ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

OCTYLPHENOL ETHOXYLATE TREATMENT WITH ZERO-VALENT ALUMINUM BASED ADVANCED OXIDATION PROCESS

M.Sc. THESIS

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Department of Environmental Engineering

Environmental science and Engineering Programme

Thesis Advisor: Assoc.Prof. Dr. Tuğba ÖLMEZ HANCI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

OKTİLFENOL ETOKSİLATIN SIFIR DEĞERLİKLİ ALÜMİNYUM BAZLI İLERİ OKSİDASYON PROSESLERİ İLE ARITIMI

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Çevre Mühendisliği Anabilim Dalı

Çevre Bilimleri ve Mühendisliği Programı

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Haziran 2016

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Date of Submission : 02 May 2016
Date of Defense : 10 June 2016

To my patient spouse,

my kind professor,

friends and family.

FOREWORD

This thesis was written for my Master degree during the period of Autumn 2015 and Spring 2016, under the co-operation of Istanbul Technical University (ITU), in Department of Environmental Engineering.

I would first like to thank my thesis advisor Dr. Tuğba Ölmez Hanci. I have been amazingly fortunate to have an advisor who gave me the freedom to explore on my own. Her patience and support helped me overcome many crisis situations and finish this dissertation. I hope that one day I would become as good an advisor to my students as Dr. Tuğba has been to me.

I am deeply grateful to Prof. Dr. İdil Arslan-Alaton for commenting on my views and helping me understand and enrich my ideas.

I would like to acknowledge to Prof. Alper Tunga Akarsubaşı for his technical assistance and support in the genotoxicity (Umu Chromo) tests.

I would like to thank my friends Hadi Fakhri, Merve Doğan and Yasaman Fallahi because of their help for my experimental studies. Their support and care helped me overcome setbacks and stay focused on my thesis.

I am also thankful to ITU environment, of being so supportive with the necessary chemicals and equipments.

Finally, I appreciate the financial support from the Scientific and Technological Research Council of Turkey (TUBITAK) under Project Nr. 111Y257 and 114Y257.

I would like to express my gratitude to my parents and my parents-in-law for their unfailing emotional support and continuous encouragement throughout my years of study.
None of this would have been possible without the love and patience of Aydin, my husband. I would like to dedicate my thesis to my lovely spouse who has been a constant source of love, materially and morally support, all these years.

June 2016

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ABBREVIATIONS

AOPs	**:** Advanced Oxidation Processes
APEs	**:** Alkylphenol ethoxylates
BPA	**:** Bisphenol A
DW	**:** Distilled water
HP	**:** Hydrogen Peroxide
HPLC	**:** High performance liquid chromatography
NPEs	**:** Nonylphenol ethoxylates
$HO^{\bullet}$	**:** Hydroxyl radicals
OPEs	**:** Octylphenol ethoxylates
PMS	**:** Peroxymonosulfate
PS	**:** Persulfate
ROS	**:** Reactive Oxygen Species
$SO_4^{\bullet -}$	**:** Sulfate radicals
SW	**:** Raw Surface Wastewater
TDS	**:**Total Dissolved Solids
TOC	**:** Total Organic Carbon
TSS	**:**Total Suspended Solids
TW	**:** Tap water
TX-45	**:** Triton X-45
WW	**:** Domestic wastewater treatment plant effluent
ZVAl	**:** Zero-Valent Aluminum

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OCTYLPHENOL ETHOXYLATE TREATMENT WITH ZERO-VALENT ALUMINUM BASED ADVANCED OXIDATION PROCESS

SUMMARY

Alkylphenol ethoxylates (APEs) are non-ionic surfactants and the more important members of them are nonylphenol (NP) and octylohenol (OP). APEs are being used in the formulations of cleaning products, paints, ink dispersants, textile and leather processing (preparation, dyeing and finishing), pulp and paper manufacturing, metal processing, cosmetics and personal care products. It has been postulated that APEs have estrogenic activity and is classified as an endocrine disrupting compound (EDC). There is growing concern on the influence of APEs, Due to their high consumption rate and adverse health effects on wildlife. APEs are discharged to wastewater treatment facilities or directly released into the environment and are a potential source of contamination in the aquatic environment. Primary degradation of APEs in wastewater treatment plants or in the environment generates more persistent shorter chain APEs. Due to the fact that biotreatment requires long retention times and connot degrade APEs completely, rapid and efficient treatment process including advanced oxidation process (AOPs) have successfully been developed to the efficient treatment of APEs. AOPs are based on the generation of very reactive species free radicals. ZVAl exhibits a capacity to degrade organic pollutants under acidic conditions. In the presence of O_2, ZVAl/oxidant showed high oxidation capacity due to the high stability of aqua-complexed Al^{3+} over a wider pH range and leads to generation of $OH^{\bullet}$ and $SO_4^{\bullet-}$ free radicals by an electron transfer mechanism from ZVAl to oxidant.

In this study, nanoscale zero-valent aluminum (nZVAl)-activated hydrogen peroxide (HP), persulfate (PS) and peroxymonosulfate (PMS) oxidation of commercially important octylphenol polyethoxylate type nonionic surfactant namely Triton™ X-45 (TX-45), was investigated. Consequently, it is of major importance to follow changes in toxicity during the application of AOPs, preferrably by conducting battery tests to examine potential toxic effects on tests organisms belonging to different trophic levels. Two different acute toxicity tests using *Vibrio fischeri* and *Pseudokirchneriella subcapitata* as well as the UMU-Chromo genotoxity test were undertaken to evaluate the ecotoxicological effects of TX-45 and its oxidation products.

In the first part of the study, TX-45 abatement with different initial concentration, oxidant consumption and pH changing were investigated in the nZVAl/O_2/H^+ system, mere oxidant process and nZVAl/Oxidant treatment methods. Thereafter, treatment performances were evaluated in distilled water (DW), raw surface water (SW), tap water (TW) and effluent from a domestic wastewater treatment plant (WW) to estimate TX-45 degrade as well as its TOC content.

TX-45 removals in the absence of nZVAl (mere HP, PS and PMS treatments) and oxidants (nZVAl/O_2/H^+ treatment) were obtained between 5%-38%. Activation of HP, PS and PMS with nZVAl enhanced TX-45 degradation substantially. Complete TX-45 degradation occurred in DW with the nZVAl/PS and nZVAl/PMS treatment combinations after 90 min and 60 min, respectively, whereas only 76% TX-45 removal was obtained with nZVAl/HP after 120 min (TX-45=2 mg/L; nZVAl=1 g/L; HP-

PMS=0.25 mM; PS=0.5 mM; pH=3). In DW, TX-45 removal efficiencies decreased as follows; nZVAl/PMS≈nZVAl/PS>nZVAl/HP and as nZVAl/PMS> nZVAl/HP> nZVAl/PS in SW and WW. Additionally, it should be mentioned that the TOC contribution of the 2 mg/L TX-45 in the SW, TW and WW samples was relatively minor (10-20%) that could not have affected the TOC removal considerably.

Toxicity test results indicated that the nZVAl/PS-treated TX-45 samples did not exhibit toxic effects on *V. fischeri*; the relative inhibition increased from 15% to 26% in DW and decreased to practically non-toxic levels (<8%) in SW after 120 min treatment. During the early stages of nZVAl/PS treatment, the growth inhibition test conducted with the microalgae *P. subcapitata* revealed that the relative inhibition value was increased from 35-39% to 44% and 52% in DW and SW samples, respectively. After 120 min treatment, it dropped back to 40 and 25% in DW and SW samples, respectively. The battery test results demonstrated not TX-45, but the oxidation products of the treatment process caused inhibitory effects and also results revealed that the most sensitive organism to TX-45 and its degradation products was *P. subcapitata.* According to the UMU-Chromo test results the original and nZVAl/PS-treated TX-45 neither exhibit cytotoxic nor genotoxic effects.

OKTİLFENOL ETOKSİLATIN SIFIR DEĞERLİKLİ ALÜMİNYUM BAZLI İLERLİ OKSİDASYON PROSESLERİ İLE ARITIMI

ÖZET

Noniyonik yüzey aktif madde kategorisinin geniş bir parçasını oluşturan alkilfenol etoksilatlar, deterjanları, temizleyicileri, yağ gidericileri, kuru temizleme yardımcılarını, petrol dağıtıcılarını, emülsiyonlaştırıcıları, ıslatma maddelerini, yapıştırıcıları, tarım ilaçlarını, pestisitleri, kozmetikleri, kağıt ve tekstil işleme formülasyonlarını, ön yıkama maddelerini, metal işleme sıvılarını, petrol sahası kimyasallarını, boya ve kaplamaları, toz kontrol maddelerini de içeren geniş bir yelpazade kullanılmaktadır. Alkilfenol etoksilatlar biyolojik olarak daha zor bozunan yüzey aktif maddelerdir ve sudaki çözünürlüklerinden dolayı atıksudan uzaklaştırılmaları zordur. Alkilfenol etoksilatlar grubundaki en çok kullanılan nonilfenol ve oktilfenol etoksilatlar, yarattıkları ciddi çevresel sorunlarla ön plana çıkmışlardır. Etoksi gruplarının kademeli olarak uzaklaşması ile parçalanan nonilfenol etoksilat (NPEO) ve oktilfenol etoksilatlar (OPEO), lipofil karakterleri ve düşük biyoayrışabilirlikleri nedeniyle biyolojik birikim gösteren alkilfenollere (nonilfenol ve oktilfenol) dönüşmektedir. Nonilfenol ve oktilfenoller suda yüksek derecede toksik etki göstermekte ve çok düşük konsantrasyonlarda dahi suda yaşayan canlıların endokrin sistemlerini bozarak üremelerini etkilemektedir. Alkil fenol etoksilatlar yaygın üretim kapasiteleri, yoğun tüketimleri, sedimentlerde ve yağ hücrelerinde birikim eğilimleri, kronik toksik etkileri ve son zamanlarda bunlara ek olarak parçalanma ürünü olan alkilfenollerin pek çok ülke ve kuruluş tarafından "endokrin bozucu kirletici madde" listelerinde sınıflandırılması nedeniyle, gündem konusu, öncelikli kirleticiler olarak dikkat çekmektedirler. Endüstriyel kaynaklı, endokrin bozucu, kanserojenik ve toksik özellik gösteren alkilfenoller ise konvansiyonel yöntemlerle giderilememekte, bu nedenle de arıtma sistemine ve/veya alıcı ortama olumsuz etkileri devam etmektedir.

İleri oksidasyon prosesleri (İOP), oksidasyon potansiyeli çok yüksek olan serbest radikallerin reaksiyon ortamında üretilmelerine dayanan prosesler ve arıtma yöntemleridir. Bu proseslerle, hedef kirleticinin kısmı oksidasyonla toksisitesi giderilmekte ve/veya kirletici biyolojik olarak daha kolay ayrıştırılabilen oksidasyon ara ürünlerine dönüştürülmekte, bazı durumlarda ise tamamen oksidasyon son ürünlerine mineralize (karbondioksit ve su) edilmektedir. Bugüne kadar hidroksil radikali ($HO^{\bullet}$) bazlı çeşitli heterojen ve homojen İOP'nin birçok organik ve inorganik kirleticinin arıtımında kullanımı detaylı olarak incelenmiş, proseslerin modellenmesi, optimizasyonu, kirleticilerin giderim mekanizmaları ve proses verimine etki eden koşullar ayrıntıları ile rapor edilmiştir. Son yıllarda ise, zor ayrışan, hatta inert ve/veya toksik kirleticilerin oksidasyon potansiyeli yüksek (2.4-2.6 eV) sülfat radikali ($SO_4^{\bullet-}$) bazlı İOP ile giderimiyle ilgili araştırmalar giderek önem kazanmıştır. Yarılanma ömrü hidroksil radikaline oranla daha uzun, su/atıksu matrisinde bulunan, reaksiyon süresinin uzamasına ve oksidan tüketimine sebep olan maddelerden daha az etkilenen sülfat radikalinin bu özellikleri $SO_4^{\bullet-}$ bazlı İOP'nin su ve atıksu arıtımında kullanımını daha avantajlı hale getirmektedir.

Yüksek yüzey alanları ve reaktiviteleri nedeniyle sıfır değerlikli demir (SDD) ve sıfır değerlikli alüminyum (SDA) gibi sıfır değerlikli metal nanopartikülleri ile arıtma uygulamaları ise son yıllarda önemli bir araştırma konusu olmuştur. Asidik ortamda oksijen varlığında SDA moleküler oksijeni aktive etmekte ve serbest radikallerin oluşumuna neden olmaktadır. Ortamda hidrojen peroksit (HP), persülfat (PS) ve peroksimonosülfat (PMS) oksidanlarının bulunması durumunda ise benzer şekilde SDA ve oksidanlar arasında gerçekleşen elektron transferi neticesinde serbest radikaller ($HO^{\bullet}$ ve $SO_4^{\bullet -}$) oluşmaktadır. SDA ile arıtma prosesinin potansiyel uygulama alanları, yeraltı sularının arıtımı (pestisitler, antibiyotikler, arsenik, nitrat ve ağır metaller, vb.) ve endüstriyel atıksuların (klorlü organik bileşikler, boyar maddeler, fenoller, klorlu fenoller) arıtımıdır. Bugüne kadar mikrokirleticilerin SDA ile arıtılabilirliği konusunda çalışmaların çoğu sentetik (saf) suda ve/veya laboratuvar ölçeğinde gerçekleştirilmiştir. Bu nedenle elde edilen arıtılabilirlik sonuçları gerçek koşulları ve söz konusu arıtma sisteminin gerçek performansını yansıtmamaktadır.

Bu bilgilerden yola çıkarak bu çalışmada, SDA kullanıldığı İOP'nin geliştirilmesine temel bilgi düzeyinde katkıda bulunmak üzere, biyolojik olarak zor ayrışan veya hiç ayrışamayan, canlı bünyesinde ve sucul ortamlarda birikme potansiyeline sahip, doğal ortamlarda potansiyel olarak toksik, kanserojen ve/veya endokrin bozucu olarak etkileri nedeniyle de pek çok ülkede üretimi ve/veya hammadde olarak kullanımında yasal düzenlemeler getirilmiş alkilfenol etoksilatlara örnek teşkil etmesi açısından seçilen OPEO'nun, SDA/HP, SDA/PS ve SDA/PMS ile arıtılabilirliğinin incelenmesi amaçlanmıştır.

Bu bilgilerden yola çıkarak, bu çalışmanın ilk aşamasının amacı, endokrin bozucu kimyasallardan olan ve toksik olduğu bilinen TX-45'in etkin arıtımını (ana madde giderimi ve mineralizasyon) sağlayabilmek için SDA/HP, SDA/PS ve SDA/PMS proseslerinin kullanılabilirliği araştırılmış ve proses performanslarının distile su ve gerçek su numunelerinde (ham yüzeysel su, arıtılmış evsel atıksu, çeşme suyu) karşılaştırılmıştır. Çalışmanın ikinci aşamasında ise su fotobakterisi *Vibrio fischeri (V. fischeri)* ve tatlı su algi *Pseudokirchneriella subcapitata (P. subcapitata)* ile reaksiyon süresi boyunca belli aralıklarla alınan numunelerde toksisite analizleri gerçekleştirilmiş ve TX-45 kirleticisinin arıtımı sırasında meydana gelen toksisite değişimlerinin belirlenmiştir. Bu çalışmalara ek olarak arıtma sonrasında genotoksik aktivitenin belirlenmesi amacı ile UMU-Choromo testi yürütülmüştür.

