
DTPMP=2.6 mM	0.0812	0.0063	0.0024	0.0123

4.5.5 Control Experiments

In this section, in order to indicate two selected sequestering agents' effect on H_2O_2/UV-C, four control experiments were run. Those are DTPMP (1.5g/L)+UV-C and DTPMP(1.5g/L)+UV-C+H_2O_2 (30mM) at pH=10.5; HEDP(1g/L)+UV-C and HEDP(1g/L)+UV-C+H_2O_2 (30mM) at pH=10.5.

COD and TOC data of these four control experiments were illustrated in Figure 4.27 and Figure 4.28.

As shown in the Figure 4.27 and Figure 4.28, HEDP and DTPMP in the absence of H_2O_2 the COD and TOC changing trend almost flat, but DTPMP had a more pronounceable removal when compare with HEDP, which demonstrated DTPMP was more serious on interfere and absorb UV-C light.

The Figure 4.27 and Figure 4.28 also showed that COD and TOC changing trend of HEDP and DTPMP in the presence of H_2O_2 had an evident removal, which proved that HEDP and DTPMP competed the $HO^{\bullet}$ with our target compound NPEO; the data also showed that COD and TOC changing trend of DTPMP in the presence of H_2O_2 was faster than HEDP's, which meant that DTPMP absorb $HO^{\bullet}$ more serious then HEDP.

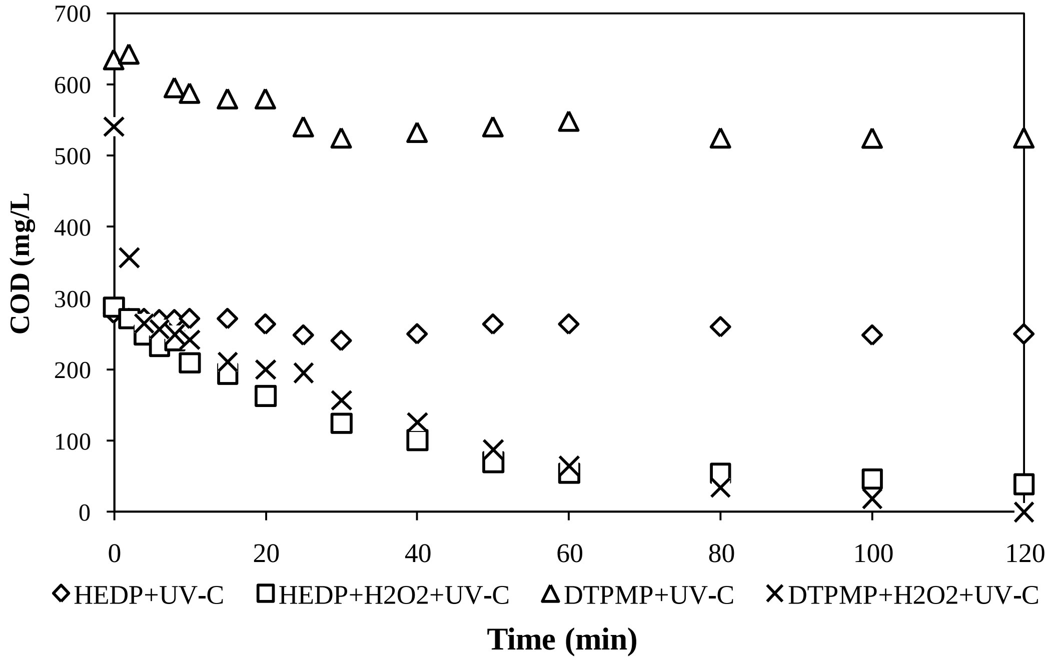


Figure 4.27 : DTPMP and HEDP degradation of COD by the UV-C and H_2O_2/UV-C treatment process.

Upon the discussions, came to the conclusion that these two selected sequestering agents HEDP and DTPMP both of them interfere with UV-C light and consume $HO^•$ and DTPMP showed more serious effect than HEDP on the H_2O_2/UV-C treatment process.

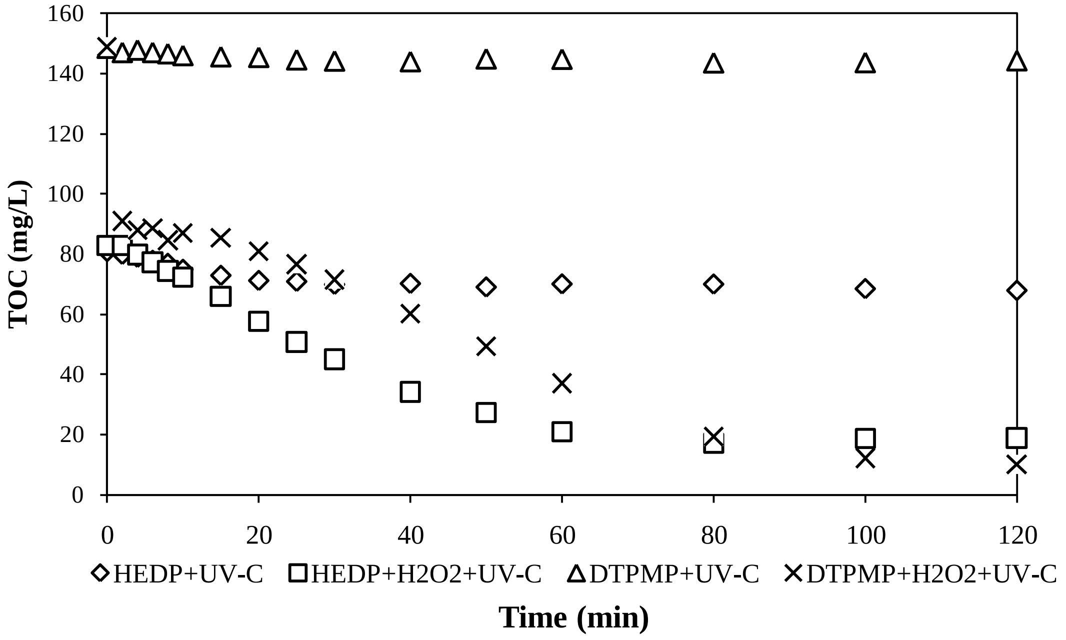


Figure 4.28 : DTPMP and HEDP degradation of TOC by the UV-C and H_2O_2/UV-C treatment process.

4.6 Effect of Textile Preparation Process Effluent I

After studied the individual effect on H_2O_2/UV-C treatment of two common salts (NaCl and Na_2CO_3) and two commercial sequestering agents (DTPMP and HEDP), in the second part of the experimental study, the application of H_2O_2/UV-C treatment on effluents originating from four different simulated textile preparation effluents were comparatively evaluated.

First textile preparation effluent recipe made up by DTPMP=1.5 g/L, Cl^-=3 g/L, and CO_3^{2-}=3.0 g/L at pH_0=10.5.

4.6.1 NPEO

The NPEO abatement during photochemical advanced oxidation in the presence of DTPMP=1.5 g/L, Cl^- =3 g/L, and CO_3^{2-}=3.0 g/L at pH_0=10.5 were illustrated in Figure 4.29.

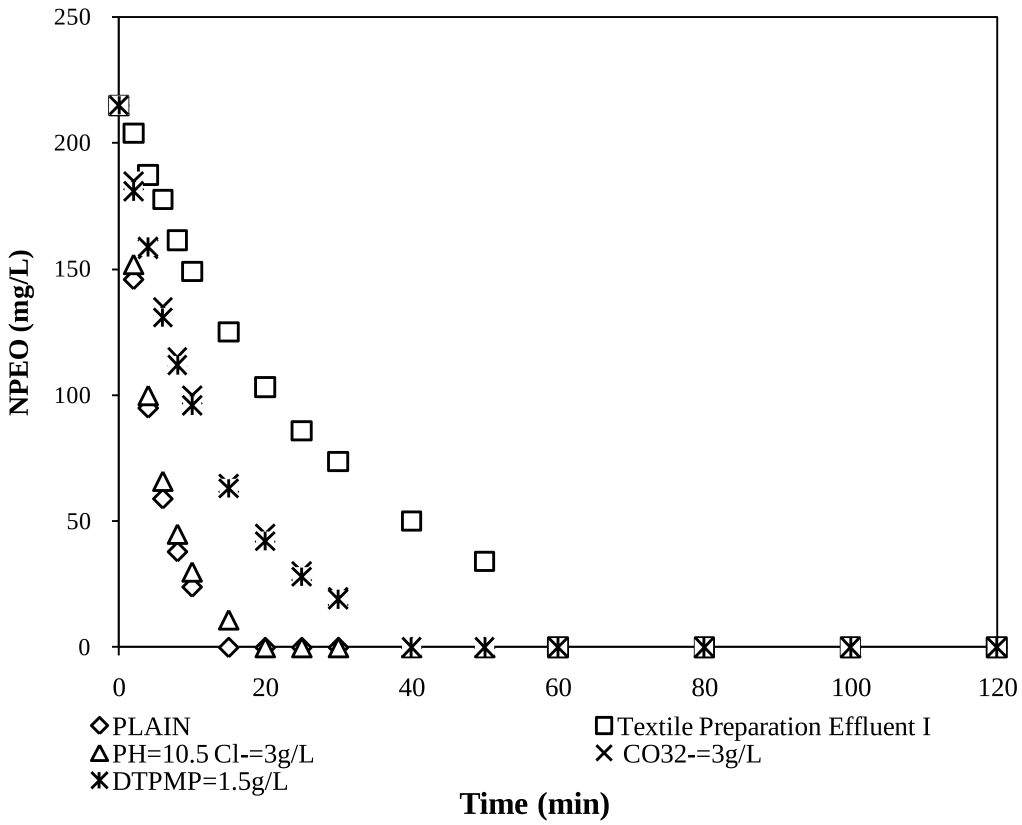


Figure 4.29 : Degradation of NPEO in the presence of Textile Preparation Process Effluent I by H_2O_2/UV-C process.

As theoretically expected that combine the DTPMP, CO_3^{2-} with Cl^- caused a strong inhibition than any other previous individual study was observed. The NPEO degradation up to 60 mins finished, whereas the plain experiment NPEO degradation only took 20 mins.