Ortamda SDA bulunmaması (HP, PS ve PMS oksidasyonu) ve herhangi bir oksidan ilavesi yapılmaması ($nZVAl/O_2/H^+$ uygulaması) durumunda TX-45 giderim verimleri %5 ve %38 arasında bulunmuştur. HP, PS ve PMS oksidanlarının SDA ile aktive edilmesi sonrasında TX-45 giderimleri artmış göstermiştir. SDA/PS ve SDA/PMS uygulamaları ile 90 ve 60 dakika sonrasında TX-45 tamamen giderilmiş, SDA/HP prosesi ile ise 120 dakika sonunda %76 giderim verimi sağlanmıştır (Arıtma koşulları: TX-45=2 mg/L; SDA=1 g/L; HP-PMS=0.25mM; PS=0.5mM; pH=3). Distile su ile yürütülen çalışmalarda TX-45 giderim verimleri nZVAl/PMS ≈ nZVAl/PS > nZVAl/HP sırası ile gerçekleşmiş, ham yüzeysel su ve arıtılmış evsel atıksu örneklerinde ise bu sıra nZVAl/PMS > nZVAl/HP > nZVAl/PS şeklinde değişmiştir.

Toksisite deneyleri sonucunda SDA/PS prosesi ile distile suda gerçekleştirilen TX-45 arıtımında *V. fischeri* fotobakterisine toksik etki gösteren ara ürünlerin oluşmadığı belirlenmiştir. Distile suda gerçekleştirilen arıtma uygulamasının ilk aşamalarında

%15 olan başlangıç inhibisyon değeri 120 dakika sonunda %26'ya yükselmiştir. Yüzeysel su numunesinde ise 120 dakika sonunda inhibisyon %8 mertebelerine düşmüştür. *P. subcapitata* tatlı su alg türü ile gerçekleştirilen toksisite deneylerinde %35-39 olarak belirlenen başlangıç inhibisyonu, oksidasyonun ilk aşamalarında distile suda %44 ham yüzeysel suda %52'ye yükselmiştir. 120 dakikalık arıtma süresi sonunda bu değerler distile suda %40, ham yüzeysel suda %25 mertebelerine düşmüştür. Farklı türler ile gerçekleştirilen toksisite analizlerinde *P. subcapitata* türünün TX-45 ve oksidasyon ürünlerine karşı daha hassas olduğu belirlenmiştir. UMU-Chromo genoksisite testi ise orijinal ve SDA/PS ile arıtılmış TX-45 numunelerinin sitotoksik ve genotoksik etki göstermediğini ortaya koymuştur.

Bu çalışma kapsamında gerçekleştirilen kapsamlı analitik ölçüm ve arıtılabilirlik çalışmaları, bilimsel açıdan özgün olmaları ve bu kirletici gruplarını içeren endüstriyel atıksulardan kaynaklanan çevresel problemlere çözüm yöntemi sunmaları nedeniyle her açıdan önemli katkılar sağlamıştır.

1. INTRODUCTION

There is growing concern on the influence of endocrine-disrupting compounds (EDCs) on public health. They are present in our environment, food, and consumer products as they were originally designed to act as a pesticide, solvent, preservative, or plasticizer. EDCs have been investigated due to their adverse effects in animals and humans inhibiting the normal action of the endocrine system. The list of these xenobiotic compounds is extensive and includes for example the following families of chemicals: alkylphenols (AP), phthalates, bisphenol A (BPA), polybromodiphenylethers, and natural and synthetic estrogens (Crini, 2007).

Alkylphenol ethoxylates (APEs) are one of the most widely used classes of nonionic surfactants and are being used in the formulations of cleaning products, paints, ink dispersants, textile and leather processing (preparation, dyeing and finishing), pulp and paper manufacturing, metal processing, cosmetics and personal care products. Octylphenol ethoxylates (OPEs) and nonylphenol ethoxylates (NPEs) are two of the most common APEs in the marketplace (Ying et al. 2002). The worldwide production of APEs was estimated around 80% of NPEs and 20% of OPEs (Renner, 1997).

APEs are discharged to wastewater treatment facilities or directly released into the environment. Many studies have reported on the wide occurrence of APE metabolites in the environment. Primary degradation of APEs in wastewater treatment plants or in the environment generates more persistent shorter chain APEs and alkylphenols (APs) such as nonylphenol (NP), octylphenol (OP) and AP mono- to triethoxylates (NPE1, NPE2 and NPE3) (Giger et al. 1984).

As a consequence of the use, discharge and biodegradation of APEs, NP and OP occur ubiquitously in the environment. For instance, NPEs and also OPEs are unstable in the environment and both undergo the same processes of degradation to yield metabolites that are generally more stable and thus more persistent. From the ecotoxicological point of view, NP is persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (Soto et al. 1991; Comber et al. 1993; Baldwin, 1997; Severin et al. 2003; David et al. 2009; Lozano et al. 2012).

Humans are largely exposed to APs by the intake of contaminated foods and drinking water. Both NP and OP have been detected in different foods (Guenther and Heinke, 2002; Yang and Ding, 2005; Lu et al. 2007).

Studies have showed that APEs metabolites are more toxic than the parent substances and possess the ability to mimic natural hormones by interacting with the estrogen receptor (Soto et al. 1991; Jobling and Sumpter, 1993; Jobling et al. 1996; Renner, 1997).

OPEs are extensively biodegraded in laboratory screening tests, but do not meet the stringent criteria for classification as readily biodegradable (Klecka et al. 2008) and biodegradability values of 0-20% have been quoted based on oxygen uptake and 0-9% based on spectroscopic techniques (Swisher, 1987; Scott and Jones, 2000). APE (and its derivatives) are not anaerobically degradable during sludge treatment (Scott and Jones, 2000). Their resistance to biodegradation at low temperatures and the generation during the degradation process of some persistent metabolites which are much more toxic than the original compound (Maguire, 1999), the use of NPEs has been banned in domestic formulations in some countries of the European Union such as Germany, Spain, and the United Kingdom, (European Commission (EC) 2003) as well as Switzerland and Canada (Soares et al. 2006).

Physical and chemical processes such as filtration, oxidation and advanced oxidation have been commonly used for the removal of endocrine disrupting contaminants from wastewater (Soares et al. 2008). Removal of APEs by filtration, membrane bioreactors, ozone, electrochemical processes and advanced oxidation techniques is reported in the literature (Perkowski and Mayer, 2005; Arslan-Alaton and Erdinc, 2006; De La Fuente et al. 2010; Olmez-Hanci et al. 2011; Nagarnaik and Boulanger, 2011; Olmez-Hanci et al. 2014).

Being widely recognized as highly efficient for the treatment of industrial chemicals, advanced oxidation processes (AOPs) are destruction technologies alternative to conventional treatment methods. These methods are based on the formation of free radicals ($HO^{\bullet}$ and $SO_4^{\bullet-}$) which are capable of degrading even the most recalcitrant molecules within a reasonable time span. AOPs that usually involve ultraviolet irradiation, ozone, hydrogen peroxide (HP), persulfate (PS) and peroxymonosulfate (PMS) to generate hydroxyl ($HO^{\bullet}$) and sulfate ($SO_4^{\bullet-}$) radicals are commonly used to

destroy organic contaminants in various types of water (Kolthoff et al. 1951; Liang et al. 2004; Litter, 2005; Rastogi et al. 2009). More recently, the application of AOPs based on sulfate radicals ($SO_4^{\bullet-}$) due to its high efficiency in the degradation and mineralization of recalcitrant and/or toxic organic pollutants has been the subject of recent interest (Zhao et al. 2010a; Lin et al. 2011; Saien et al. 2011; Olmez-Hanci et al. 2013; Sharma et al. 2015; Sharma et al. 2016).

Several treatability studies have already demonstrated that $HO^{\bullet-}$ and $SO_4^{\bullet-}$ -based AOPs are more promising options for the efficient degradation and mineralization of APE's found in water and wastewater (De La Fuente et al. 2010; Antoniou et al. 2010; Olmez-Hanci et al. 2011; Ghauch et al. 2013; Olmez-Hanci et al. 2014; Karci, 2014).

In recent years, innovative AOPs using zero-valent metal, such as zero-valent iron (ZVI) and zero-valent aluminum (ZVAl) to generate reactive oxygen species (ROS) to degrade and even mineralize refractory organic pollutants have received increasing interest (Bokare and Choi, 2009; XR and XZ, 2010; Kusic et al. 2011; Lin et al. 2013; Fu et al. 2014).

In the absence of oxidants, the zero-valent metal/H^+/O_2 oxidation systems are relatively slow and inefficient processes (Joo et al. 2005; Zhao et al. 2010; Temiz et al. 2015). External addition of oxidants is expected to substantially improve the degradation rates (Bokare and Choi, 2009; Temiz et al. 2015).

Prior to selection of the most appropriate AOP, it should be considered that the efficiency and performance of these processes may change dramatically when they are applied to real water and wastewater matrices that contain significant amounts of organic as well as inorganic substances, besides the target pollutant. Consequently, it is important to test the selected AOP under real treatment conditions, namely in the natural environment of the pollutant under investigation.

It should be kept in mind that during the application of AOPs, there is always the risk of producing degradation intermediates that could potentially be more toxic than the original/parent pollutant (Munter, 2001; Arslan-Alaton and Olmez-Hanci, 2011; Marugán et al. 2012). Consequently, toxicity tests serve as integral tools to decide whether a treatment process is ecotoxicologically safe or not.

1.1 Aim and Motivation of the Study

Considering the above mentioned issues, the aim and motivation of the present experimental study was the treatment of a commercially important octylphenol polyethoxylate type nonionic surfactant namely Triton™ X-45 (TX-45) solutions by HP, PS and PMS as well as their combinations with nanoscale ZVAl-mediated heterogeneous treatment systems under acidic pH (=3). The present M.Sc. thesis is thought to be the first of its kind, dealing with the degradation of a nonionic, octylphenol polyethoxylate surfactant with the nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment combinations. A series of oxidation experiments were conducted in distilled water (DW), raw surface water (SW), tap water (TW) and domestic wastewater treatment plant effluent (WW) spiked with TX-45 in order to examine the treatability of TX-45 in real water/wastewater matrices. The effectiveness of the investigated processes was examined in terms of TX-45 and TOC removals as well as oxidant consumption rates. In the final part of the study changes in acute toxicity and genotoxic activity during application of the optimized treatment systems were evaluated by employing *Vibrio fischeri* (*V. fischeri*) and *Pseudokirchneriella subcapitata* (*P. subcapitata*) bioassays and the Umu-Chromo test, respectively.

1.2 Scope of the Study

Within the scope of the experimental study, the most suitable values of process parameters for nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment combinations was firstly determined on the basis of TX-45 and TOC removal rates and efficiencies. For this purpose, experiments were carried out with aqueous 2 mg/L of TX-45 solutions under varying treatment conditions at a fixed reaction duration of 120 min. For these experiments, the application ranges were as follows; TX-45= 2 mg/L; H_2O_2= 0.25 and 0.50 mM; PS= 0.25 and 0.50 mM; PMS= 0.25 and 0.50 mM; nZVAl= 1 g/L; pH= 3; and T= 25ºC. The effects of process parameters on treatment efficiency was evaluated on the basis of TX-45 and TOC removals. At the same time, H_2O_2, PS and PMS consumption rates were compared under different process conditions in distilled water (DW).

After these experimental studies, an experimental set was conducted for 120 min in the presence of 0.50 mM PS, 0.25 mM H_2O_2, 0.25 mM PMS and 1 g/L nZVAl at pH=3 and T= 25˚C by dissolving 2 mg/L of TX-45 in water matrix (raw surface water (SW), tap water (TW) and domestic wastewater treatment plant effluent (WW)), also in order to evaluate the acute toxicity of TX-45 and its intermediate products by using the *Vibrio fischeri* (*V. fischeri*) and *Pseudokirchneriella subcapitata* (*P. subcapitata*) as the test organism, 0.50 mM PS and 1 g/L nZVAl at pH=3 and T= 25˚C experimental set was selected in distilled water (DW) and raw surface water (SW). The set condition which was selected for acute toxicity evaluation also was used for genotoxicity test in distilled water (DW).

2. THEORETICAL BACKGROUND

2.1 Alkylphenol Ethoxylates (APEs)

Alkylphenol ethoxylates (APEs) are non-ionic surfactants, consisting of a branched-chain alkylphenol which has been reacted with ethylene oxide, producing an ethoxylate chain and the most important members of APEs are ethoxylates of nonylphenol (NP) and octylphenol (OP) **(Figure 2.1).** Alkylphenol (AP) is fairly nonpolar portion of APE molecule which allows to dissolve grease and other materials that have small water solubility, and the ethoxylate (EO) is water-soluble portion of the surfactant and aids in the transfer of material to the aqueous phase. This structure makes most of polar APEs soluble in water and helps disperse dirt and grease from soiled surfaces into water (Snyder et al. 2001).

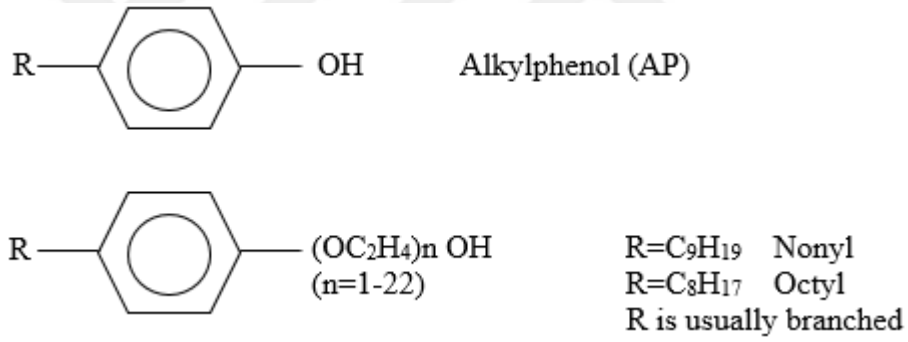


Figure 2.1: Chemical structures of APEs.

2.1.1 History of alkylphenol ethoxylates

APEs widely used as raw material to formulate products such as detergents, paints, cleaning products ($AP_{10-12}EOs$), dispersing agents, wetting products ($AP_{8-9}EOs$), pesticides ($AP_{n>15}EOs$), and petroleum recovery chemicals in the household, industry and agriculture and **Figure 2.2** shows the percentage of APEs which used in marketplace (Månsson et al. 2008; Arslan-Alaton and Olmez-Hanci, 2012).

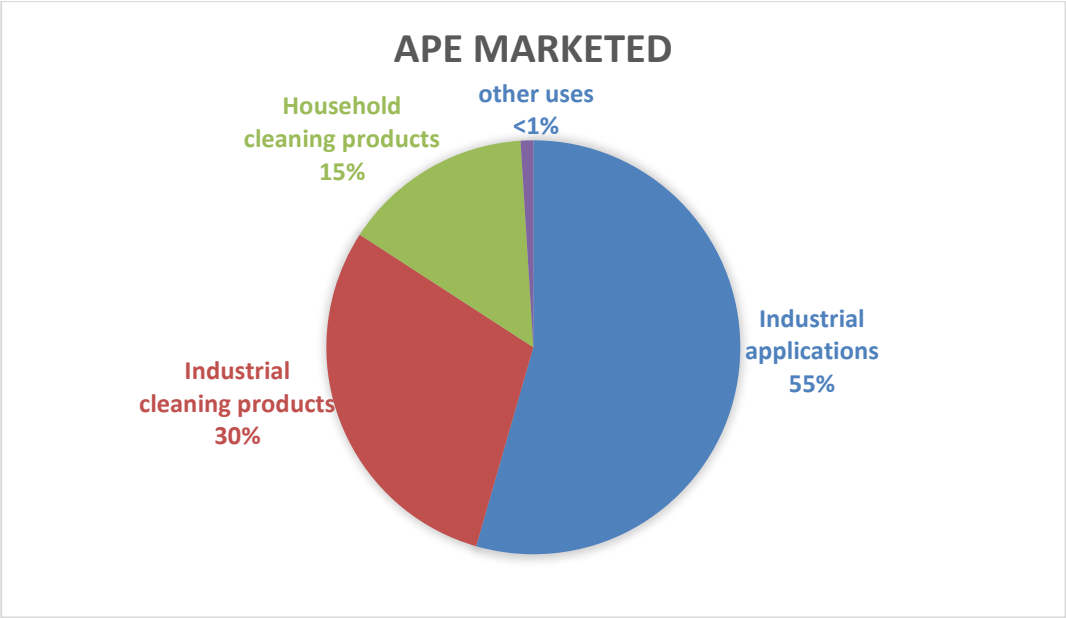


Figure 2.2: Distribution of APEs in the marketplaces. (Kovarova et al. 2013)

Worldwide, about 500,000 tons of APEs are produced annually and 60% of which ends up in the aquatic environment (Renner, 1997; Sole et al. 2000). it makes APEs the world's third largest group of surfactants in terms of production and use (Ying et al. 2002).

In 2012, the total amount of surfactants (not including soaps) consumed in Europe was 2.92 Mt and around %48 (1.397 Mt) of them were non-ionic, according to statistics published by the European Committee of Surfactants and their Organic Intermediates (CESIO) (2012).

Restrictions on the use of APE have arisen since the discovery in 1984 that their breakdown products are more toxic to aquatic organisms than the APE themselves. Biodegradation of APE leads to the shortening of the ethoxylate chains to alkyl phenol carboxylates leading ultimately to NP and OP, which have low water solubility and adsorb to suspended solids and sediments (Scott and Jones, 2000).

In 1987, reacting to EPAs interest in APEs, the Chemical Manufacturers Association (CMA) formed the Alkylphenol and Ethoxylates Panel to conduct research on APEs. Armed with data about the toxicity and fate of APEs, the panel has been fighting European regulatory trends that have reduced APE sales.

APEs "have been demonized in Europe," according to Carter Naylor, a member of the panel and a chemist with APE manufacturer Huntsman Corporation, Salt Lake City, Utah (Renner, 1997), APE are still being used because of their excellent performances and low production costs for many industrial applications (Jonkers, 2001). However, using of APEs- based chemicals were stopped in household applications of a lot of companies even voluntarily (Karahan et al. 2010).

Concentrations of ΣAPE metabolites in treated wastewater effluents, for example in the US, ranged from < 0.1 to 369 µg/L (Rudel et al. 1998), in Spain they were between 6 and 343 µg/L (Sole et al. 2000) and concentrations up to 330 µg/L were found in the UK (Blackburn and Waldock, 1995).

According to Environmental Quality Standards (EQS) annual average concentration, for NP and OP in water surface were proposed to 0.3 µg/L and 0.1 µg/L, respectively (European Commission, 2006). In USA, the Environmental Protection Agency (EPA) detected the NP concentration should not exceed 6.6 µg/L in freshwater and 1.7 µg/L in saltwater (Brooke, 2005).

2.1.2 Toxicity of APEs

In the literature, Giger et al. (1984) from Switzerland were found that nonylphenol ethoxylates and products of degradation were more toxic to aquatic life than their precursors. These substances are also recognized as endocrine disrupters and have more endocrine activity than their parent products by Berryman et al. (2004) works. Subsequently other studies demonstrated that the toxicity of APEs is increased with decreasing ethoxylate chain length (Staples et al. 2004; Barber et al. 2007).

Soto et al. (1991) observed inadvertently that nonylphenol was capable of inducing breast tumour cell proliferation. Nonylphenol was found to mimic the natural hormone 17β-estradiol by competing for the binding site of the receptor for the natural estrogens (White et al. 1994; Lee and Lee, 1996).

APs are not estrogenic; however, upon degradation during sewage treatment they may release estrogenic alkylphenols and mimic to effect of the hormone estrogens (Sonnenschein and Soto, 1998). According to Kovarova et al. (2013), APEs have endocrine disruption activity, hepatotoxic, genotoxic and other negative effects on animal and human health, Also NPs in wastewater extracted from digested sewage sludge can pass into rivers. It has been hypothesized that endocrine disruptors may be responsible for a decreasing male sperm count, testicular and breast cancers (Scott and Jones, 2000).

2.1.3 Environmental fate of APEs

APEs and their degradation products (e.g., NP and OP) are not produced naturally and the source of them are usually anthropogenic activities (Kovarova et al. 2013). APs and APEs enter the environment primarily via industrial and municipal wastewater treatment plant effluents (liquid and sludge), landfill leachates but also due to direct discharge such as through pesticide application. The reviews of Soares et al. (2008), Ying et al. (2002) and Ying (2006) noted that waste discharges from sewage treatment plants (STW) and industries are the main sources of APs and APEs found in aquatic environments.

APEs as common environmental contaminants found in surface water (Scullion et al. 1996; Ying et al. 2002), groundwater (Zoller, 1990; Soares et al. 2008), wastewater (Ying, 2006; Månsson et al. 2008; Petrovi‘c and Barceló 2010) and air (Dachs et al. 1999). Following their release in to the environment, degradation and sorption are two ways which strongly impacted these substances behavior and fate (Ying et al. 2002).

Lower APEs oligomers (EO < 5) are usually water-insoluble or lipophilic and higher oligomers are described as water-soluble and hydrophilic (Ahel and Giger, 1993). Because of low partition coefficient (log K_{ow} for APEs metabolites between 3.90 and 4.48) of them, they able to attach with organic matter and adsorb onto sediment and soil (Ying et al. 2002).

APEs are readily biodegraded under both aerobic and anaerobic conditions in the environment including microbial degradation (Paasivirta and Rantio, 1991) and it has been demonstrated that finally APEs, in sewage sludge or the natural environment, can

breakdown to shorter-chain APEs and losing most of EO (ethoxy) groups to form short-chain APEs (1–2 EO units), alkylphenoxy carboxylic acid, and APs (Maguire 1999). Ahel (1994) examined NPEs with (EO > 8) are readily degraded, usually with >92% efficiency. Previous investigations showed that APOs metabolites degraded more easily under aerobic, than under anaerobic conditions (Brunner et al. 1988; Ying et al. 2002).

2.2 Advanced Oxidation Process

Advanced Oxidation Processes (AOPs) have received increasing attention in the research and development of wastewater treatment technologies in the last decades. These processes can be applied for the removal or degradation of toxic pollutants and mineralization of many organics from industrial and municipal wastewater including resistant organics (pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals) (Arslan-Alaton and Olmez-Hanci, 2012; Wang and Xu, 2011; Stasinakis, 2008; Munter, 2001) also used as pretreatment to convert recalcitrant pollutants into biodegradable compounds that can then be treated by conventional biological methods (Stasinakis, 2008; Vincenzo Naddeo, 2013).

2.2.1 Definition and general principles

AOPs are based on the generation of very reactive species free radicals. Between various free radicals like superoxide radical ($O_2^{\bullet-}$), hydroperoxyl radical ($HO_2^{\bullet}$), hydroxyl radical ($HO^{\bullet}$), peroxyl radical ($ROO^{\bullet}$), sulfate radical ($SO_4^{\bullet-}$) and alkoxyl radical ($RO^{\bullet}$), hydroxyl and sulfate radicals have a key role and more promising options for the efficient degradation and mineralization of organic pollutants found in water and wastewater (De La Fuente et al. 2010; Olmez-Hanci et al. 2014).

Table 2.1 summarizes some oxidizing species and their relative oxidation power as well as oxidation potential. As can be seen from **Table 2.1**, HO• and $SO_4^{\bullet-}$ are two powerful, and hence non-selective oxidizing agents (Yang and Zhao, 2015; Trapido, 2008; Carey, 1992).

Table 2.1: Relative oxidation power and oxidation potential of some oxidizing species.

Oxidizing Species	Oxidation Potential (eVolts)	Relative Oxidation Power (Chlorine as reference)
Hydroxyl Radical ($HO^{\bullet}$)	2.80	2.05
Sulfate Radical ($SO_4^{\bullet -}$)	2.60	1.88
Ozon (O_3)	2.00	1.52
Persulfate ($S_2O_8^{2-}$)	2.01	1.46
Hydrogen Peroxide (H_2O_2)	1.77	1.30
Perhydroxyl Radical ($HOO^{\bullet}$)	1.70	1.25
Permanganate (MnO^{4-})	1.69	1.24
Chlorine (Cl_2)	1.38	1.00
Oxygen	1.20	0.90

2.2.2 Major AOPs types

Free radicals in AOPs, may be produced by photochemically and non-photochemically. **Table 2.2** lists some of the most frequently reported AOPs for application in water and wastewater treatment. Most of them use a combination of strong oxidizing agents (e.g , hydrogen peroxide and ozone) with catalysts (e.g. transition metal ions, zero-valent metal) and irradiation (e.g. ultraviolet, visible). According to (Stasinakis, 2008) among different available AOPs producing hydroxyl radicals, TiO_2/UV light process, H_2O_2/UV light process and Fenton's reactions seem to be some of the most popular technologies for wastewater treatment.

Table 2.2: Classification of most established AOPs

Photochemical AOPs	Non-photochemical AOPs
H_2O_2/UV, H_2O_2/Fe^{2+}/UV	Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, AL_0/ H_2O_2
$S_2O_8^{2-}$/UV	$Fe^{2+}/S_2O_8^{2-}$, AL_0/ $S_2O_8^{2-}$
O_3/UV, H_2O_2/O_3/UV	TiO_2/O_3, H_2O_2/O_3, H_2O_2/O_3/ TiO_2
TiO_2/UV, H_2O_2/TiO_2/UV	Ozonation at high pH
	Wet air oxidation (WAO)
	Sonolysis
	Supercritical water oxidation (SCWO)
	Electrochemical oxidation

2.2.3 Advantage and disadvantage of AOPs

Gabardo Filho (2005) and Domenech et al. (2001) listed number of advantages of AOPs when compared to conventional oxidation processes.

- Able to assimilate large variety of organic compounds;
- Full Mineralization of pollutants;
- Employed in the destruction of refractory compounds resistant to other treatments, such as the biologic;
- Can be integrated with other processes such as pre or post treatment;
- Used in high toxicity wastewater that can cause some difficulty in the treatment of biological process;
- Allow in situ treatment;
- Develop byproducts reaction intermediates that submitted to a post treatment may be mineralized;
- Improve organoleptic properties of treated water;
- Present high power with high oxidizing reaction kinetics.

But AOPs can be applied to certain types of waste under some restrictions, as follows (Domenèch et al. 2001; Kommineni et al. 2008).

- Some processes are not available at appropriate scales.

- Costs can be high due to energy consumption.
- Some types do not apply to wastewater with high organic capability, turbidity, optical or color.
- Potential for accumulation of oxidation by-products.
- Potencial for bromate formation.
- Radical scavenging by interfering compounds can reduce effectivnece of AOPs.

Also Kommineni et al. (2008) briefly describe advantage and disadvantage of some known AOPs types:

Table 2.3: Advantage and disadvantage of some AOPs types

AOP types	Advantages	Disadvantages
H_2O_2/O_3	More effective for waters with high Methyl tert-butyl ether (MTBE) amount	Potential for bromate formation
	More effective than O_3 or H_2O_2 alone	Need to treatment more H_2O_2 because of potential of microbial growth
	Complementary disinfection	
	Used for remediation applications	Need to treatment ozone off-gas
O_3/UV	More efficiency in compare with H_2O_2/UV process in same oxidant concentration	Interference of turbidity with UV lights
		Potential for bromate formation
	More effective than O_3 or UV alone.	High cost and energy required
		Need to treatment ozone off-gas
		Competition of compounds in UV lights adsorption
	Complementary disinfection	In pre-post chlorination potential for formation disinfection by products

Table 2.3 (continued): Advantage and disadvantage of some AOPs types

H_2O_2/UV	No potential for bromate formation	Interference of turbidity with UV lights
	No need to treatment ozone off-gas	Less stoichiometrically efficient in the formation of $HO^{\bullet}$ than O_3/UV process
	More efficiency for oxidize MTBE (>95%)	Competition of compounds in UV lights adsorption
	Not limited by mass transfer compared to O_3 processes	In pre-post chlorination potential for formation disinfection by products
TiO_2 Catalyzed/ UV	No potential for bromate formation	Pre-treatment need for elude TiO_2 sedimentation
		No full scale application exist
	In compare with other UV process can performed in high wavelength	Separation need if TiO_2 added as a slurry
		Necessity of oxygen sparging
		Reaction efficiency is highly pH-dependent, requiring close observing and control
	No need to treatment ozone off-gas	Potential for rapid loss of TiO_2 effectiveness, necessity of catalyst on-site storage or regeneration method
Fenton's reaction	No potential for bromate formation	Very low pH (<2.5) is required to keep the iron in solution
	No need to treatment ozone off-gas	No full scale application exist
	Low energy need in compare with O_3 or UV process	Need iron exploitation system

2.2.4 ZVAl/Oxidant system

Using of ZVI is solely beneficial due to its abundance, low toxicity and low cost also generating strongly oxidizing hydroxyl radicals in reaction ZVI+O_2 via the Fenton reaction (Joo et al. 2004; Joo et al. 2005; Kang and Choi, 2009). However, corrosion of ZVI in exciting oxygen cause; a) enhancing the pH value due to the generation of hydroxide ions and as a result the overall oxidative capacity decrease because ZVI-mediated H_2O_2 formation and the following Fenton reaction is effective only at acidic pH (pH<3) also, b) iron hydroxide precipitate and the accumulation of hydroxide precipitates on the metal surface leads to surface passivation and loss of metal reactivity (Bokare and Choi, 2009).

Similar to ZVI, ZVAl exhibits a capacity to degrade organic pollutants under acidic conditions. In the presence of O_2, ZVAl/O_2/H^+ showed higher oxidation capacity compared to ZVI/O_2/H^+ due to the higher stability of aqua-complexed Al^{3+} over a wider pH range (Bokare and Choi, 2009). The choice of alternative zero-valent metals with higher capacity to produce reactive oxygen species (ROS) depends on the rate of electron transfer to O_2 or externally added oxidants (ie. hydrogen peroxide, HP; persulfate, PS; peroxymonosulfate, PMS). For instance, ZVAl can provide a greater thermodynamic driving force for electron transfer as compared with ZVI due to its higher reduction potential (-1.67 V, Al^{3+}/Al; -0.44 V Fe^{2+}/Fe).

2.2.5 ZVAl/Oxidant mechanisms

The commercially available ZVAl powders normally contain an aluminum oxide (Al_2O_3) layer on the surface for protect the inside of the ZVAl from oxidized and inhibit the activation of dioxygen to ROS. The ZVAl/H^+/O_2 oxidation system involves two major processes, the (i) corrosive dissolution of Al^{3+} and simultaneous reduction of O_2 to hydroperoxyl radical(s), $HO_2^{\bullet}$, that leads the formation of HP and (ii) generation of $HO^{\bullet}$ by an electron transfer mechanism from ZVAl to HP;

$$Al^0 \rightarrow Al^{3+} + 3e^- \tag{2.1}$$

$$O_2 + H^+ + e^- \rightarrow HO_2^{\bullet} \tag{2.2}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{2.3}$$

$$Al^0 + 3H_2O_2 \rightarrow Al^{3+} + 3HO^{\bullet} + 3OH^- \tag{2.4}$$

Both ZVAl-induced HP production **(Eqns. 2.1-2.3)** and the generation of $HO^{\bullet}$ **(Eqn. 2.4)** are highly favored under acidic pH conditions (pH 2-4) due to the enhanced corrosion of ZVAl (Cheng et al. 2015; Liu et al. 2011; Bokare and Choi, 2009). However, ZVAl corrosion is accompanied by an increase in solution pH **(Eqns. 2.2 and 2.4)** as a consequence of hydroxide ion generation and $Al(OH)_3$ precipitation.