As aforementioned, CO_3^{2-} and Cl^- are $HO^•$ scavengers which react with $HO^•$ accordingly, they competed with target compound-NPEO for $HO^•$, chloride's scavenging effect is negligible at a very high pH, hence NPEO degradation rate decreased. In the Textile Preparation Effluent I solution combined these two scavengers at pH=10.5 which can counteract the effect of chloride whenas carbonate played the role as a pH buffer and strong $HO^•$ scavenger. DTPMP was also introduced into the Textile Preparation Effluent I, which hindered H_2O_2 photolysis by interfered with the UV light. Due to those negative effects, unsurprisingly, the treatment received a strong retardation on degradation of NPEO, COD and TOC. The degradation rate constants are given in the Table 4.6.

4.6.2 COD

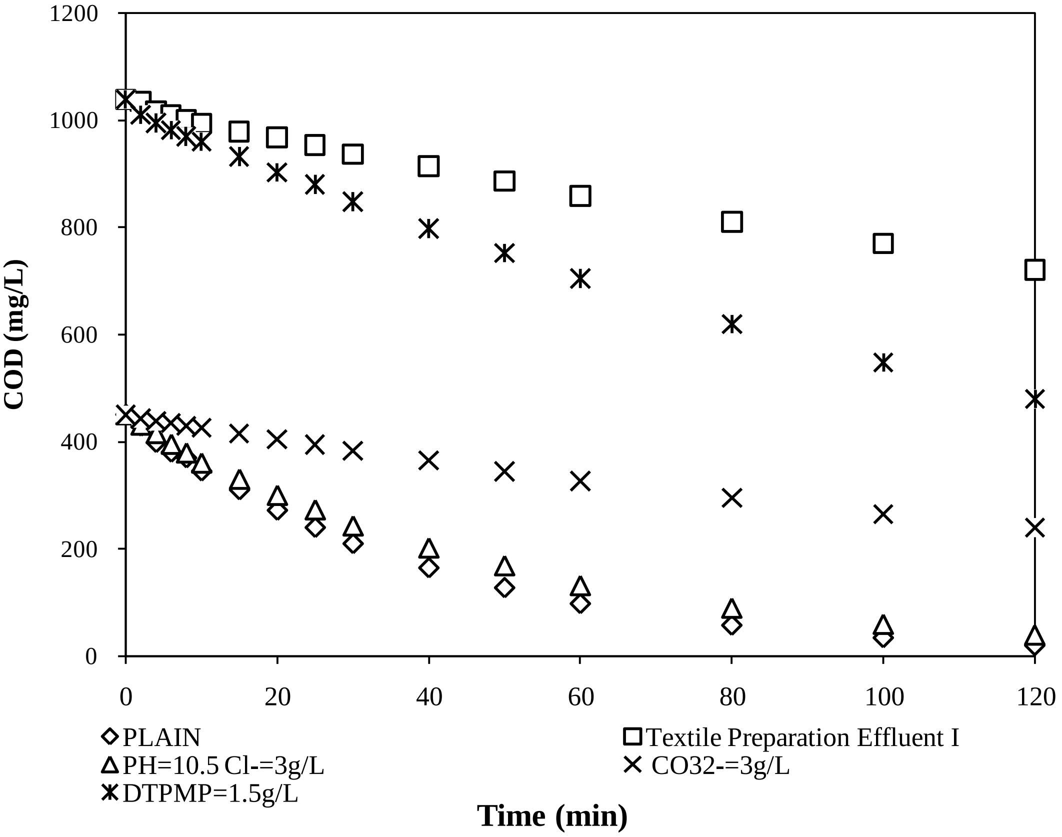


Figure 4.30 : COD abatement in the presence of Textile Preparation Effluent I during NPEO degradation by H_2O_2/UV-C process.

The COD abatement during NPEO photochemical advanced oxidation in the presence of DTPMP, Cl^- and CO_3^{2-} was illustrated in Figure 4.30.

As Figure 4.30 shown the changes in COD value, the Textile Preparation Effluent I (DTPMP=1.5 g/L+Cl^- =3.0 g/L+ CO_3^{2-}=3.0 g/L) showed the most inhibition which removal efficiency of COD is 17% at 60 mins. Normally, without any textile preparation auxiliary introducing in the solution the removal efficiency of COD is 78% at 60 mins. The rate coefficient of COD abatement in the presence with Textile Preparation Effluent I at pH_0=10.5 is 0.0030 min^{-1} almost come to zero.

The low degradation rate can attributed to two reasons, first one, scavenger effect by Cl^- and CO_3^{2-} also the fact that sequestering agent-DTPMP's interference UV-C lights and hindering H_2O_2; second one is the fact that DTPMP is organic who caused high initial COD value but the H_2O_2 was limited.

4.6.3 TOC

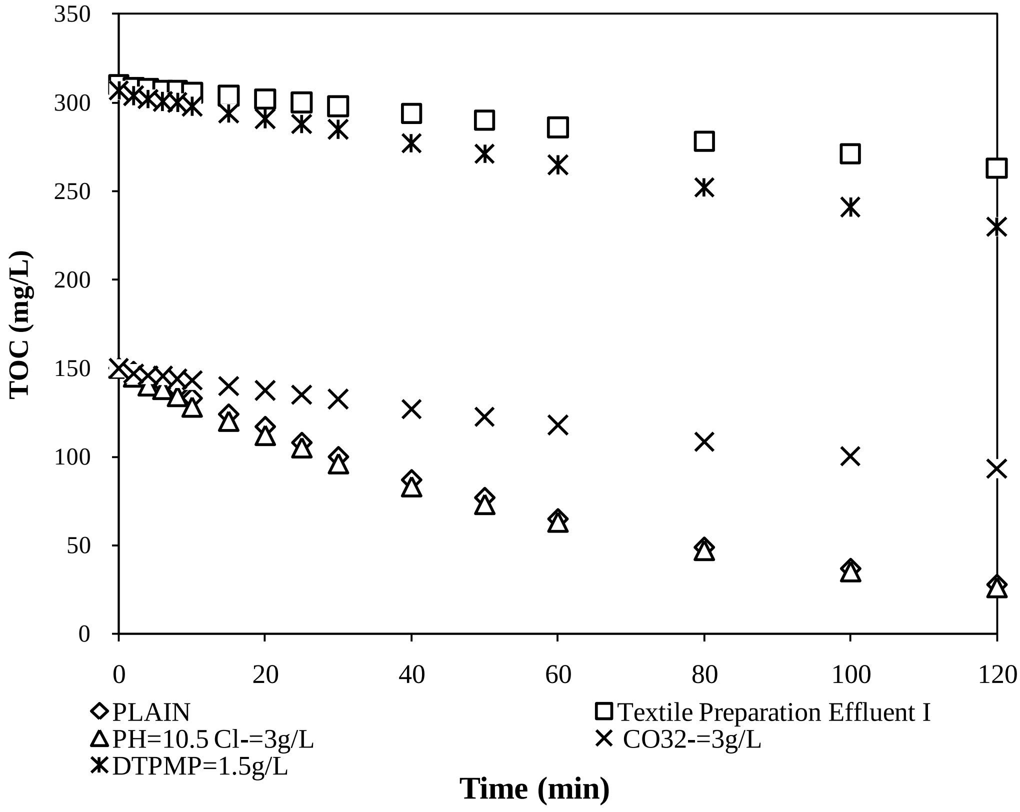


Figure 4.31 : TOC abatement in the presence of Textile Preparation Effluent I during NPEO degradation by H_2O_2/UV-C process.

The TOC abatement during NPEO photochemical advanced oxidation in the presence of DTPMP, Cl^- and CO_3^{2-} was illustrated in Figure 4.31.

As Figure 4.31 shown the changes in TOC value, the Textile Preparation Effluent I (DTPMP=1.5 g/L+Cl^- =3 g/L+ CO_3^{2-}=3.0 g/L) caused significant inhibition, which removal efficiency of TOC was 8% at 60 mins. Normally, without any textile preparation auxiliary introducing into the solution, the removal efficiency of TOC was 59% at 60 mins. The rate coefficient of TOC abatement in the presence with Textile Preparation Effluent I at pH_0=10.5 is 0.0014 min^{-1} almost come to zero which revealed that very restricted mineralization occurred.

The reasons caused low rate of COD degradation are also can be used for explaining low TOC degradation rate caused by Textile Preparation Effluent I.

4.6.4 H_2O_2

As is evident in Figure 4.32, in the presence of DTPMP in solution H_2O_2 consumption is retarded, which is because DTPMP competed the UV-C light with H_2O_2 accordingly H_2O_2 photolysis got inhibited.

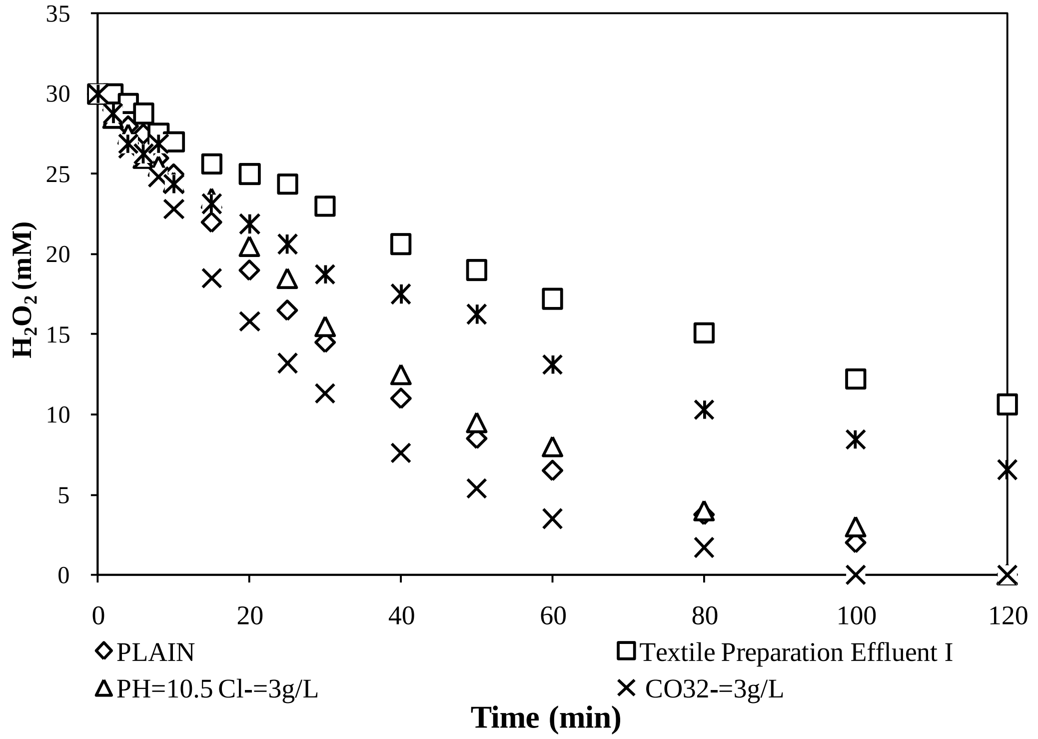


Figure 4.32 : Consumption of H_2O_2 in the presence of Textile Preparation Effluent I during NPEO degradation by H_2O_2/UV-C process.

Table 4.6: Pseudo-first order rate constants in the presence of Textile Preparation Effluent I for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k (min^{-1})			
Experimental conditions	NPEO	COD	TOC	H_2O_2
Plain (only NPEO)	0.2211	0.0255	0.0142	0.0270
Textile Preparation Effluent I	0.0369	0.0030	0.0014	0.0088
Cl^- =3 g/L	0.1995	0.0201	0.0145	0.0231
CO_3^{2-}=3.0 g/L	0.0792	0.0052	0.0039	0.0367
DTPMP =1.5 g/L	0.0812	0.0063	0.0024	0.0123

4.6.5 pH

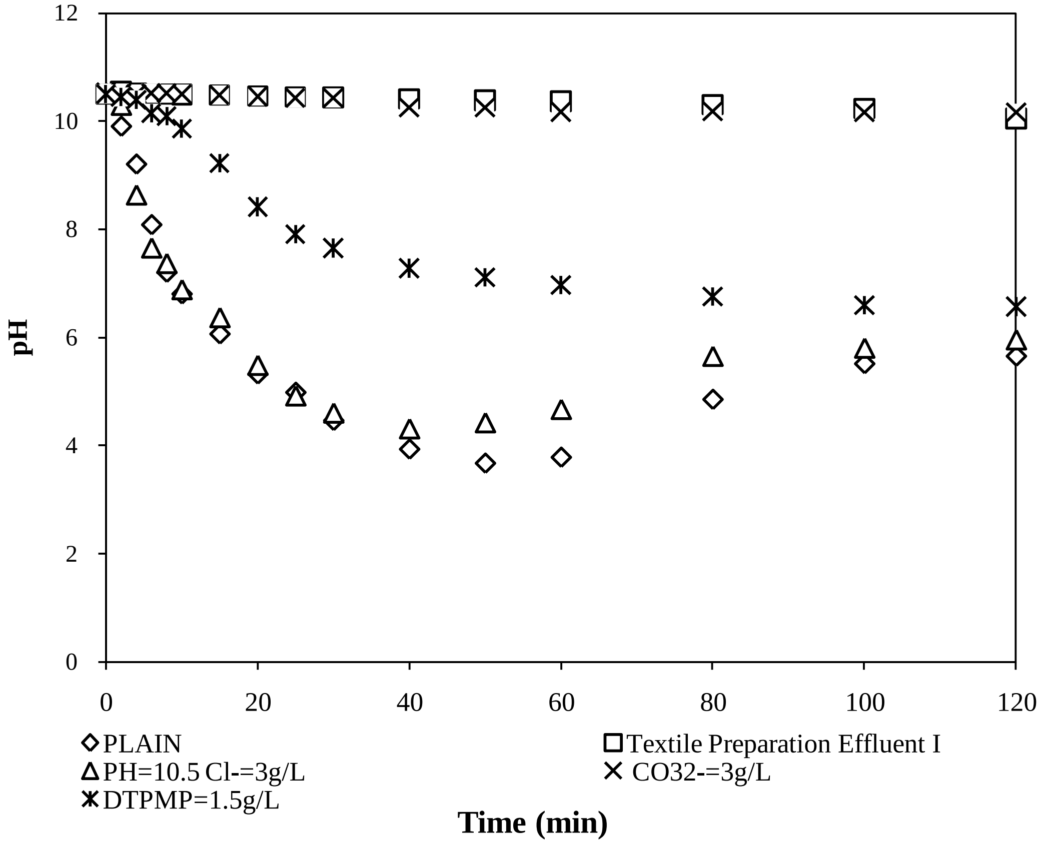


Figure 4.33 : pH value in the presence of Textile Preparation Effluent I during NPEO degradation by H_2O_2/UV-C process.

As is shown in Figure 4.33, pH values of Textile Preparation Effluent I retained around 10.5, that because of the presence of carbonate which is a good pH buffer, also might be because of the retardation of photochemical oxidation.

4.7 Effect of Textile Preparation Process Effluent II

In this set, the 1.5 g/L HEDP instead of DTPMP was introduced into the Textile Preparation Effluent II which combined with Cl^-=3.0 g/L and CO_3^{2-}=3.0 g/L at pH 10.5.

4.7.1 NPEO

The NPEO abatement during NPEO photochemical advanced oxidation in the presence of HEDP=1.5 g/L, Cl^- =3.0 g/L, and CO_3^{2-}=3.0 g/L at pH_0=10.5 were illustrated in Figure 4.34.

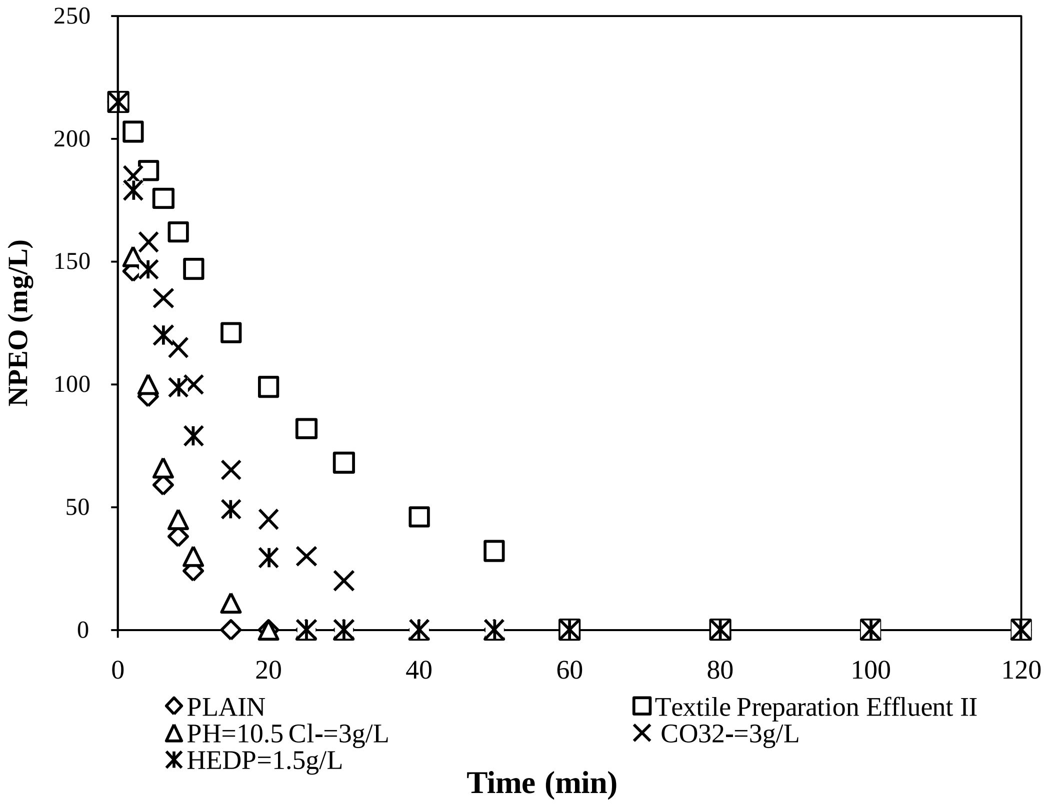


Figure 4.34 : Degradation of NPEO in the presence of Textile Preparation Process Effluent II by H_2O_2/UV-C process.

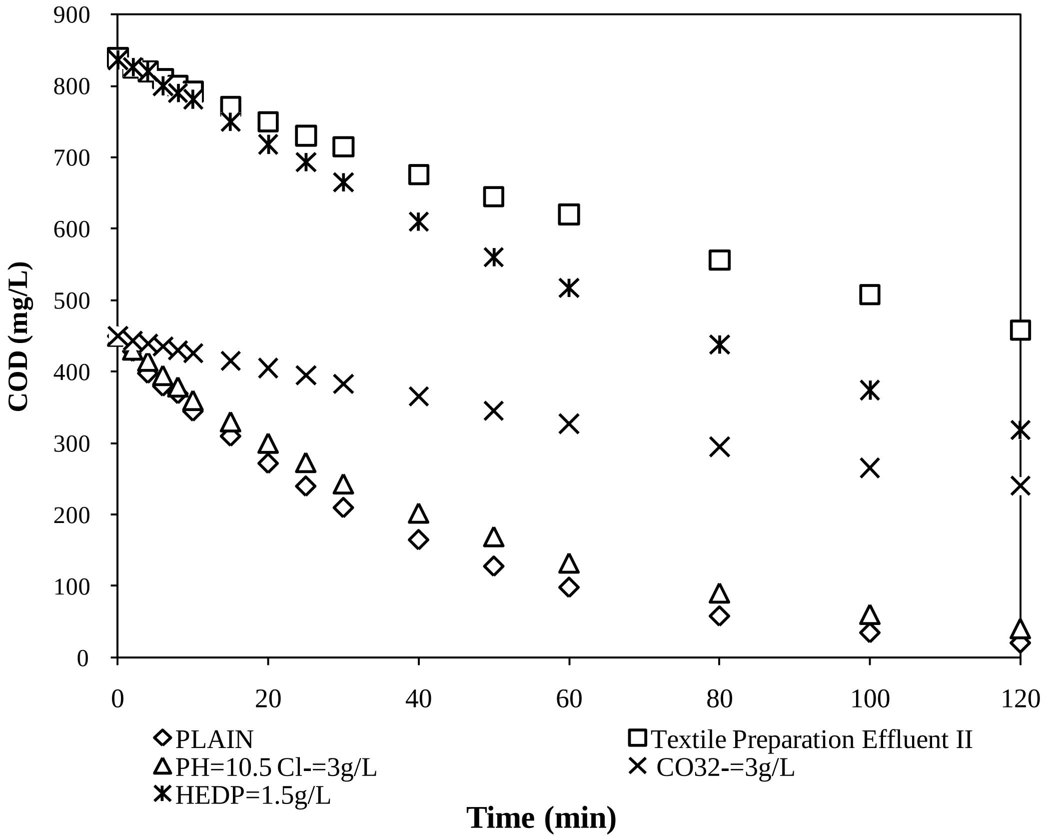
As Figure 4.34 displayed, Textile Preparation Effluent II induced significant inhibition. The possible reasons could be under the scavenger effect by carbonate and chloride, whereas chloride only causes inhibition at the acidic pH circumstance, hence at pH=10.5 the inhibitory effect caused by chloride was negligible; at same time sequestering agent played the role of interfered with the UV absorbance.