In the absence of oxidants, the zero-valent metal/O_2/ H^+ oxidation systems are relatively slow and inefficient (Temiz et al. 2015; Zhao et al. 2010; Joo et al. 2005). The addition of oxidants is expected to substantially improve the degradation rates (Bokare and Choi, 2009; Cheng et al. 2015; Temiz et al. 2015). The mechanism of enhanced $HO^{\bullet}$ and $SO_4^{\bullet-}$ formation in the presence of the oxidants HP (**Eqn. 2.4)**, PS **(Eqn. 2.5)** and PMS **(Eqn. 2.6)** starts with the direct electron transfer from the Al^0 surface to the oxidants under acidic pH conditions;

$$2Al^0 + S_2O_8^{2-} + 6H^+ + 1.5O_2 \rightarrow 2Al^{3+} + 2SO_4^{\bullet-} + 3H_2O \ \textit{(tentative)} \tag{2.5}$$

$$Al^0 + 3HSO_5^- + 3H^+ \rightarrow Al^{3+} + 3SO_4^{\bullet-} + 3H_2O \ \textit{(tentative)} \tag{2.6}$$

Figure 2.3 showed the schematically of ZVAl/Oxidant mechanism which occurs during this process.

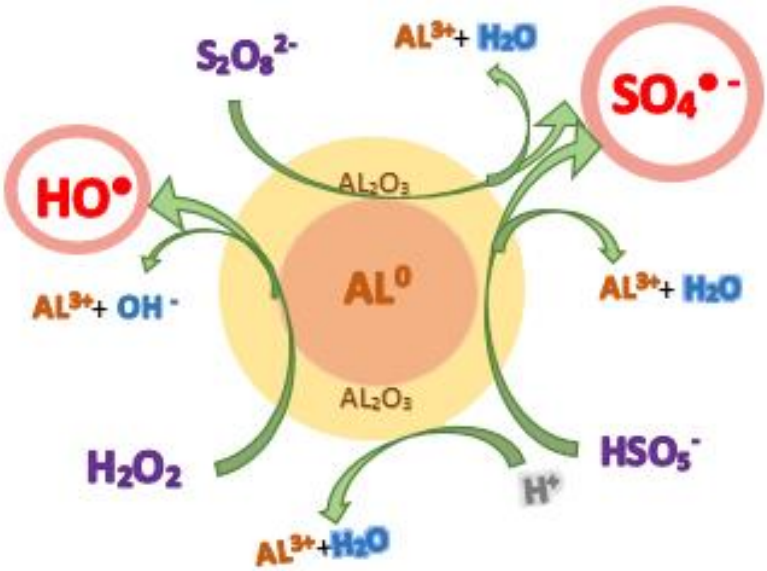


Figure 2.3: ZVAl/Oxidant mechanisms during process.

Fundamentally, the procedure of ZVAl/Oxidant requires; adjusting the pH (2.5-3.5), adding the zero valent aluminum catalyst (as a nanoparticle), adding the oxidant (e.g. H_2O_2, PS and PMS) and after that oxidization reactions, adjusting pH (6.5-7.5) and precipitation to remove Al ions as $Al(OH)_3$ after the reactions.

2.2.6 Some of AOPs application

Since AOPs were first defined in 1987, the field has witnessed a rapid development both in theory and in application. However, there are still many research needs on these existing AOPs. Recent trends are the development of new, modified AOPs that are efficient and economical. Some of AOPs are explained below, mainly remarked process with hydrogen peroxide (HP), persulfate (PS) and peroxymonosulfate (PMS) as an oxidant and zero valent aluminum (ZVAl) as a catalysis. There are lots of studies according to using HP, PS and PMS as an oxidant but ZVAl was established in recent years as a catalysis and is novel method in combined with oxidant, so there are limited source of scientific literature on ZVAl/Oxidant treatment system.

Removal of phenol by acid-washed ZVAl (AW-ZVAl) in the presence of HP was evaluated by Cheng et al. (2015). Experimental results showed that under pH of 2.5-3.5, AW-ZVAl demonstrated an excellent capacity to remove phenol. In the presence of 4.0 mM HP, the phenol concentration decreased from initial 20.0 mg/L to 0.3 mg/L

by 6.0 g/L AW-ZVAl in 3h at initial pH 2.7. The addition of HP into AW-ZVAl/Air/H^+ system facilitated the reaction due to the enhancement of $HO^{\bullet}$ generation (Cheng et al. 2015). Additionally, Lin and Lin (2016) conducted experiments with AW-ZVAl system focusing on the treatment of water contaminated with bromate. In this study, ZVAl is used as the first time to remove bromate from water. As a conclusion, ZVAl could completely remove bromate present in water (*i.e.*, 78.1 μmol/L) at 60 °C and pH = 3, while it became ineffective for removing bromate under alkaline conditions.

In the study of Temiz et al. (2015), 20 mg/L aqueous TX-45 in solution with 14 mg/L TOC, degraded within short treatment periods (<60 min) accompanied with significant (>40%) TOC removals during ZVI/PS types of AOPs.

Girit et al. (2015) compared treatment efficiency of zero valent iron (ZVI)/HP and ZVI/PS for the removal of BPA and TOC of the solution. In their study complete BPA removal and around 80% TOC degradation were achieved in ZVI/PS system, whereas 16% BPA reduced in only mere PS system (all systems performed in 50 C). About ZVI/HP system BPA totally degraded after 40 min in 25 °C and poor TOC reduction was obtained during this process.

Olmez-Hanci et al. (2014) examined degradation of TX-45 by PS/UV-C, HP/UV-C and only UV-C process and results showed that application of PS/UV-C and HP/UV-C treatment appeared to be successful in the degradation of a TX-45. It could be demonstrated that surfactant abatement was rapid and complete under all studied reaction conditions, whereas a minimum, threshold initial oxidant concentration of at least 2.5mM was required for remarkable (>80%) TOC removals.

Sánchez-Polo et al. (2013) compared the treatment efficiency of (UV, UV/H_2O_2, UV/$K_2S_2O_8$, and UV/Na_2CO_3) to remove bisphenol A (BPA) from aqueous solution. Results demonstrated that the UV/$K_2S_2O_8$ system was more effective than UV/H_2O_2 to degrade BPA, achieving a higher percentage removal in a shorter time due to the generation of $SO_4^{\bullet-}$ and $HO^{\bullet}$ radicals and the lowest diminution were obtained in UV/Na_2CO_3.

Liu et al. (2011) reported application of zero valent aluminum-acid system to the treatment of BPA. According to results under pH <3.5 acidic conditions, ZVAl

demonstrated an excellent capacity to remove more than 75% BPA. (experimental conditions: pH =1.5, reaction solutions initially containing 4.0 g/L aluminum and 2.0 mg/L BPA at 25 ± 1 °C within 12h).

TiO_2/UV, H_2O_2/UV and $S_2O_8^{2-}$/UV were employed and compared for removal of TX-100 by Saien et al. (2011). It was concluded that the effectiveness of each AOP as follows: $S_2O_8^{2-}$/UV (98.5% in 30 min)> H_2O_2/UV (81% in 60 min)> TiO_2/UV (72% in 60 min).

Bokare and Choi (2009) investigated degradation of aqueous organic pollution (4-chlorophenol) under ZVAl/O_2 treatment system. It was concluded that >95% of 4-CP degradation was achieved in 10 h in air-equilibrated conditions. Also, they mentioned that higher oxidation efficiency of ZVAl/ O_2 was obtained compared to ZVI/O_2 system, which is discussed in terms of pH dependent metal ion solubility and precipitation characteristics.

2.3 Toxicity Test

One of the very significant subjects in environmental pollution monitoring is toxicity measurement of wastewater, sediments, and contaminated water bodies. The exposure of living organisms to toxic levels of pollutants can cause disease to human and animals. Toxic chemicals can change the rates of natural biological processes and in the long-term cause to inhibition of growth, reproduction, and migration of species. Thus, the monitoring and detection of toxic chemicals is very important for the overall safety and security of humans and all biota on earth (Hassan et al. 2016).

2.3.1 Necessity of toxicity test

Generally, pollution monitoring and evaluation of effluent quality can measure with some parameters like pH, DO, COD, BOD, TOC, TDS and TSS, but these parameters only indicate the nature of the pollutants and are limited in terms of information about the biological effects. Estimate of biological effects using a rapid, simple, sensitive and cost effective method can demonstrate specific information on toxicity and ecotoxicity. Prevalent, plants, animals, algae, fish and invertebrates maybe used for aquatic toxicity measurement.

The tests based on these organisms require large exposure time and sample volume. Therefore, toxicity measurements based on microorganisms are gaining popularity due to short doubling time, high sensitivity and simplicity (Parvez et al. 2006; Movahedian et al. 2005). Foundation of bioassays is the response of organisms exposed to contaminants relative to a control and used for determine the toxicity level of specific pollution and complex aqueous matrices like surface water, groundwater and wastewater for aquatic organisms (Rizzo, 2011).

2.3.2 Biotox luminescent bacteria test with pohotobacteria *Vibrio fischeri*

Vibrio fischeri also known formerly as *Photobacterium phosphoreum* is one of the luminescent microorganisms and bioluminescence inhibition assays has been widely used for acute toxicity estimation and several commercial test kits. Microtox, LUMIStox, and ToxAlert are based on this strain (Ren, 2004). Amount of light emitted by these bacteria being an indicator of metabolism. Therefore, a water toxicity parameter can be measured as a reduction of light emission caused by the presence of hazardous component(s) in the sample (Zadorozhnaya et al. 2015). It has been standardized (ISO, 1998) and it is commercially available in different versions as well.

Table 2.4: Advantage and disadvantage of using biotox (Zadorozhnaya et al. 2015).

Advantage	Disadvantage
• Rather simple • Based on very few elements • No need for preculturing of test biota • Long term stability of the culture • Elimination of maintenance cost • Express method in comparison with other bioassays • Screening tool for a wide range of ecotoxicological problems	• Complexity of bringing the lyophilized bacteria in working conditions • Range of dangerous substances and degree of their toxicity that can vary for different biotests and human beings

2.3.3 Algal growth inhibition test with green microalgae *Pseudokirchneriella subcapitata* (*Selenastrum Capricornutum*)

Algal biossays are often used in toxicity testing because of their ecological importance and sensitivity to many substances, especially herbicides and metals. Green microalgae are kept in static conditions in the vessels, which contain control nutrient medium and nutrient medium, which the test material is added. Evaluation of endpoints using microalgae for acute and persistent tests includes esterase inhibition, ATP energy loss, growth inhibition, motility inhibition, and chlorophyll fluorescence (Hassan et al. 2016).

Many algal bioassays are used to assess the toxicity of organic pollutants, herbicides, oil dispersants, effluents, solid waste leachates, groundwater, and organic extracts (Kong et al. 1998; Radix et al. 2000; Pehlivanoglu and Sedlak, 2004; Hong et al. 2008; B. Liu et al. 2011; Hassan et al. 2016).

Table 2.5 monitors some advantage and disadvantage of toxicity test with algae group (Karci, 2014). In the following, **Table 2.6** shows two bioassays, which are used in this study with their method and some of their application in water matrices (Rizzo, 2011).

Table 2.5: Advantage and disadvantage of using algae in toxicity test.

Advantage	Disadvantage
• Short test duration when photosynthetic activity is effective • Standard method are available for this test	• The ecological relevance of laboratory-derived toxicity results for single species of cultured freshwater algae is not known for most chemicals. • The large interspecific variation in response observed for many chemicals and unrealistic experimental conditions in the standard toxicity test

Table 2.6: Bioassays method and application in different water matrices.

Bioassays Organisms	Bioassays Group	Method	Application	Reference
Vibrio fischeri	Microorganism	ISO, 2008	Disinfection of Hospital wastewater	(Emmanuel et al. 2004)
			Industrial wastewater treatment	(Tisler et al. 2004)
			Urban wastewater treatment	(Hernando et al. 2005)
Pseudo. subcapitata	Algae	ISO, 2012	Industrial wastewater treatment	(Walsh et al. 1980; Tisler et al. 2004; Oral et al. 2007)
			Urban wastewater treatment	(Hernando et al. 2005)

2.3.4 Application of acute toxicity test in APEs degradation methods

Farre et al. (2001) investigated toxicity properties of NPEO-R_9E_6 measuring with bioluminescence inhibition of *V. fischeri* , EC_{50}= 95 was estimated and these group known as a harmful substances according to the European Union Directive (European Economic Community (EEC), 1967; Farré et al. 2001).

Liwarska et al. (2005) studied acute toxicity of nonionic surfactant with *P. subcapitata* algae. Results demonstrated AE-$R_{11\text{-}13}E_{10}$ with EC_{50}= 6.87 belong to toxic or even to highly toxic substances and APE-R_8E_7 with EC_{50}= 24.90 classified as a harmful material.

Ledakowicz et al. (2005) evaluated ozonation impact on toxicity of nonionic surfactant by inhibition of *V. fischeri*. They reported toxicity of the tested Triton X-100 solution increased abruptly already at the beginning of the ozonation process from 68% to around 95%. A very long polyethoxylate chain reaching 70 mers on average characterizes the molecule of Triton X-705. Toxicity of the initial solutions of Tritons X-100 and X-705 was similar and the inhibition of bioluminescence was 60% for TX-705 but, with increasing length of polyethoxylate chain a distinct decrease in toxicity could be observed and reached to 90% at the end of the toxicity test.

Jurado et al. (2009) expressed the evolution of the toxicity over the biodegradation process as a percentage of inhibition of *V. fischeri*. For all the nonionic surfactants assayed, except for the nonylphenol polyethoxylate, a major decline was found in toxicity during the first days of the biodegradation assay and at all the concentrations tested.

Toxic effect on *V. fischeri* during nonylphenol polyethoxylate treatment in synthetic freshwater with H_2O_2/UV-C and Photo-Fenton process were investigated with Karci et al. (2014). Experimental results showed percentage of inhibition of *V. fischeri* initially increased from 10 (±0.16)% to 30 (±1.3)% and 19 (±5.0)% during H_2O_2/UV-C and Photo-Fenton treatments, respectively. However, the inhibitory effect decreased back to 10% for both processes at the end of treatment (Karci et al. 2014).

Recently investigation from Olmez-Hanci et al. (2015) demonstrated degradation and toxicity assessment of the nonionic surfactant Triton™ X-45 by the peroxymonosulfate/UV-C process. As a conclusion from their results, in the *V. fischeri* toxicity bioassay, a prompt increase in relative inhibition from 33% to 61% after 1 min was followed by a sharp decrease to 8% after 10 min in PMS/ UV-C treatment. Thereafter, the inhibitory effect slightly re-increased to 18% after 120 min treatment. Additionally, the bioassay performed with *P. subcapitata* appeared to be more sensitive to OPEO oxidation products among the examined toxicity tests.