4.7.2 COD

The COD abatement during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent II was illustrated in Figure 4.35.

Comparing Textile Preparation Effluent II with HEDP only which started in the same initial COD, it was so obviously, Textile Preparation Effluent II leaded to a evident retardation. The rate coefficient of COD abatement in the presence with Textile Preparation Effluent II at pH_0=10.5 is 0.0050 min^{-1} almost come to zero.

Low COD degradation rate can be attributed to two reasons, those are chloride and carbonate scavenger effect affected the oxidation rate; the sequestering agent-HEDP interfered the photolysis of H_2O_2 and caused the high initial COD value.



4.7.3

Figure 4.35 : COD abatement in the presence of Textile Preparation Effluent II during NPEO degradation by H_2O_2/UV-C process.

4.7.4 TOC

The TOC abatement during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent II was illustrated in Figure 4.36.

Textile Preparation Effluent II caused the lowest removal efficiency, which is 11% at 60 mins. Normally, without any textile auxiliary introducing in the solution the removal efficiency of TOC at 60 mins is 59%. The rate coefficient of TOC abatement in the presence with Textile Preparation Effluent II at $pH_0=10.5$ is 0.0019 min^{-1} almost come to zero.

The reasons caused low rate of COD degradation are also can be used for explaining low TOC degradation rate caused by Textile Preparation Effluent II.

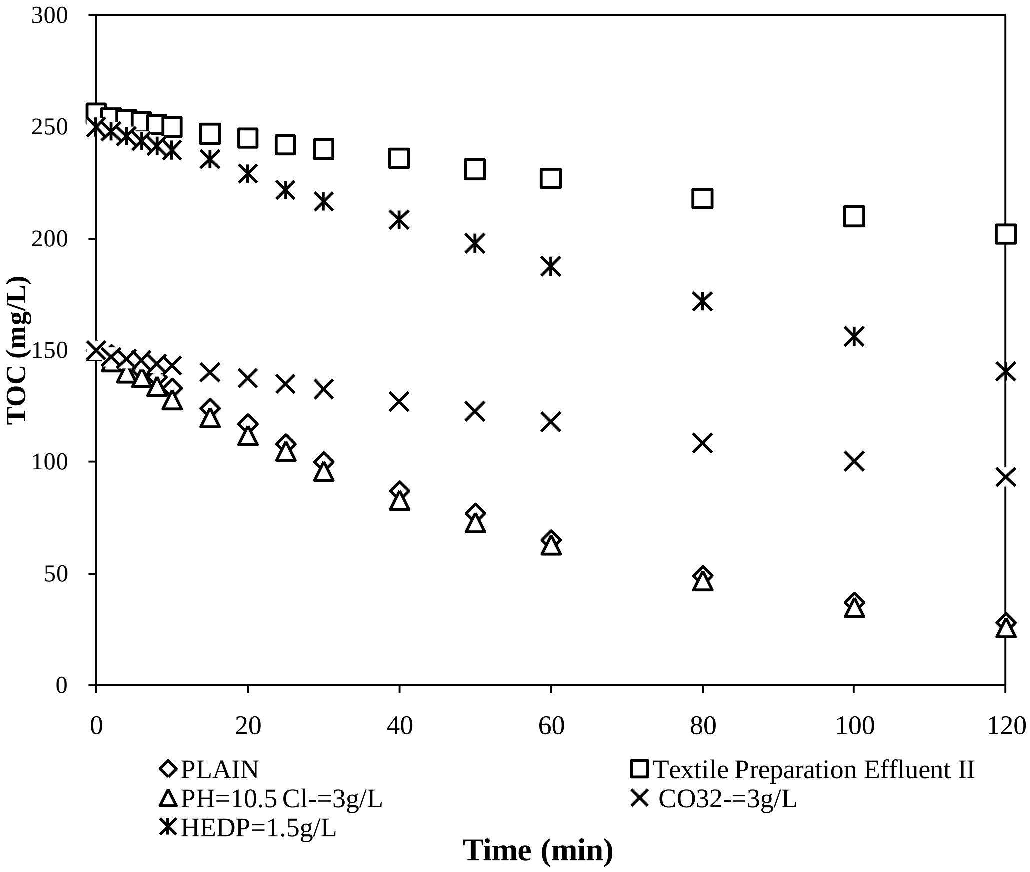


Figure 4.36 : TOC abatement for H_2O_2/UV-C Treatment of Textile Preparation Effluent II and respective Control Experiments.

4.7.5 H_2O_2

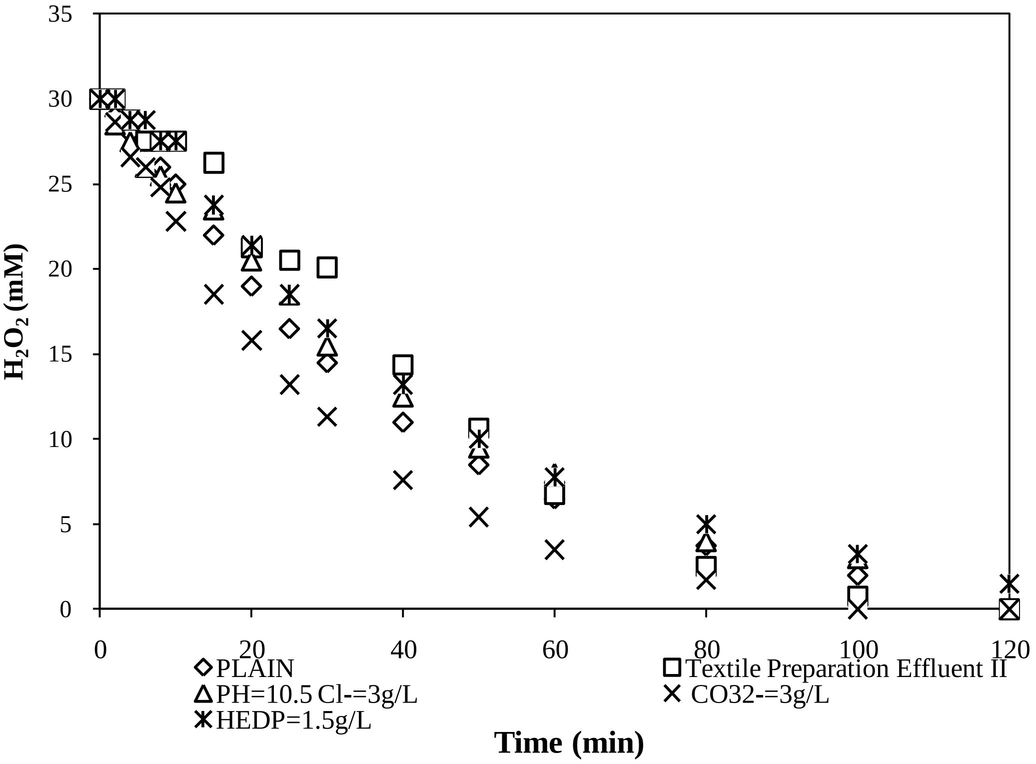


Figure 4.37 : H_2O_2 consumption in the presence of Textile Preparation Effluent II by H_2O_2/UV-C process.

As shown in the Figure 4.37, in the presence of HEDP in solution the photolysis of H_2O_2 retarded because HEDP competed the UV-lights with H_2O_2. As aforementioned, HEDP has less inhibitory effect on H_2O_2 decomposition compared with another sequestering agent- DTPMP.

4.7.6 pH

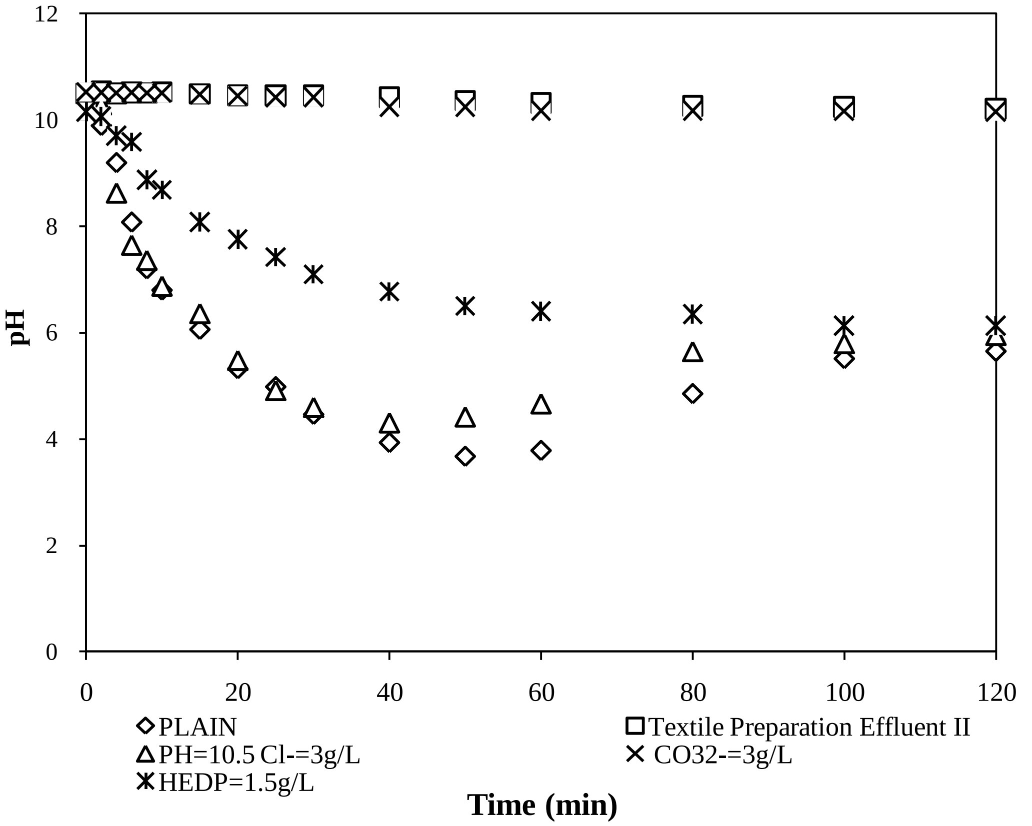


Figure 4.38 : pH value in the presence of Textile Preparation Effluent II during NPEO degradation by H_2O_2/UV-C process.

As is shown in the Figure 4.38, pH value kept around 10.5 with the carbonate presence in solution, which is a good pH buffer. The flat pH-changing trend also implied that limited oxidation occurred.

Table 4.7: Pseudo-first order rate constants in the presence of Textile Preparation Effluent II for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k (min^{-1})			
Experimental conditions	NPEO	COD	TOC	H_2O_2
Plain(NPEO only)	0.2211	0.0255	0.0142	0.0270
Textile Preparation Effluent II	0.0387	0.0050	0.0019	0.0213
Cl^- =3 g/L	0.1995	0.0201	0.0145	0.0231
CO_3^{2-}=3.0 g/L	0.0792	0.0052	0.0039	0.0367
HEDP =1.5 g/L	0.0998	0.0081	0.0048	0.0244

4.8 Effect of Textile Preparation Process Effluent III

In Textile Preparation Effluent Recipe III, NaOH instead of carbonate was introduced into solution in order to investigate the performance of H_2O_2/UV-C treatment in the absence of strong $HO^{\bullet}$ scavenger carbonate.

4.8.1 NPEO

The NPEO abatement during photochemical advanced oxidation in the presence of DTPMP=1.0 g/L, Cl^- =3.0 g/L, and NaOH=1.5 g/L at pH_0=11.5 were illustrated in Figure 4.39.

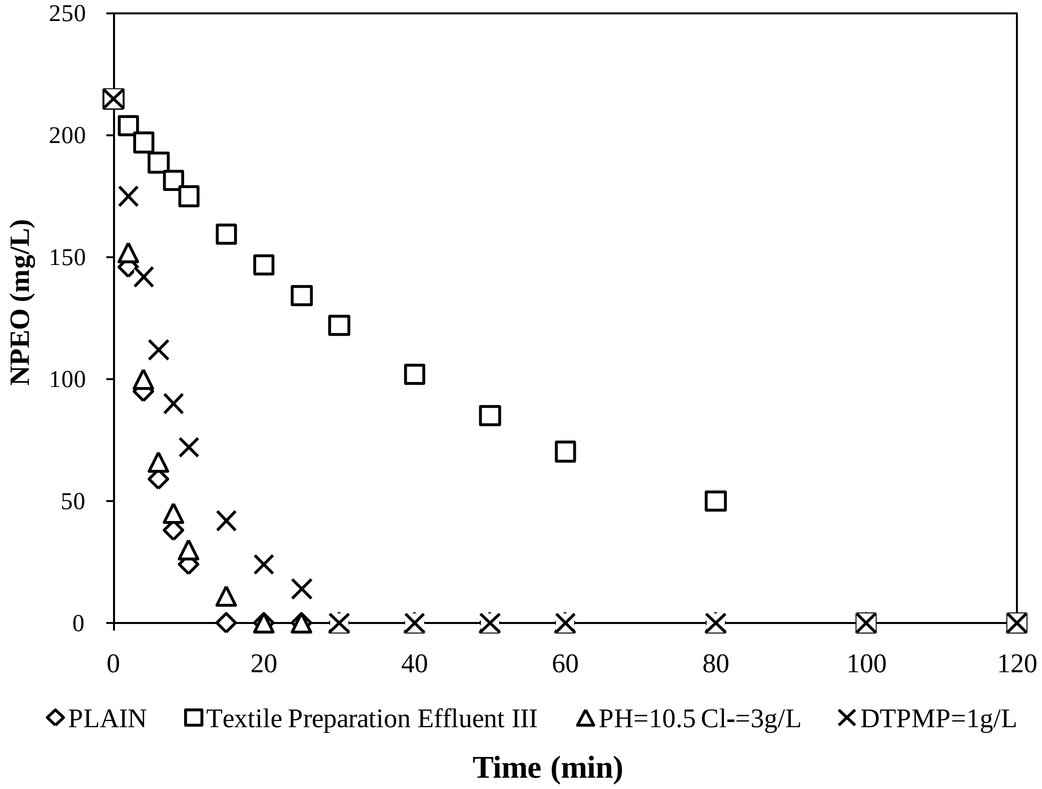


Figure 4.39 : Degradation of NPEO in the presence of Textile Preparation Process Effluent III by H_2O_2/UV-C process.

The Figure 4.39 showed the changes in degradation of NPEO, which Textile Preparation Effluent III showed the most serious inhibition. The possible reason could be both effects of pH and DTPMP. Textile Preparation Effluent III the initial pH value was adjusted to 11.5 which was leaded to an extra problem- H_2O_2 dissociation.

H_2O_2 dissociated with pK_a =11.6. Therefore, at pH=11.5, 77% H_2O_2 dissociated into HO_2^-, only 23% H_2O_2 are available for photolysis. Since DTPMP was introduced in Textile Preparation Effluent III which interferes with the UV light absorption, though 23% H_2O_2 available in solution, because limitation of the UV light, H_2O_2 photolysis rate got retarded.

So, even use of NaOH instead of the strong scavenger CO_3^{2-} for the Effluent III, however, due to the dual effects of pH and DTPMP, the system reaction rate was limited.

Therefore, pH’s effect is stronger than sequestering agents are according to the experimental results.

4.8.2 COD

The COD abatement during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent III was illustrated in Figure 4.40.

It was so obvious that Textile Preparation Effluent III leaded to the serious retardation. The rate coefficient of COD abatement in the presence with Textile Preparation Effluent III at pH_0=11.5 is 0.0028 min^{-1} almost come to zero.

Low COD degradation rate can be attributed to two reasons, high initial pH caused the limited H_2O_2 are available for the generation of $HO^\bullet$; the sequestering agent-HEDP interfered the photolysis of H_2O_2 and caused the high initial COD value.

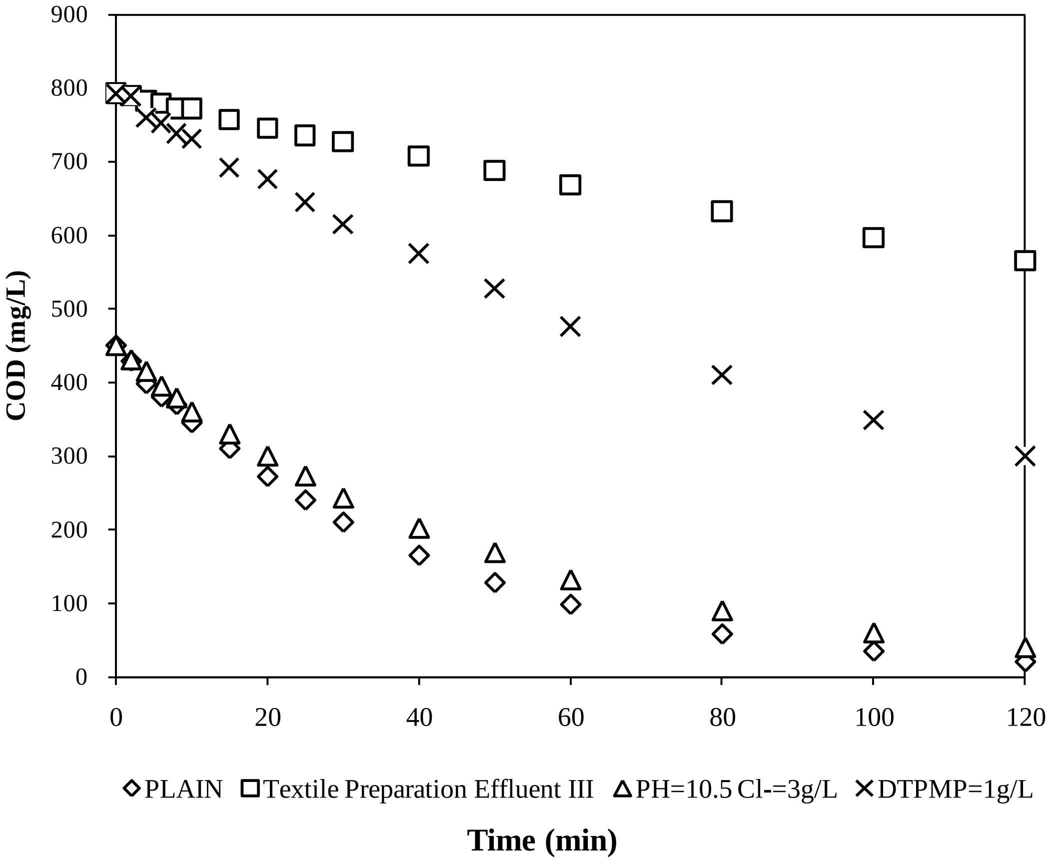


Figure 4.40 : COD abatement in the presence of Textile Preparation Effluent III during NPEO degradation by H_2O_2/UV-C process.

4.8.3 TOC

The TOC abatement during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent III was illustrated in Figure 4.41.

As Figure 4.41 presented the changes in TOC value, Textile Preparation Effluent III caused the lowest removal efficiency, which is 8% at 60 mins. Normally, without any introducing of textile preparation auxiliary into the solution the TOC removal efficiency at 60 mins is 59%.