2.3.5 Genotoxicity test

Undoubted, degenerative changes of the genetic apparatus cause to the formation of a variety of further diseases. Micro-scale toxicity tests based on the use of microorganisms provide the possibility for a first screening of suspicious samples. In addition these method should be sensitive and reliable to detect toxins and be ecologically friendly, economically cost and also producing as little waste as possible (Toolaram et al. 2012).

The umu-assay is a test system developed by Oda et al. (1985) and later modified by Whong et al. (1986). The umu test are colorimetric assays based on, the production of β-galactosidase (β-gal) as a response to DNA damage. The umuC-gene is essentially involved in bacterial mutagenesis via the so-called SOS-pathway (Little and Mount,

1982; Rajagopalan et al. 1992). The high correlation between the Umu Chromotest and traditional Ames test for mutagenicity supports it as a reasonable alternative for early-stage testing of the thousands of new pharmaceutical, agricultural and industrial chemicals synthesized every year. Most large chemical manufacturers have the ability to screen 100 or more synthetic chemicals per year with the traditional Ames test, which requires the use of several Salmonella strains. The umu test, using only a single Salmonella strain, could potentially test a greater range of new chemicals with the same resources. The reduction in material expense and labor, as well as its robustness also position it as a suitable screen for complex environmental samples (Yasunaga et al. 2004).

Karci et al. (2014) used umuC-test to determine genotoxicity of nonylphenol polyethoxylate (NP-10) after H_2O_2/UV-C and Photo-Fenton process. According to the umu-test results, in particular H_2O_2/UV-C oxidation of NP-10 resulted in the formation of weakly to moderately genotoxic degradation products with and without metabolic activation and the induction factors recorded during Photo-Fenton treatment were in general lower than those found during H_2O_2/UV-C treatment. However, the Photo-Fenton-treated reaction solution still exerted a weak genotoxic potential with and without metabolic activation at the end of the treatment period.

Cupi and Baun (2016) investigated the feasibility of high-throughput (96-well plate) umu assay to test the genotoxic effect of TiO_2 engineered nanoparticles (ENPs) under UV light (full spectrum) and visible light (455 nm). They obtained the employment of umu assay might not be sensitive enough to quantify the photo-genotoxicity of nanomaterials.

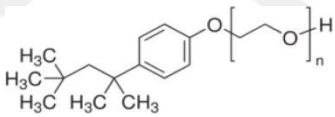
3. MATERIALS AND METHODS

3.1 Materials

OPPE (Triton™X-45, average ethoxylate chain length of 4.5) was purchased Sigma; (CAS 9002-93-1, USA with 427 molecular weight). Some of the chemical and physical properties of Triton X-45 are summarized in **Table 3.1**.

Triton X-45 ($C_{14}H_{22}O(C_2H_4O)_n$) is a nonionic surfactant that has a hydrophilic polyethylene oxide chain (on average it has 4.5~ 5 ethylene oxide units) and an aromatic hydrocarbon lipophilic or hydrophobic group.

Table 3.1: Physicochemical properties of Triton X-45.

Physicochemical Parameters	
IUPAC name	2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol
Molecular structure	
CAS No.	9002-93-1
Molecular formula	$(C_2H_4O)_{(\sim 5)}C_{14}H_{22}O$
Molecular weight	427 g/mol
Water solubility	Soluble
Appearance (Color)	Colorless to faint yellow
Appearance (Form)	Viscous liquid
Cloud Point	39.4 - 44.8 °C
Flash point	218°C 425°F
Density	1.031 g/mL at 25 ˚C
Viscosity	290 CP at 25 ˚C
Pour Point	26 °C

Commercial-grade nZVAl particles with a specific surface area of 10-20 m^2/g, a particle size of 100 nm and a purity of >99.9% were purchased from US Research Nanomaterials, Inc. (Houston, USA). Potassium persulfate (PS, $K_2S_2O_8$, >99.5%) and potassium peroxymonosulfate (PMS, $2KHSO_5 \cdot 3KHSO_4 \cdot 3K_2SO_4$ available as Oxone®, ≥99.5%) were purchased from Sigma-Aldrich, (USA), H_2O_2 (HP, 35%, w/w) from Merck (Germany). Aqueous TX-45 solutions were prepared in distilled water (Arium 61316RO, Sartorius AG, Germany). Ultrapure water for the chromatographic measurements was prepared with an Arium 611UV water purification system (Sartorius AG, Germany). All other reagents and solvents were of at least analytical grade and obtained from Merck (Germany), Fluka (USA) or Sigma-Aldrich (USA).

TX-45 removals were also followed in real effluent samples (SW, WW and TW). The SW used in the present work was taken from the influent of a local water treatment plant serving approximately 4.5 million people. The WW was the effluent of a local advanced domestic wastewater treatment plant practicing combined carbon, nitrogen and phosphorus removal. The SW and WW samples were transported to the laboratory in a cooler at 4°C and kept refrigerated until used. TW was also used as a real water sample for comparative purposes. The environmental characteristics of the different water and wastewater samples are presented in **Table 3.2.**

Table 3.2: Environmental characterization of water and wastewater samples.

Parameter	Unit	TW	SW	WW
pH	-	7.3	7.9	7.3
TX-45	(mg/L)	< 0.2	< 0.2	< 0.2
TOC	(mg/L)	5.5	7.6	10.4
DOC	(mg/L)	5.0	7.2	9.9
Alkalinity	(mg $CaCO_3$/L)	78	115	176
Hardness	(mg $CaCO_3$/L)	135	110	113
Colour	(Pt-Co)	1	48	40
COD	(mg O_2/L)	nd[1]	nd[1]	<30
Total Kjeldahl Nitrogen	(mg N/L)	nd[1]	nd[1]	5.3
Total Phosphorus	(mg P/L)	nd[1]	nd[1]	1.2
Suspended Solids	(mg/L)	<10	12	14
A254	(cm^{-1})	0.031	0.043	0.202
A280	(cm^{-1})	0.025	0.119	0.154
A350	(cm^{-1})	0.040	0.039	0.051
Cl^-	(mg/L)	40	21	120
Nitrite	(mg N/L)	<0.07	<0.07	0.38
Nitrate	(mg N/L)	2.7	2.2	18.8
Sulfate	(mg/L)	71	16	119
Phosphate	(mg P/L)	<0.1	0.17	3.21
Fluoride	(mg/L)	0.06	0.08	0.13

[1]nd: not determined

3.2 Experimental Procedure

Aqueous TX-45 solutions were treated in a 500 mL-capacity borosilicate glass reactor at room temperature (25±2 °C) at a fixed TX-45 concentration of 2 mg/L (4.7 µM). Although this TX-45 concentration is relatively high compared to environmentally relevant concentrations being mostly reported in the (European commission 2003), it was decided to work at this concentration to ensure accurate kinetic, toxicological and analytical assessment of TX-45. HP, PS and PMS oxidation (in the absence of nZVAl) of TX-45 was examined at pH 3 for 120 min. Thereafter, the more conventional nZVAl/O_2/H^+ (in the absence of oxidants) treatment was explored at pH 3 with 1 g/L ZVAl as a control experiment. Then, aqueous TX-45 solutions were subjected to the nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment combinations. After process optimization, TX-45-spiked DW, SW, TW and WW samples were subjected to the combined treatment systems. The selection of the studied working conditions was based on preliminary experiments and former related works that have been reported recently (Bokare and Choi, 2009; Girit et al. 2015). In the optimization experiments, the effect of initially added oxidant concentration was examined in detail. According to these baseline experiments, 0.25 mM (8.5 mg/L) HP, 0.25 mM (28.25 mg/L) PMS and 0.50 mM PS (96 mg/L) activated with nZVAl gave the highest TX-45 removal rates and efficiencies. Therefore, in the present study TX-45 abatement results were presented particularly for the concentrations of 0.25 mM and 0.50 mM for all oxidants. The experimental procedure of a typical run was described elsewhere (Girit et al. 2015). Samples were taken at regular time intervals from the reactor and filtered through 0.22 µm Millipore membranes (Millipore Corp., USA) to separate nZVAl from the reaction solution. All filtered samples were analyzed for the parameters residual TX-45, TOC, oxidant (HP, PS and PMS) concentrations and pH. All experiments were conducted in duplicate and average values were taken when presenting the results.

3.3 Analytical Procedure

The amount of TX-45 in the aqueous solution was measured by high-performance liquid chromotography (HPLC; Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array detector (DAD; G1315A, Agilent Series) and a Novapack C18 (3.9 mm×150 mm, Waters, USA) reversed phase column. The detection wavelength and column temperature were set at 225 nm and 25°C, respectively. The mobile phase consisted of 0.01% phosphoric acid/acetonitrile in water (65:35, v/v) at a flow rate of 1.0 mL/min. The instrument detection and quantification limits for TX-45 (100 μL injection volume) were calculated as 78 μg/L and 234 μg/L, respectively and The correlation coefficients of the established calibration curves for TX-45 were found as 0.999.

TOC was measured on a Shimadzu V_{CPN} analyzer (Japan) equipped with an autosampler. The instruments were equipped with autosamplers and Infrared (IR) detectors, and were calibrated with standard potassium hydrogen phthalate solutions.

Residual HP and PS concentrations were traced by employing the colorimetric method according to Klassen et al. (Klassen et al. 1994) and Villegas et al. (Villegas et al. 1963), respectively, whereas PMS was measured iodometrically (Wahba et al. 1959) and Jenway 6300 Spectrophotometry instrument (wavelength 320∼1000nm, accuracy ±1 %T, light source: Tungsten Halogen lamp, designed in UK) was used to measure the total PS and HP concentration in the samples. 615nm and 351nm wavelength was adjusted for PS and HP, respectively.

An Orion (USA) 720+ model pH-meter was used for pH measurements. Anion analysis was conducted using a Dionex ICS-1500 ion chromatography unit equipped with a conductivity detector, a Dionex IonPac AG14A (4×50 mm) guard column and a Dionex IonPac AS14A (4×250 mm) analytical column. Released Al^{3+} measurements were made with an Analytik Jena ContrAA®700 model atomic absorption spectrophotometer. All analytical measurements were carried out in triplicate and respective standard deviations were found to be within the ranges of the relevant test procedures.

3.4 Acute Toxicity and Genotoxicity Activity

Before conducting the toxicity tests, residual oxidant in the test samples were removed with suitable quenching agents to eliminate the interference of oxidants in bioassays. Sodium thiosulfate was recommended as suitable quenching agent for the removal of PS and PMS in the *V. fischeri* and *P. subcapitata* bioassays (Olmez-Hanci et al. 2014). In case of HP enzyme catalase and manganese oxide were found to be suitable quenching agents for *V. fischeri* and *P. subcapitata* bioassays, respectively (Olmez-Hanci et al. 2014). In order to eliminate its interference with the toxicity and genotoxicity test results Al^{3+} residuals in the reaction solutions were removed in the form of $Al(OH)_3$ flocs by pH adjustment, precipitation and filtration steps prior to toxicity analysis. The concentration of Al^{3+} in the treated TX-45 solutions was below 0.02 mg/L for the bioassays.

3.4.1 Biotox-Luminescence: Test method based on measurement of light emission from the marine photobacteria *Vibrio fischeri*

The biotox test was performed according to the (ISO 11348-3:2008) and it was based on determining the inhibition of the luminescence emitted by the marine bacterium *V. fischeri*. The BioToxTM Kit (Aboatox Oy, Finland) was derived as freeze dried bacteria.

The inhibition of light emission by cultures of *V. fischeri* is determined by means of a batch test. This is accomplished by combining specified volumes of the test sample or the diluted sample with the luminescent bacteria suspension in a test tube. The light emission from the bacteria is measured photometrically by a spectrophotometer.

Sodium thiosulfate (6.2 mg for 25 ml samples) were added to the all samples also to the neutralized water samples (control samples) and tempered to room temperature for 1 day to remove oxidant from solutions. Thereafter oxidant elimination were control with iodometrically (Wahba et al. 1959) method. Before starting the test, NaCl was added to obtain a final chloride concentration of 2%, w/v in the samples. pH was adjusted in 7.0 ± 0.2 range with NaOH or H_2SO_4 solutions. Two replicates of each sample were tested. Freeze dried bacteria and samples vials were put in IC 20 chilling/heating dry bath instrument for half hour in 4 ˚C and 30 min in 15 ˚C. After

adding 500 μL of the bacteria suspension into each of the test vials, the vials were placed in the luminometer (Luminoskan TL Plus, Thermo Lab Systems, Finland) starting with controls and measured their luminescence (t_0). Thereafter, 500 μL of the samples were added into the vials and measurements were repeated after 0 (t_0) and 15 min (t_{15}).

3.4.2 Growth inhibition test with *Pseudokirchneriella subcapitata*

The acute toxicity towards the freshwater microalgae *P. subcapitata* was determined using Algal tox kit F™ (MicroBioTests, Inc., Gent, Belgium) micro-biotests according to the procedure described in (ISO 8692) and (OECD 201). Exponentially growing test organisms are exposed to the test substance in batch cultures over a period of normally 72 hours.

The initial biomass in the test cultures must be the same in all test cultures and sufficiently low to allow exponential growth throughout the incubation period without risk of nutrient depletion. The initial biomass should not exceed 0.5 mg/L as dry weight. Each flask was inoculated with microalgae from the concentrated suspension to obtain 1×10^4 cells/ml as the start concentration and pH must be adjust to 8.1 ± 0.2 (with either 1 M HCl or 1 M NaOH).

Three replicates were prepared containing 25 mL of each concentration. The replicates were placed in an algal growth chamber under continuous fluorescent illumination (sideway illumination=10000 LUX) and incubated at 22 ± 1 ˚C. The cell density of the algal cultures was measured at 24-h intervals over 72 h. In each case, the cell density was calculated from the optical density of the algae in different samples, measured in 10 cm path-length cuvettes at 670 nm, using a Jenway 6300 model spectrophotometer. During the course of the experiments (72 h) the algal cultures remained in the exponential growth phase. A series of controls containing only growth media and the algal inocula were also prepared.

The growth of biomass was calculated as follows;

$$\mu = (LnN_L - LnN_0)/(t_L - t_0) \tag{3.5}$$

where;

N_0 is the initial cell density, N_L is the measured cell density at time t_L, t_0 is the time of test start and t_L is the time of test termination (or the time of the last measurement within the exponential growth period in the control batches). For percentage inhibition of growth, **(Equ. 3.6)** was used as follows;

$$I_{\mu i} = \frac{(\mu_c - \mu_i)}{\mu_c} \times 100 \tag{3.6}$$

μ_i is the growth rate for test batch I and μ_c is the mean growth rate for the control batches.