The reasons caused low rate of COD degradation are also can be used for explaining low TOC degradation rate caused by Textile Preparation Effluent III.

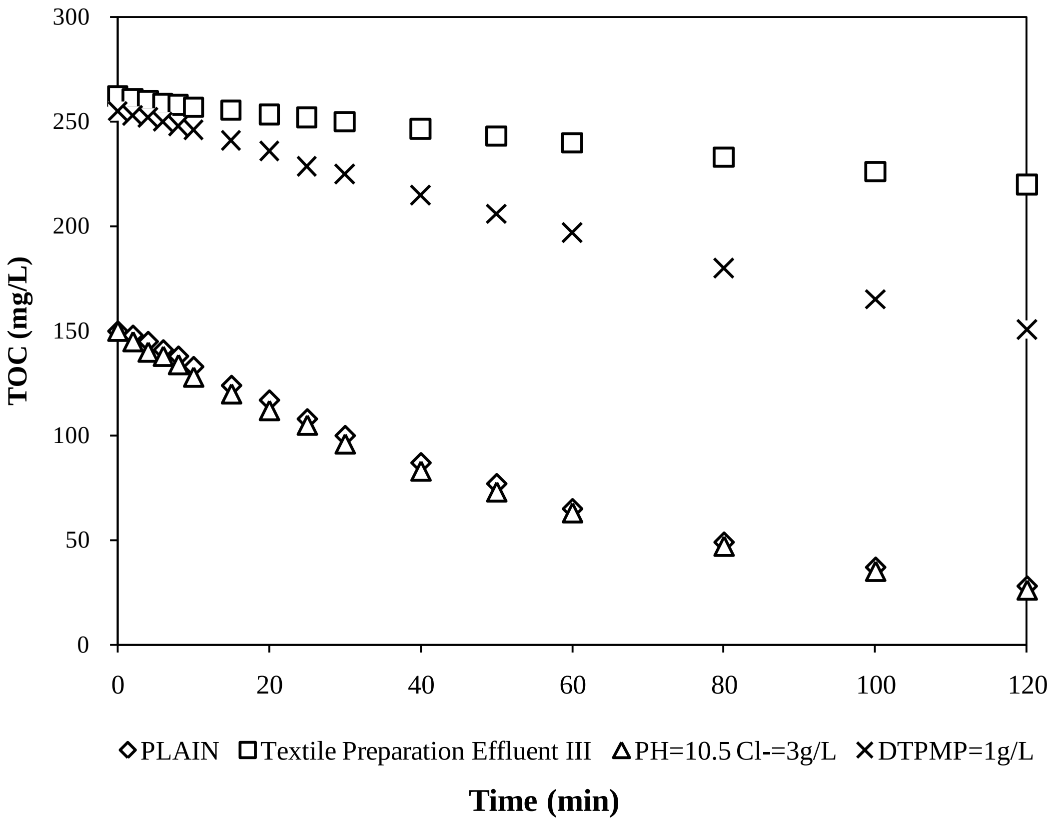


Figure 4.41 : TOC abatement for H_2O_2/UV-C Treatment of Textile Preparation Effluent III and respective Control Experiments.

4.8.4 H_2O_2

The H_2O_2 consumption during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent III was illustrated in Figure 4.42.

As presented, that Textile Preparation Effluent III leaded to a serious inhibition.

Since in the presence of DTPMP in Textile Preparation Effluent III, which competed UV light with H_2O_2, unsurprisingly, H_2O_2 consumption rate had been inhibited.

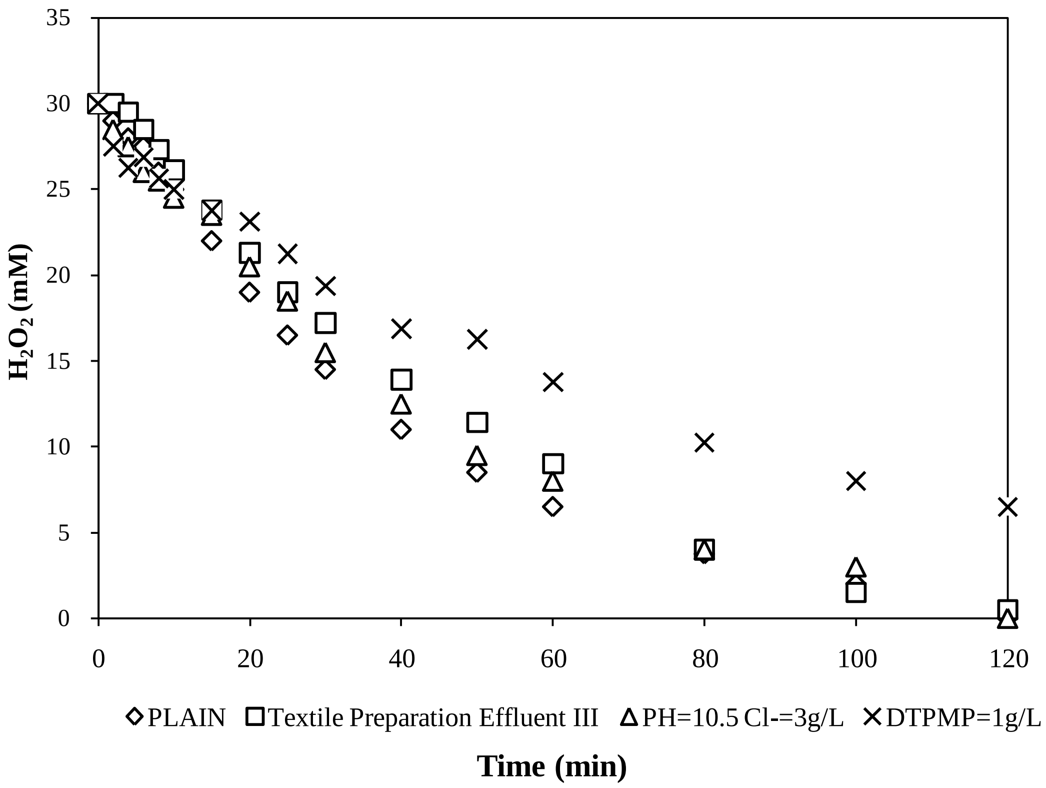


Figure 4.42 : H_2O_2 concentration for H_2O_2/UV-C Treatment of Textile Preparation Effluent III and respective Control Experiments.

Table 4.8: Pseudo-first order rate constants in the presence of Textile Preparation Effluent III for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k (min^{-1})			
Experimental conditions	NPEO	COD	TOC	H_2O_2
Plain(NPEO only)	0.2211	0.0255	0.0142	0.0270
Textile Preparation Effluent III	0.0183	0.0028	0.0014	0.0206
Cl^- =3 g/L	0.1995	0.0201	0.0145	0.0231
DTPMP=1.0 g/L	0.1098	0.0082	0.0044	0.0125

4.8.5 pH

The changes in pH (pH_0=11.5) value during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent III was illustrated in Figure 4.43.

Figure 4.43 showed Textile Preparation Effluent III has a stable pH even in the absence of carbonate in solution. The pH trend implied that the oxidation rate was inhibited and NaOH can play the role as a pH buffer instead of carbonate.

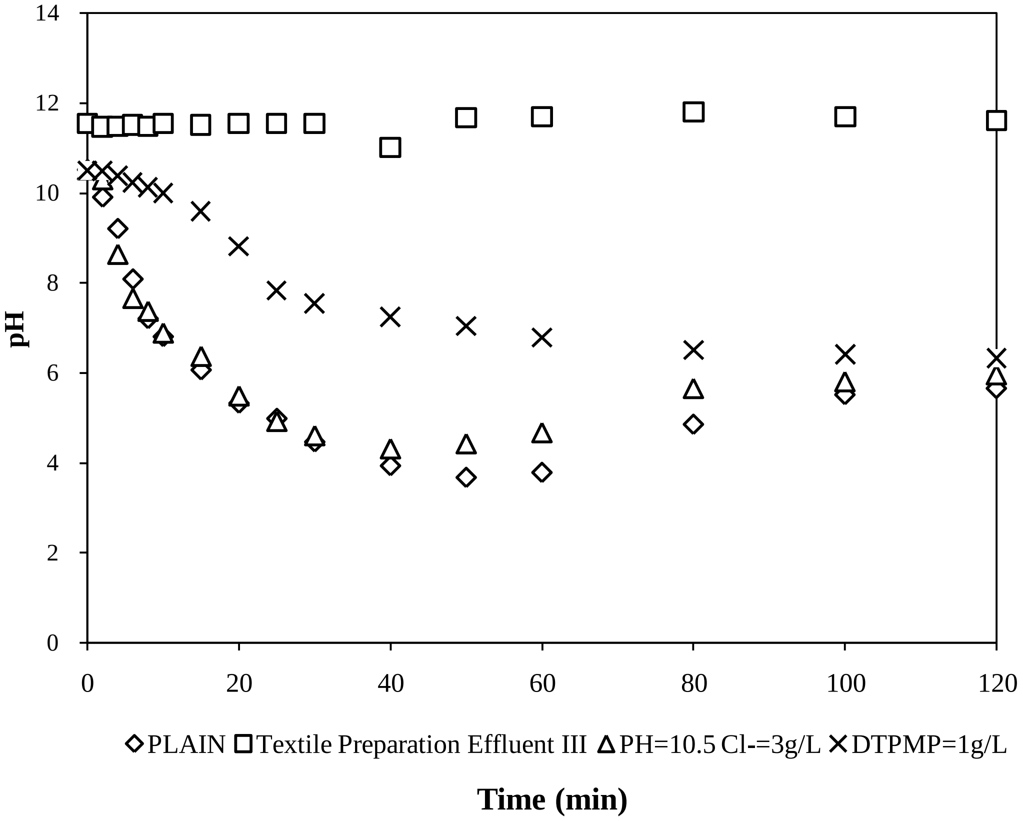


Figure 4.43 : pH value in the presence of Textile Preparation Effluent III during NPEO degradation by H_2O_2/UV-C process.

4.9 Effect of Textile Preparation Process Effluent IV

In this part, the 1.0 g/L HEDP instead of DTPMP was introduced into the Textile Preparation Effluent IV which combined with Cl^-=3.0 g/L and NaOH=1.5 g/L at pH_0=11.5.

4.9.1 NPEO

The NPEO abatement during photochemical advanced oxidation in the presence of Textile Preparation Effluent IV was illustrated in Figure 4.44.

As shown in Figure 4.44, Textile Preparation Effluent IV caused more serious inhibitory effect than any other control experiments. The reasons are same with the Textile Preparation Effluent IV, which is because of pH and sequestering agent UV-C absorbance effects.

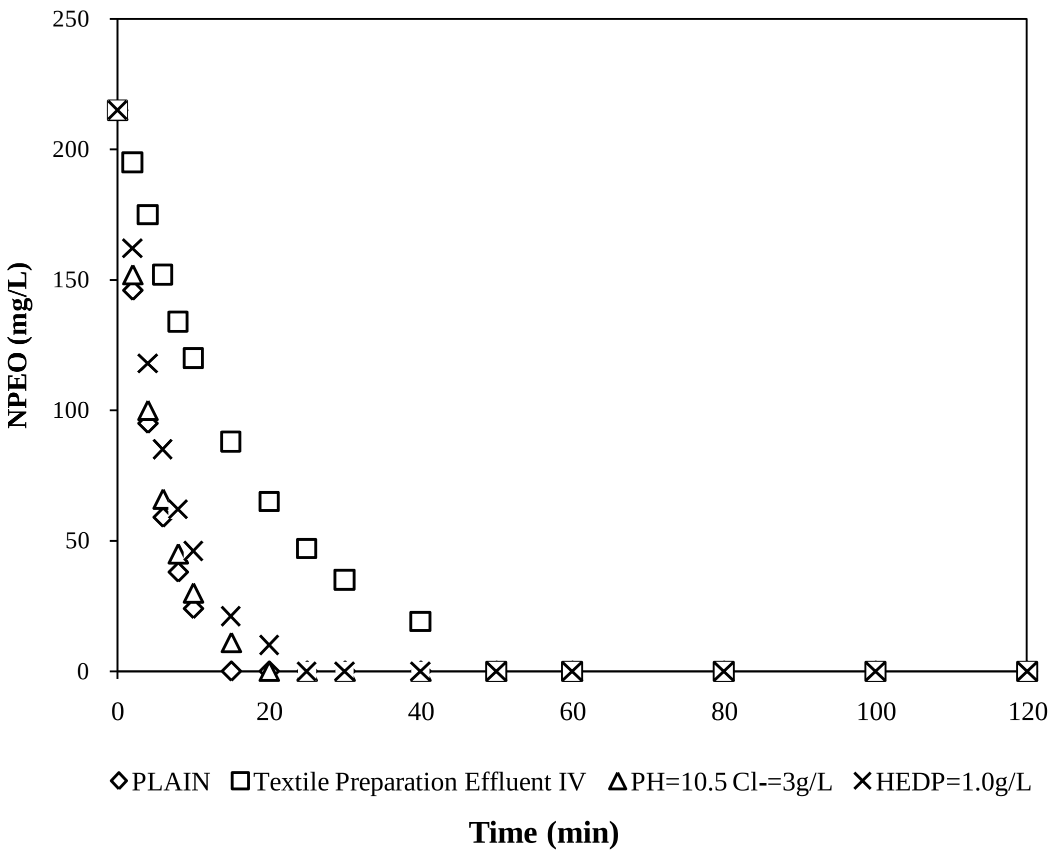


Figure 4.44 : Degradation of NPEO in the presence of Textile Preparation Process Effluent IV by H_2O_2/UV-C process.

4.9.2 COD

The COD abatement during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent IV was illustrated in Figure 4.45.

Textile Preparation Effluent IV has a similar COD changing trend with HEDP only, which showed Textile Preparation Effluent IV caused the comparatively tiny effect. The removal efficiency of COD is 32% at 60 mins, which was higher than Textile Preparation Effluent III's,

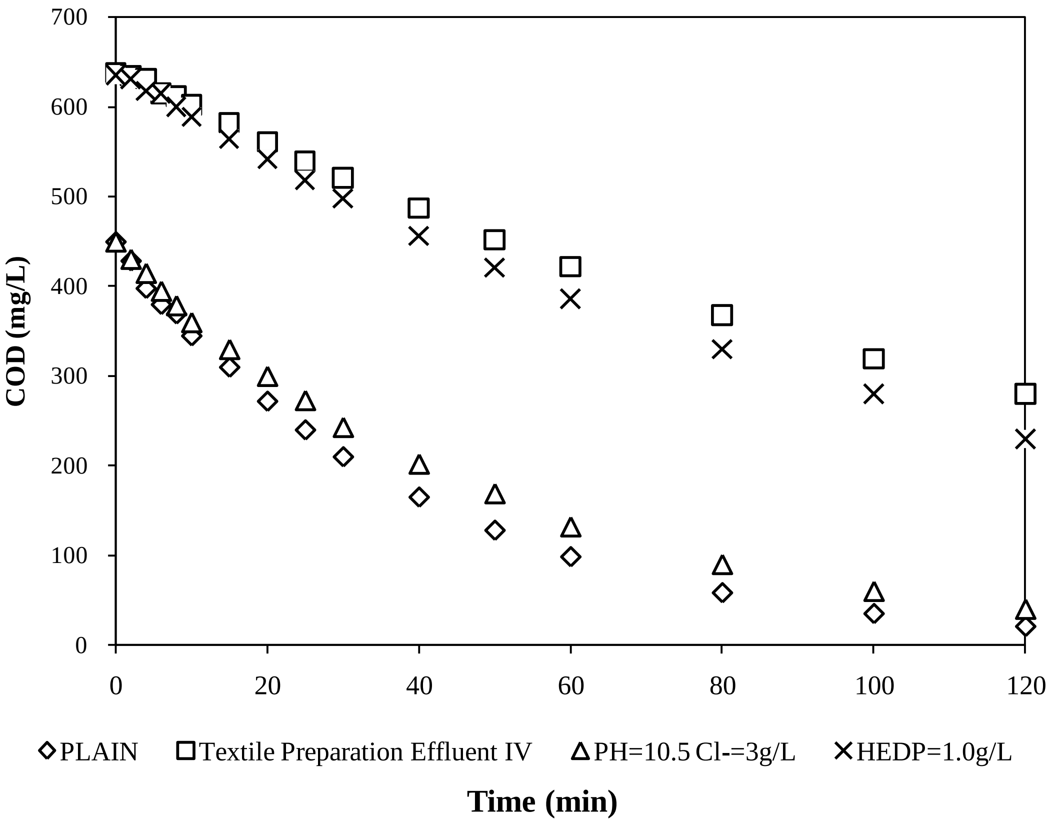


Figure 4.45 : COD abatement for H_2O_2/UV-C Treatment of Textile Preparation Effluent IV and respective Control Experiments.

4.9.3 TOC

The TOC abatement during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent IV was illustrated in Figure 4.46.

Degradation of Textile Preparation Effluent IV TOC showed the same situation with COD, which is TOC changing trend is similar with HEDP only. The removal efficiency of TOC is 28% at 60 mins, which was higher than Textile Preparation Effluent III’s.

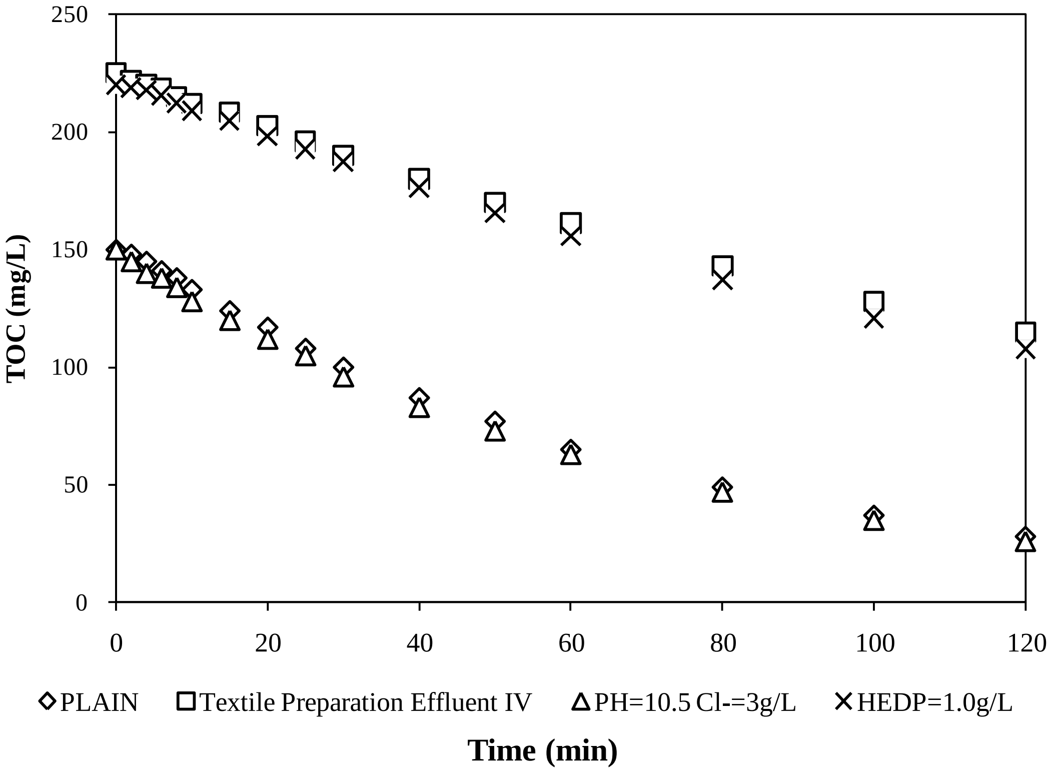


Figure 4.46 : TOC abatement for H_2O_2/UV-C Treatment of Textile Preparation Effluent IV and respective Control Experiments.

4.9.4 H_2O_2

The H_2O_2 consumption during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent IV was illustrated in Figure 4.47.

As presented, that Textile Preparation Effluent IV leaded to a recognizable inhibition. Since in the presence with HEDP in Textile Preparation Effluent IV, which competed UV light with H_2O_2, unsurprisingly, H_2O_2 consumption rate had been inhibited.