3.4.3 Genotoxicity

The umuC assay was carried out according to the procedure described by (ISO 13829). The UMU-Chromo TestTM test kit was supplied by EBPI Environmental Bio-Detection Products Inc. (Canada). According to the (ISO 13829) protocol, genotoxicity is measured by quantifying the induction ratio as the ratio of β-galactosidase activity of samples and controls in relation to the growth inhibition of the bacteria *Salmonella typhimurium* TA1535 [pSK1002]. In the present study, several dilutions (namely 1:1.5, 1:3.0, 1:6 and 1:12) of the original and treated TX-45 samples together with two positive controls (4-nitroquinoline-Noxide (4-NQO) and 2-aminoanthracene (2-AA)), negative and solvent controls were tested. For each sample dilution, the growth factor (G), the β-galactosidase activity (US) and the induction ratio (IR) were calculated as given below:

$$G = [(A_{600,S} - A_{600,B}) / (A_{600,NC} - A_{600,B})] \tag{3.7}$$

$$U_S = [(A_{420,S} - A_{420,B}) / (A_{600,S} - A_{600,B})] \tag{3.8}$$

$$I_R = (1/G) \times [(A_{420,S} - A_{420,B}) / (A_{420,NC} - A_{420,B})] \tag{3.9}$$

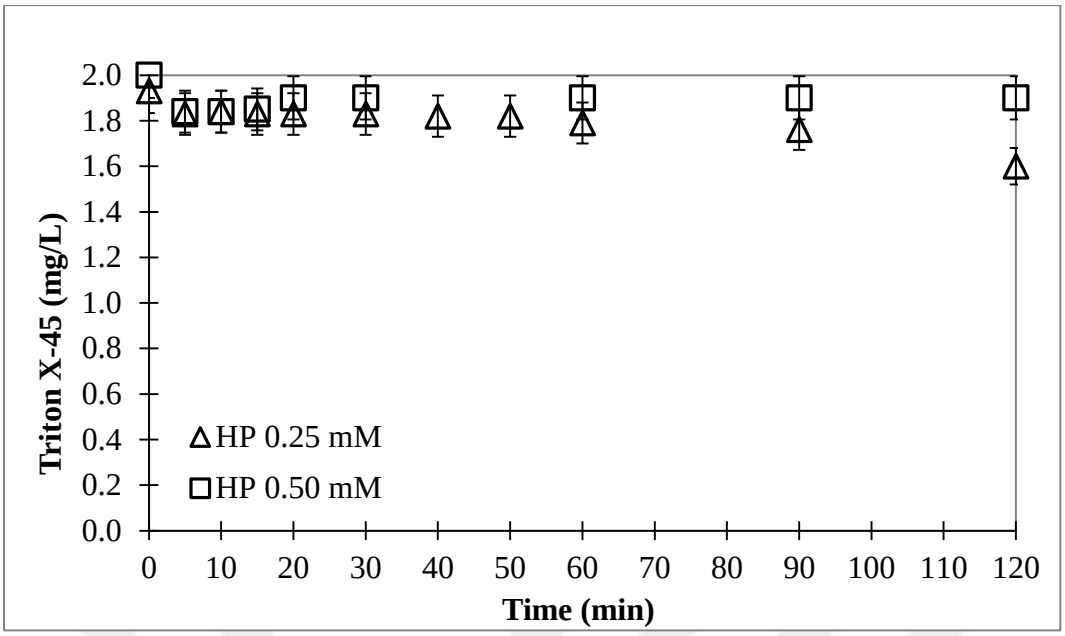
where $A_{600,S}$ and $A_{420,S}$ are the absorbance of sample S at 600 nm and 420 nm; $A_{600,B}$ and $A_{420,B}$ are the absorbance of the blank B at 600 nm and 420 nm; $A_{600,NC}$ and $A_{420,NC}$ are the absorbance of the negative control NC at 600 nm and 420 nm. Wavelengths of 600 nm and 420 nm were used to measure bacterial growth and quantify β-galactosidase activity, respectively. The optical density was measured using Bio Rad Benchmark Plus microplate spectrophotometer for the determination of the β-galactosidase activity and induction ratio. The whole test was considered valid if the positive controls reach an I_R of >2. Calculation of G allowed to identify toxic growth inhibitory effects and G<0.5, representing>50% inhibition of the biomass growth, was considered to be indicative of samples being cytotoxic. An I_R of >1.5 was taken as the threshold at which the sample was considered as genotoxic (ISO 13829; UMU-Chromo Test™, Kit ISO).

4. RESULTS AND DISCUSSION

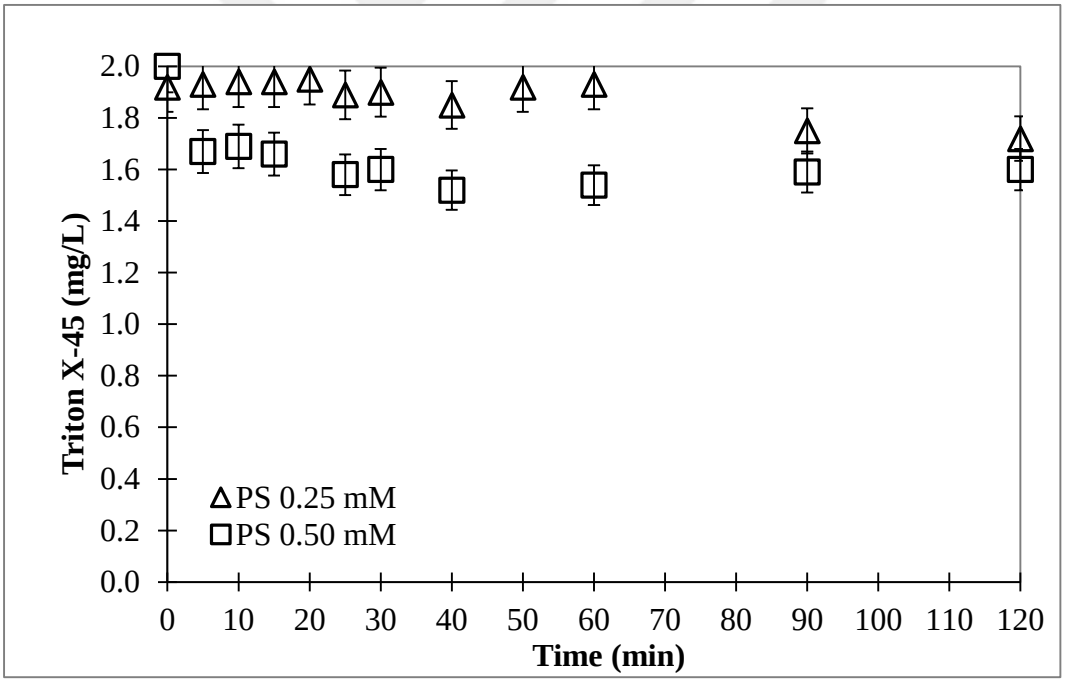
4.1 HP, PS and PMS Oxidation of Aqueous TX-45

In order to determine the most suitable initial HP, PS and PMS concentrations a set of experiments was carried out in 0.25 and 0.50 mM initial HP, PS and PMS concentration while maintaining the concentration of TX-45 constant at 2 mg/L at an initial pH of 3 as well as room temperature during 120 min treatment time.

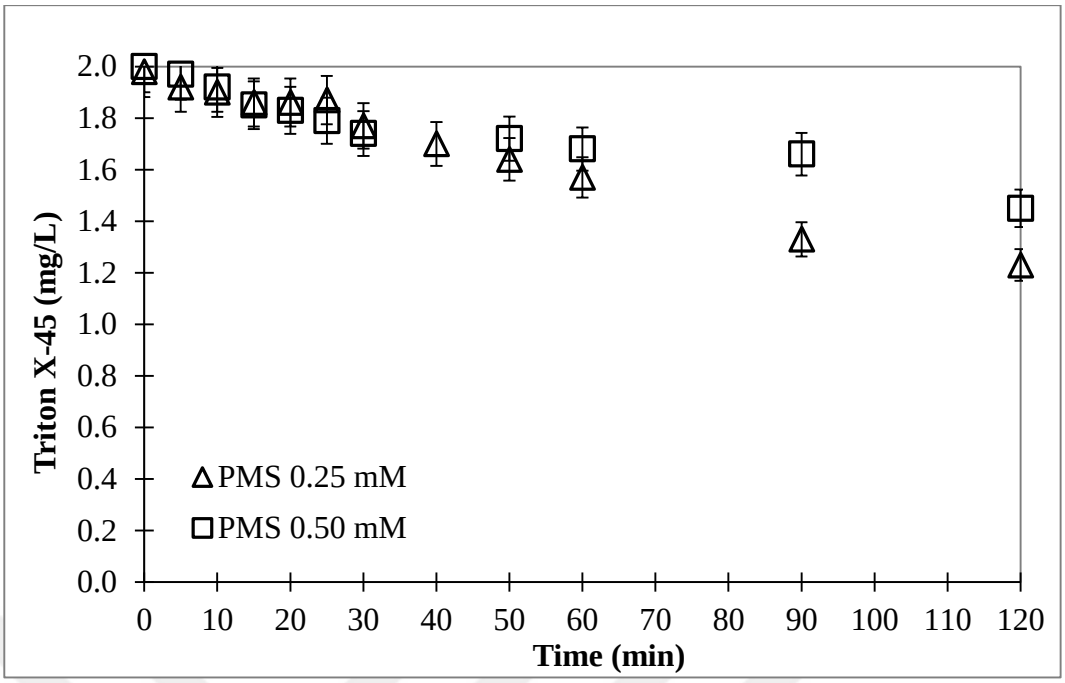
Figure 4.1 depicts changes in TX-45 concentrations (data are shown in Table A.1) observed during mere HP (a), PS (b) and PMS (c) oxidations. As it is evident in **Figure 4.1**, HP, PS and PMS treatment of TX-45 was poor and hence limited to 5%-38%. The highest overall TX-45 removal was obtained as 38% for PMS oxidation at 0.25 mM followed by 20% and 11% TX-45 removals after PS (at 0.50 mM) and HP (at 0.25 mM) treatments, respectively. As can be seen from **Figure 4.1b** increasing the initial PS concentrations increased the TX-45 removal efficiency from 10% to 20% for 0.25 mM and 0.50 mM PS concentrations, respectively. As is evident from **Figure 4.1a** and **4.1c**, increasing HP and PMS concentrations from 0.25 to 0.50 mM reduced TX-45 removal rates. As expected, HP, PS or PMS was not capable of degrading complex organics including TX-45 due to their limited oxidation potential compared to free radicals ($HO^{\bullet}$, $SO_4^{\bullet-}$).


Triton X-45 (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
HP 0.25 mM
HP 0.50 mM
0
10
20
30
40
50
60
70
80
90
100
110
120
Time (min)

(a)


Triton X-45 (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
PS 0.25 mM
PS 0.50 mM
0
10
20
30
40
50
60
70
80
90
100
110
120
Time (min)

(b)



(c)

Figure 4.1: Triton X-45 removals observed during mere HP (a), PS (b) and PMS oxidation experiments. Experimental Conditions: TX-45=2mg/L; HP,PS, PMS=0.25 and 0.50mM; pH=3; T=25°C.

Remaining oxidant concentrations were also followed during HP, PS and PMS treatments (data are shown in Table A.2). HP, PS and PMS consumptions were poor (< 10%), an observation being parallel to limited TX-45 degradation rates.

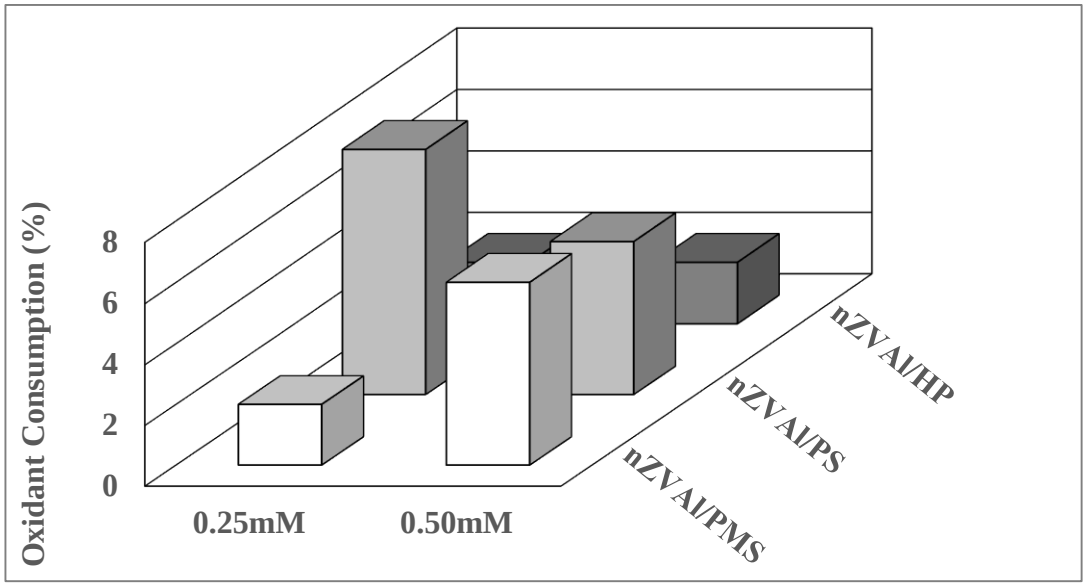


Figure 4.2: Oxidant Consumption in percent during mere HP, PS and PMS oxidation experiments.

The specific oxidation efficiencies (SOE values; calculated as g of TX-45 removed per g of oxidant consumed) for the mere oxidant treatment systems were also determined for the examined treatment combinations. The SOE values of HP, PS and PMS systems for initial oxidant concentration of 0.25 mM were found as 1.6, 0.06 and 1.06 g TX-45/g oxidant, respectively. Increasing the initial HP and PMS concentration to 0.50 mM decreased the SOE value to 0.3 and 0.15 g TX-45/g oxidant for the HP and PMS treatment, respectively. However, SOE values did not change considerably for the PS treatment systems when the initial oxidant concentration was increased from 0.25 to 0.50 mM.

The pH changing during process was determined and results showed did not change in solution pH in HP, PS and PMS treatment after 120 min. (data are shown in Table A.2).

Table 4.1 and **Figure 4.3** summarize TX-45 abatements and oxidant consumptions after 120 min during HP, PS and PMS treatments.

Table 4.1: Summary of the obtained results for TX-45 abatements, oxidants consumption and SOE value during HP, PS and PMS treatments. Experimental Conditions: TX-45= 2mg/L; HP, PS, PMS=0.25 and 0.50 mM; pH=3; T=25°C.