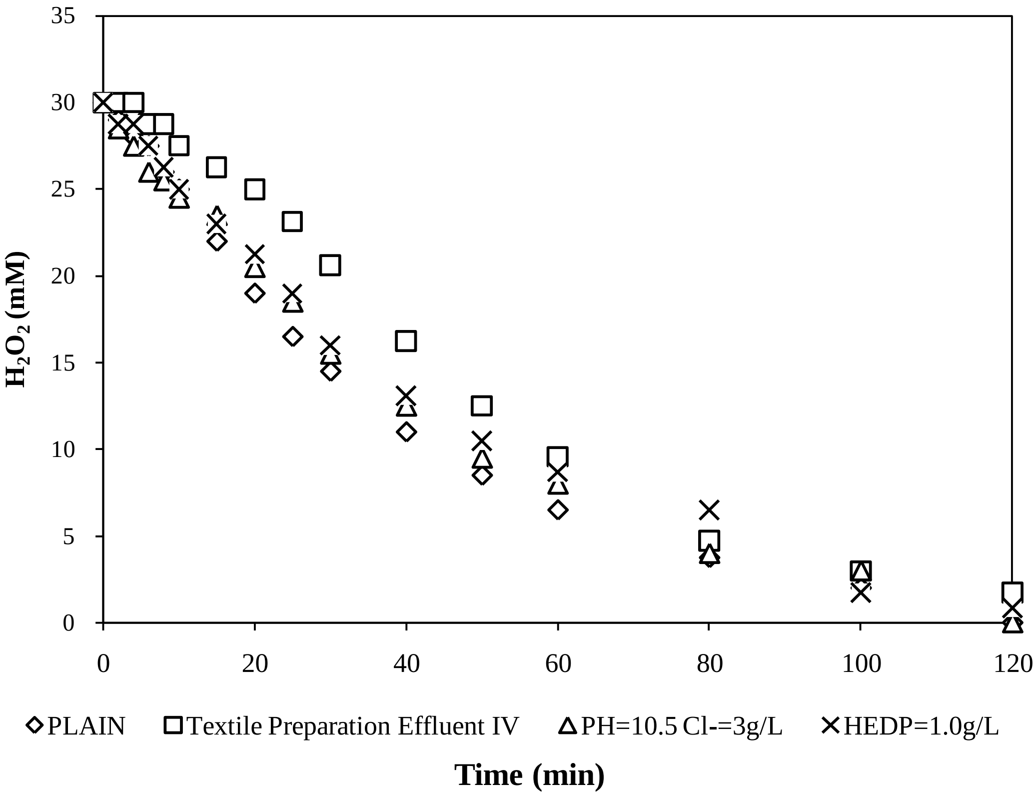


Figure 4.47 : H_2O_2 concentration for H_2O_2/UV-C Treatment of Textile Preparation Effluent IV and respective Control Experiments.

Table 4.9: Pseudo-first order rate constants in the presence of Textile Preparation Effluent IV for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k (min^{-1})			
Experimental conditions	NPEO	COD	TOC	H_2O_2
Plain(NPEO only)	0.2211	0.0255	0.0142	0.0270
Textile Preparation Effluent IV	0.0183	0.0028	0.0014	0.0206
Cl^- =3 g/L	0.1995	0.0201	0.0145	0.0231
HEDP=1.0 g/L	0.1098	0.0082	0.0044	0.0125

4.9.5 pH

The changes in pH (pH_0=11.5) value during NPEO photochemical advanced oxidation in the presence of Textile Preparation Effluent IV was illustrated in Figure 4.48.

Textile Preparation Effluent IV initial pH is 11.5 as the oxidation occurs the pH has decreased which shows that in the presence of HEDP and only 23% H_2O_2 available in solution, in the absence of carbonate, the oxidation occurred. The trend of pH changing is the evidence to prove it.

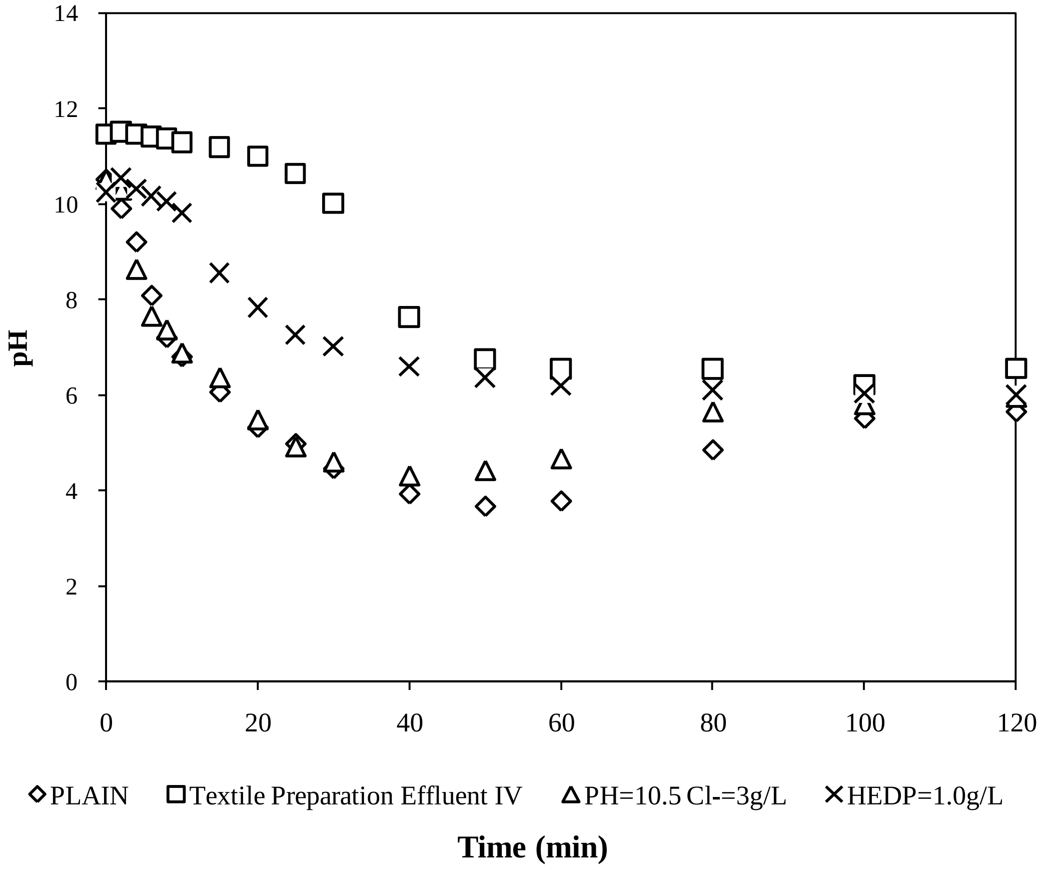


Figure 4.48 : pH value in the presence of Textile Preparation Effluent III during NPEO degradation by H_2O_2/UV-C process.

Table 4.10: Pseudo-first order rate constants in the presence of Textile Preparation Effluent IV for the NPEO degradation by the H_2O_2/UV-C treatment process of the plain experiment

	k (min^{-1})			
Alternative Textile Preparation Effluent	NPEO	COD	TOC	H_2O_2
I	0.0369	0.0030	0.0014	0.0088
II	0.0387	0.0050	0.0019	0.0088
III	0.0183	0.0028	0.0014	0.0206
IV	0.0612	0.0070	0.0056	0.0257

Table 4.10 displayed completely four Effluents' oxidation rate k value. Data obtained that Effluent IV has the best performance when comparing with other three Effluents.

The possible reason could be the difference of those two sequestering agents-DTPMP and HEDP. Comparing with Effluent III, same fraction of H_2O_2 (23%) is available, the only different thing is between these two sets are the sequestering agents' properties which in the table 4.1 shows us that DTPMP gets the stronger ability to absorb the UV lights than HEDP does.

So, even less H_2O_2 available for the treatment at pH=11.5 for the Effluent IV, however because of HEDP does not interfere with UV lights that much, besides scavenger carbonate is absence, so it can be assumed that inside reactor still have enough $HO^{\bullet}$ be generated through H_2O_2 photolysis. As a result, that can explain the reason of the Effluent IV has the best performance than others.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The purpose of this experimental study was to assess the performance of the H_2O_2/UV-C treatment process for the degradation of the commercial nonionic textile surfactant NPEO under different reaction conditions by introducing common organic and inorganic textile preparation chemicals (NaCl, Na_2CO_3, the phosphpnic acid-based sequestering agents DTPMP and HEDP) in order to predict the efficiency of advanced photochemical oxidation process under actual textile preparation conditions. These experimental results delineated that H_2O_2/UV-C oxidation is a very promising option for the efficient degradation of aqueous NPEO. However, in the presence of the textile preparation chemicals, NPEO degradation was considerably suppressed and the oxidative treatment performance of the H_2O_2/UV-C process was seriously inhibited. The following conclusions could be drawn from the experimental work:

- Chloride was not a serious $HO^\bullet$ scavenger at alkaline pH (10.5). However, a slightly inhibitory effect was observed at acidic pH (3.5).
- Carbonate (soda-ash), known as a serious $HO^\bullet$ scavenger, considerably negatively affected H_2O_2/UV-C oxidation rates and efficiencies, as expected.
- The organic sequestering agents negatively influenced H_2O_2/UV-C oxidation rates and efficiencies; the negative effect of the sequestering agent DTPMP was more serious than that of HEDP, which has a simpler molecular structure that does not hinder UV light absorption of H_2O_2 at 245 nm. Both organic sequestering agents compete with NPEO for $HO^\bullet$.
- The initial reaction pH not only influenced the carbonate/bicarbonate equilibrium but also H_2O_2 speciation. Consequently, the reaction pH had a major impact on NPEO photochemical oxidation by the H_2O_2/UV-C process.

5.2 Recommendations

The use of Textile Preparation Effluent IV is highly recommended if H_2O_2/UV-C oxidation is being considered for its treatment at source as a segregated waste stream. This textile preparation recipe does not contain the $HO^{\bullet}$ scavengers carbonate and DTPMP, but NaOH and HEDP instead, that imparted less negative influence on NPEO and its organic matter degradation.

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