Oxidants Reagent	Oxidant Concentration (mM)	TX-45 Removal Efficiency (%)	Oxidant Consumption (%)	SOE value (g TX-45/g oxidant)
HP	0.25	11	2	1.6
	0.50	5	2	0.3
PS	0.25	10	8	0.06
	0.50	20	5	0.08
PMS	0.25	38	2	1.06
	0.50	28	6	0.15

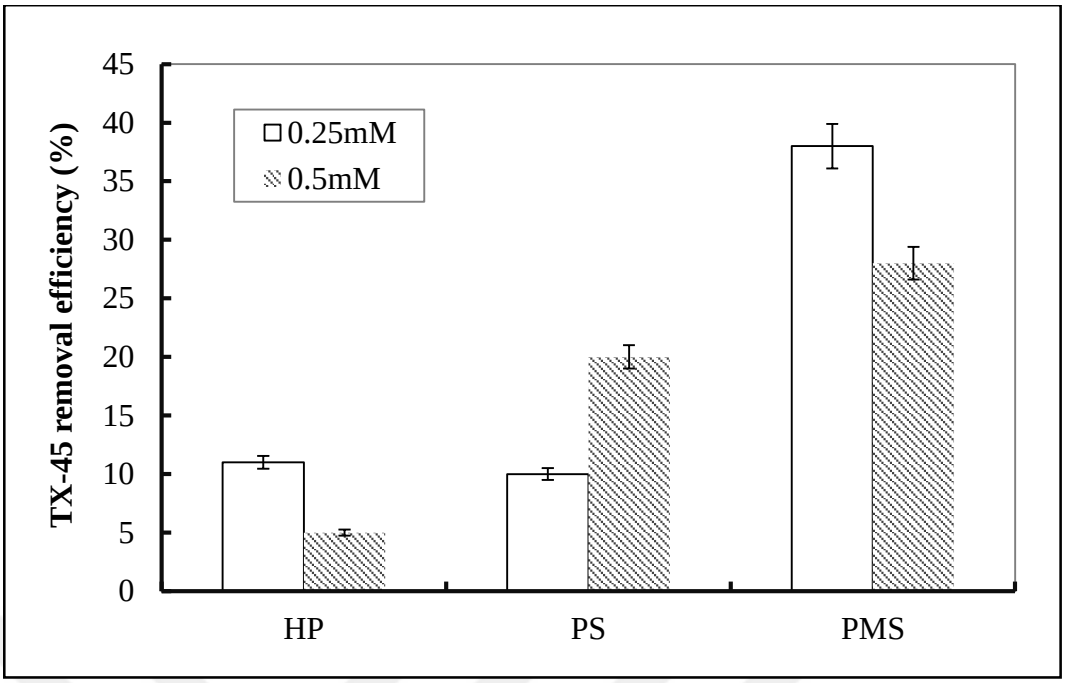
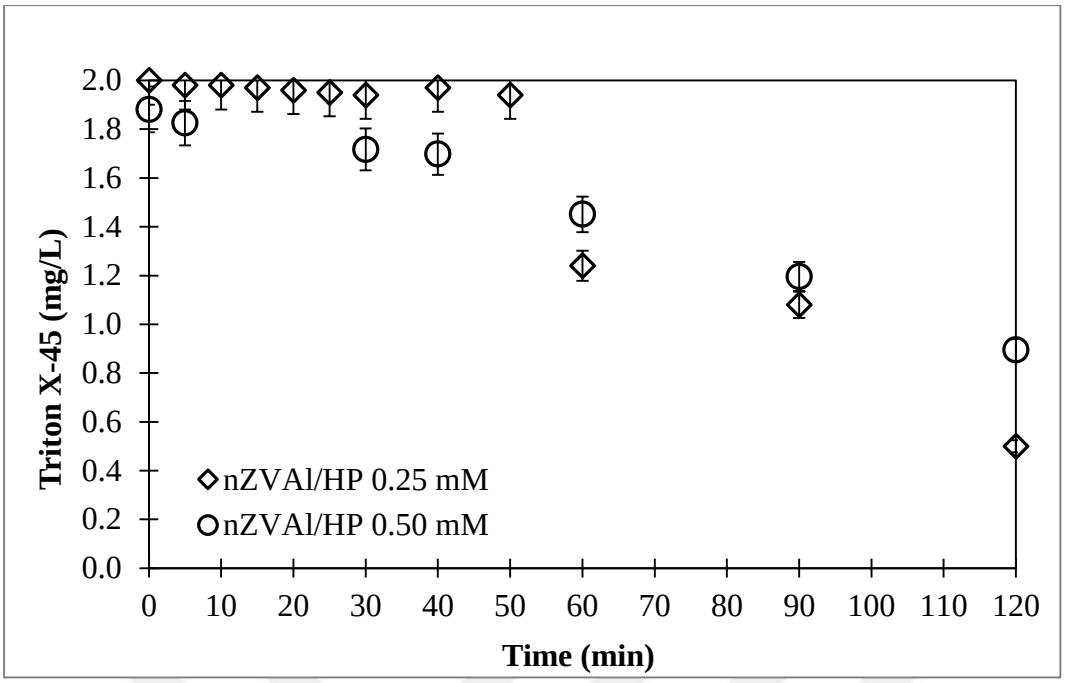


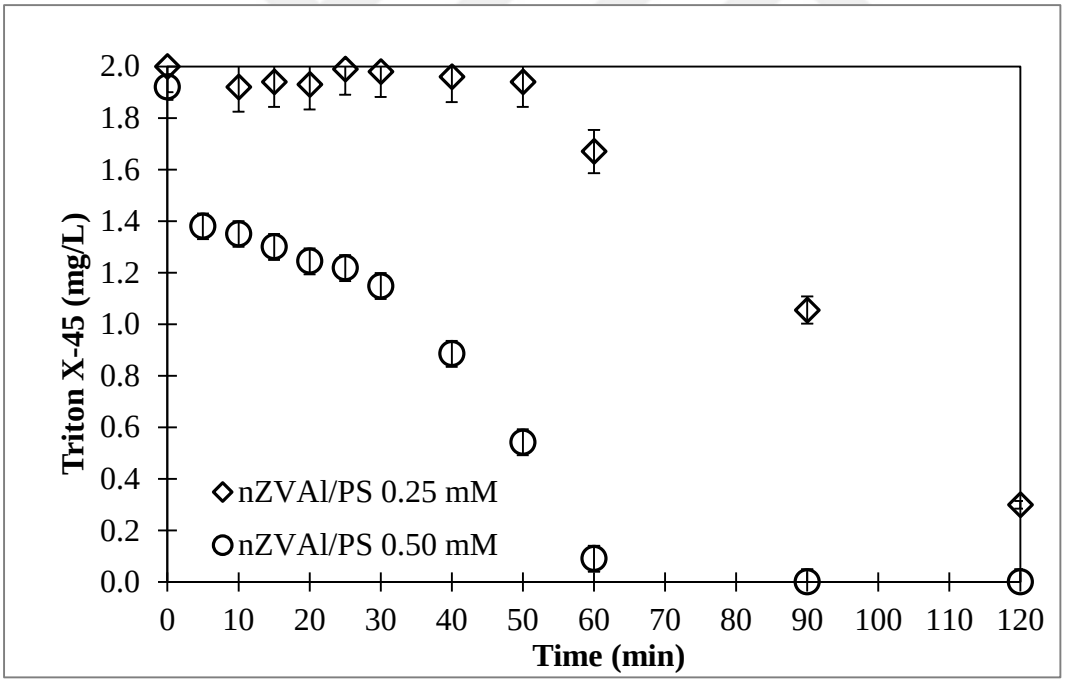
Figure 4.3: Triton X-45 removal efficiency during mere HP, PS and PMS oxidation experiments.

4.2 Aqueous TX-45 Treatment with nZVAl/HP, nZVAl/PS and nZVAl/PMS

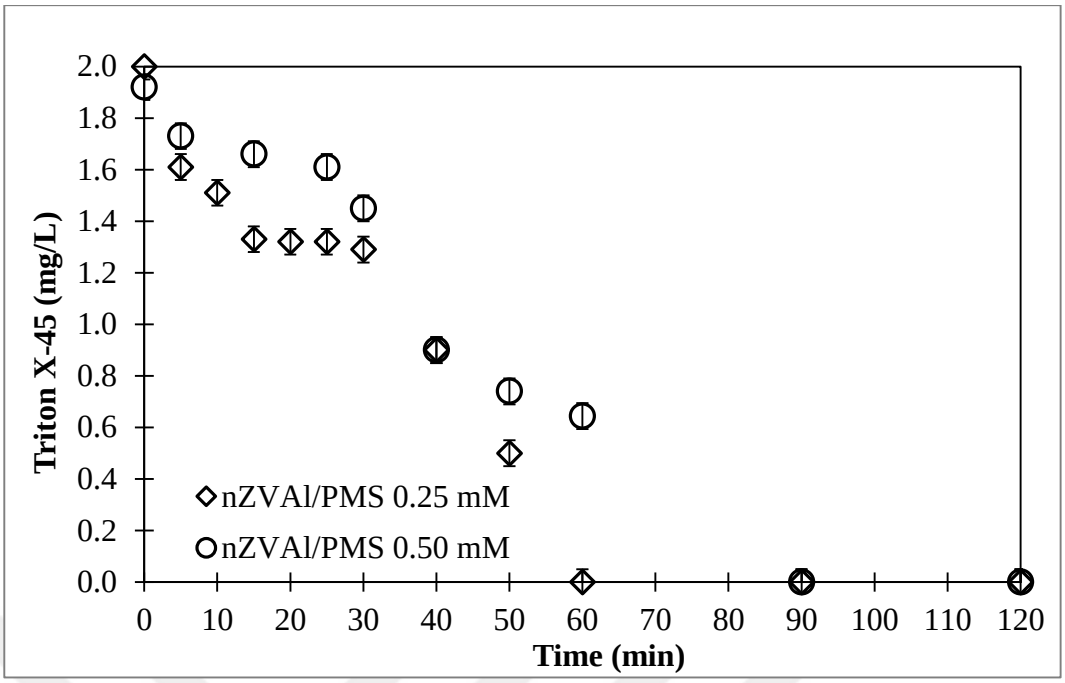
In order to assess the oxidative capacities of the nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment systems, experiments were conducted with 2 mg/L aqueous TX-45 solutions in the presence of 1 g/L nZVAl at pH3 **(Figure 4.4).** In addition to nZVAl/HP, nZVAl/PS and nZVAl/PMS combinations, the performance of the nZVAl/O_2/H^+ treatment was also examined at pH 3 **(Figure 4.4d).** Only 22% TX-45 removal could be achieved by nZVAl/O_2/H^+ treatment in the absence of HP, PS or PMS after 120 min.


Triton X-45 (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time (min)
nZVAl/HP 0.25 mM
nZVAl/HP 0.50 mM

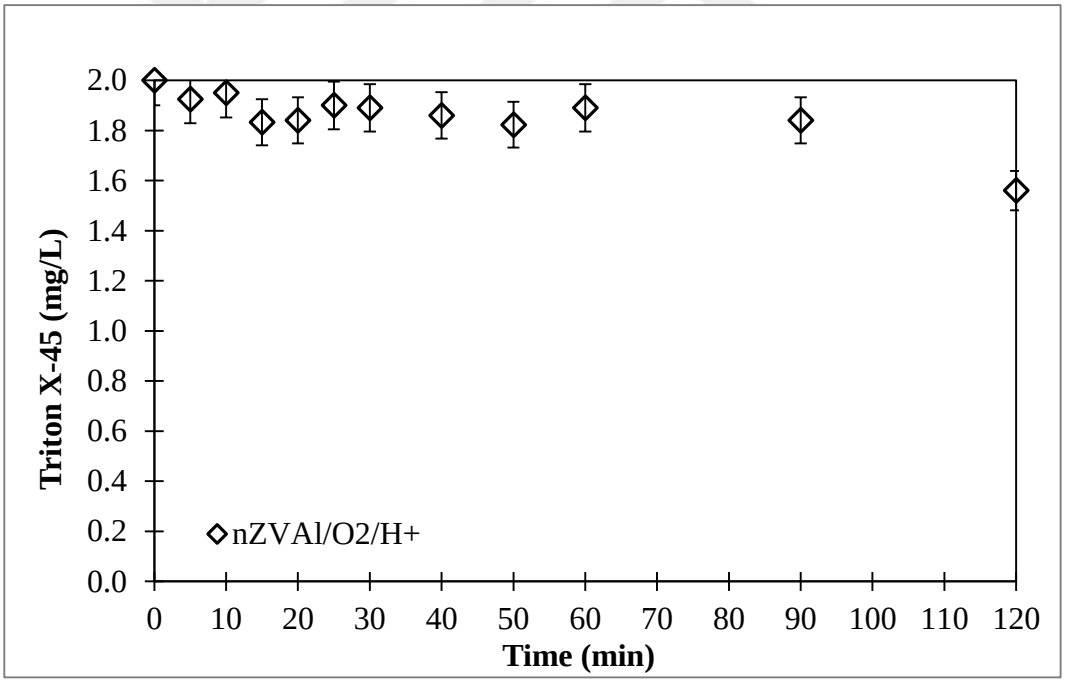
(a)


Triton X-45 (mg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time (min)
nZVAl/PS 0.25 mM
nZVAl/PS 0.50 mM

(b)



(c)



(d)

Figure 4.4: Triton X-45 removals observed during nZVAl/HP (a), nZVAl/PS (b) ,nZVAl/PMS (c) and nZVAl/O_2/H^+ (d) oxidation experiments. Experimental Conditions: TX-45=2mg/L; HP, PS and PMS=0.25 and 0.50 mM; nZVAl=1g/L; pH=3; T=25°C.

HP, PS and PMS activation with nZVAl dramatically enhanced the oxidation rate of TX-45 (data are shown in Table A.3) as compared to HP, PS, PMS and nZVAl/O_2/H^+ treatments. TX-45 was degraded completely after 90 and 60 min treatment with nZVAl/PS (0.50 mM) and nZVAl/PMS (0.25 mM), respectively. whereas 76% TX-45 removal was achieved with nZVAl/HP (0.25 mM) after 120 min. Similar to PS oxidation, TX-45 removal increased at the higher PS concentration, which can be explained by an increase in the steady-state concentration of $SO_4^{\bullet -}$ being responsible for TX-45 degradation. TX-45 was completely degraded after 90 min with the nZVAl/PS combination in the presence of 0.50 mM PS, whereas 86% TX-45 removal was observed for 0.25 mM PS after 120 min. On the other hand, increasing the HP concentration decreased the TX-45 removal from 76% to 52% for nZVAl/HP treatment system, whereas for nZVAl/PMS treatment, complete degradation of TX-45 was achieved in 60 min and 90 min at initial PMS concentrations of 0.25 mM and 0.50 mM, respectively. This is thought to be a consequence of the well-known free radical scavenging effect of excessive oxidant concentrations (Buxton et al. 1988; Fernandez et al. 2004; Criquet and Leitner, 2009). The respective scavenging reaction for HP, PS and PMS oxidants are given in **(Eqns. 4.1-4.3)**, respectively.

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad K=1.2\text{-}4.5 \times 10^7\ M^{-1}\ S^{-1} \tag{4.1}$$

$$S_2O_8^{2-} + SO_4^{-\bullet} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \qquad K=6.1 \times 10^9\ M^{-1}\ S^{-1} \tag{4.2}$$

$$HSO_5^- + HO^{\bullet} or SO_4^{-\bullet} \rightarrow SO_5^{\bullet -} + OH^- or SO_4^{2-} + H^+ \qquad K=1.0 \times 10^5\ M^{-1}\ S^{-1} \tag{4.3}$$

Oxidant consumption rates that were followed during TX-45 degradation with the nZVAl/oxidant combinations revealed that a sufficient amount of oxidant was always available during the course of the reaction. For nZVAl/HP treatment, increasing the initial oxidant concentration from 0.25 mM to 0.50 mM increased HP consumption from 27% to 98%.

In case of nZVAl/PS and nZVAl/PMS treatments, PS and PMS consumption was relatively poor; only 32% and 15% of initially added PS and 22% and 11% of initially

PMS concentration were consumed after 120 min for initial PS and PMS concentrations of 0.25 mM and 0.50 mM, respectively.

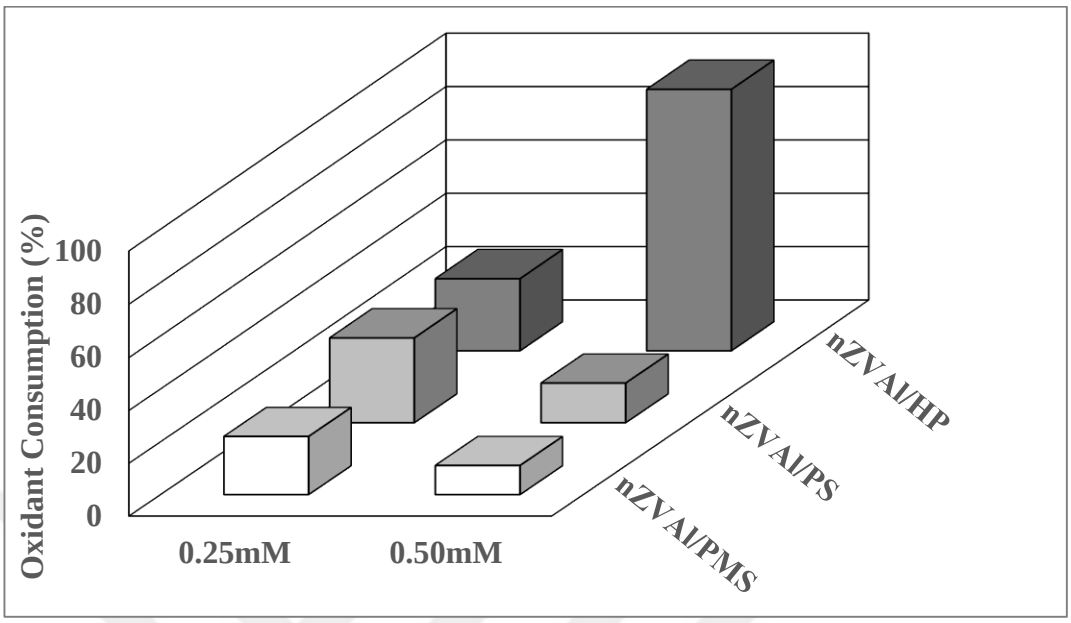


Figure 4.5: Oxidant Consumption in percent during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments.

The SOE values of nZVAl/HP, nZVAl/PS and nZVAl/PMS systems for initial oxidant concentration of 0.25 mM were found as 0.65, 0.12 and 0.28 g TX-45/g oxidant, respectively. Increasing the initial HP concentration to 0.50 mM decreased the SOE value to 0.05 g TX-45/g oxidant for the nZVAl/HP treatment. However, SOE values did not change considerably for the nZVAl/PS and nZVAl/PMS treatment systems when the initial oxidant concentration were increased from 0.25 to 0.50 mM.

Table 4.2 and **Figure 4.6** display briefly TX-45 removal, oxidant consumptions and calculated SOE values after 120 min for nZVAl/HP, nZVAl/PS and nZVAl/PMS treatments.

Table 4.2: Summary of the obtained results for TX-45 abatements, oxidants consumption and SOE values during nZVAl/HP, nZVAl/PS and nZVAl/PMS treatments. Experimental Conditions: TX-45=2 mg/L; HP, PS, PMS=0.25 and 0.50 mM; nZVAl=1 g/L; pH=3; T=25°C.

Oxidants Reagent	Oxidant Concentration (mM)	TX-45 Removal Efficiency (%)	Oxidant Consumption (%)	SOE value (g TX-45/g oxidant)
nZVAl/HP	0.25	76	27	0.65
	0.50	52	98	0.05
nZVAl/PS	0.25	86	32	0.12
	0.50	100	15	0.13
nZVAl/PMS	0.25	100	22	0.28
	0.50	100	11	0.3

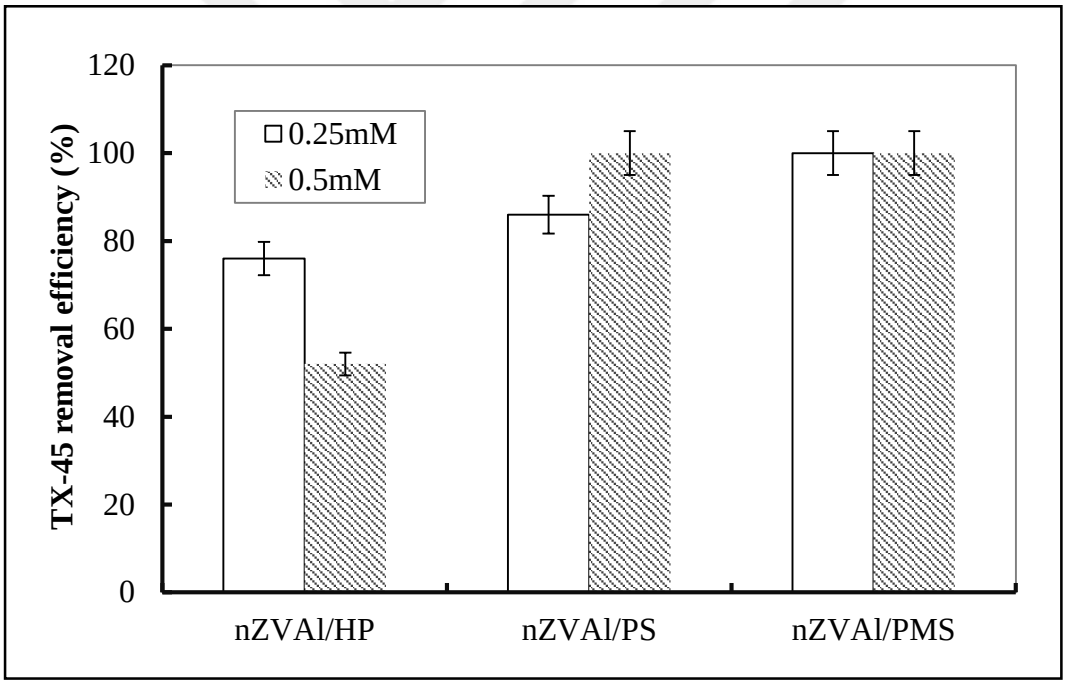


Figure 4.6: Triton X-45 removal efficiency during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments.

Changes in pH values were also followed during the time course of the nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment (data are shown in Table A.4). Degradation efficiency of target contaminant might have affected with increase in solution pH due to changes in aluminum ion speciation, precipitation of aluminum hydroxide floc and self-dissociation of oxidant through non-radical pathways. Bokare and Choi (2009)

stated that as long as solution remains below a value of 4 during the reaction, Al dissolution and hence oxidation reactions will continue. In the present study, an overall, slight increase in the solution pH from 3 to 4 was observed.

4.3 Aqueous TX-45 Treatment in Different Water and Wastewater Matrices

In the present study, four different water matrices (DW, SW, WW and TW) were investigated to evaluate their effect on TX-45 removal with the nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment systems. For these treatability experiments the initial HP and PMS concentrations were fixed at 0.25 mM for nZVAl/HP and nZVAl/PMS combinations and 0.50 mM PS for the nZVAl/PS treatment system. **Figure 4.7-4.9** presents time dependent changes in TX-45 concentrations (data are shown in Table A.5) during nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment combinations, respectively in DW, SW, TW and WW. For ZVAl/HP treatment, TX-45 removal rates were higher in SW (84% TX-45 removal after 120 min) and TW (complete TX-45 removal after 90 min) than in DW **(Figure 4.7)**, probably due to the additional ROS produced during oxidative reactions in SW and TW. As can be seen in this figure, lowest TX-45 removal rate was obtained in WW samples as 58%.

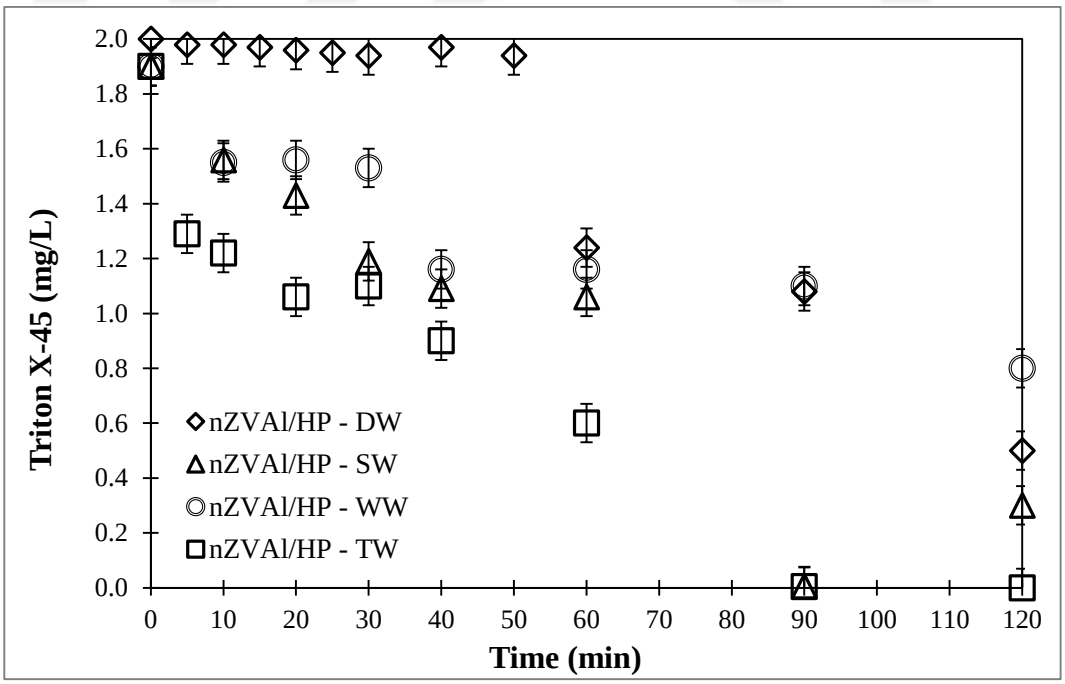


Figure 4.7: Triton X-45 removal during nZVAl/HP treatment systems in distilled water (DW), raw surface water (SW), tap water (TW) and domestic wastewater treatment plant effluent (WW). Experimental Conditions: TX-45=2 mg/L; nZVAl=1 g/L; HP =0.25 mM; pH=3; T=25°C.

During nZVAl/PS treatment significant inhibition was observed for TX-45 degradation; TX-45 removal decreased from 100% in DW (after 90 min) to 58% and even 12% in SW and WW, respectively **(Figure 4.8).** On the other hand, TX-45 treatment in the TW sample was complete in 120 min. These observations point out that the nZVAl/PS combination effectively removed TX-45 in DW and TW but its efficacy was reduced in SW and mainly in WW, speculatively due to the presence of higher concentrations of inorganic ions in these samples inhibiting the treatment performance. The fair TX-45 removal observed in the WW sample might be also attributable to its higher, relatively easily oxidisable organic matter content which was more prone to oxidation than TX-45.

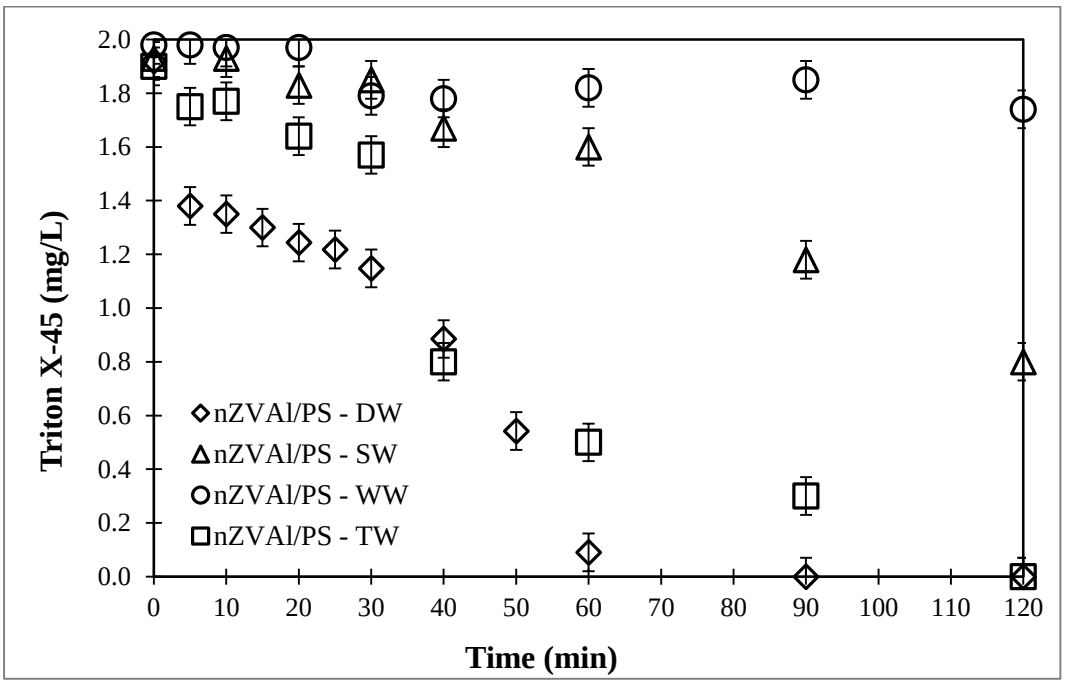


Figure 4.8: Triton X-45 removal during nZVAl/PS treatment systems in distilled water (DW), raw surface water (SW), tap water (TW) and domestic wastewater treatment plant effluent (WW). Experimental Conditions: TX-45= 2 mg/L; nZVAl=1 g/L; PS =0.50 mM; pH=3; T=25°C.

Figure 4.9 presents TX-45 abatements during nZVAl/PMS treatment in DW, SW, WW and TW. As can be seen from **Figure 4.9**, during nZVAl/PMS treatment, the fastest TX-45 degradation was obtained in DW, followed by WW, TW and SW. For this treatment combination complete TX-45 removal was achieved after 60 min and 90 min in DW and WW, respectively, whereas 93% and 98% TX-45 removals were observed in the SW and TW samples after 120 min.

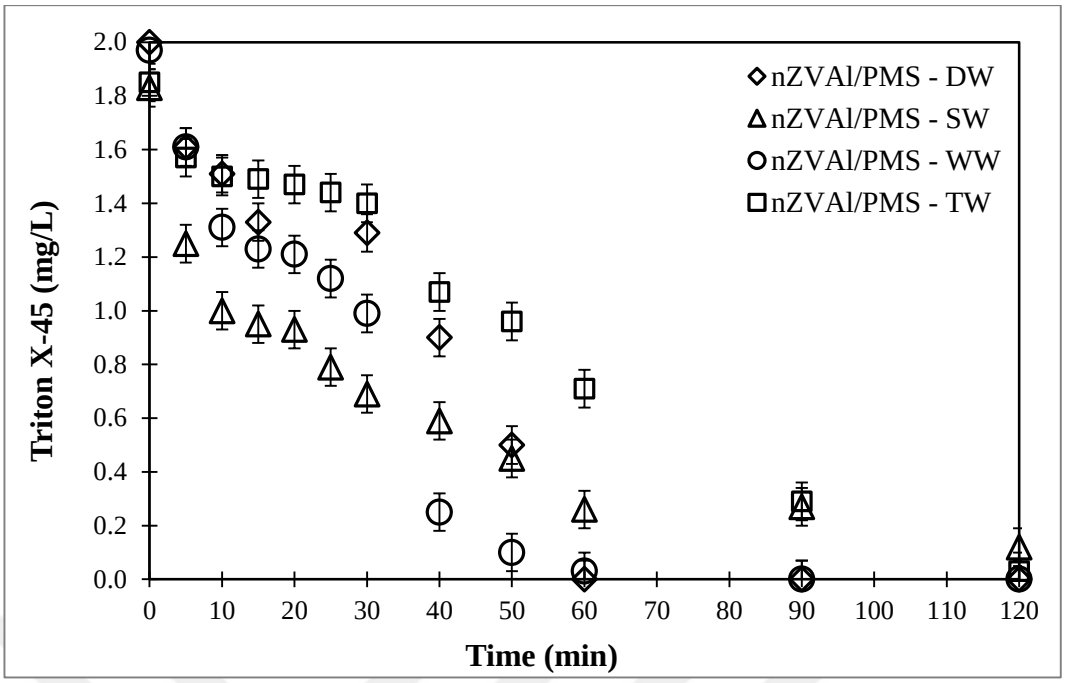


Figure 4.9: Triton X-45 removal during nZVAl/PMS treatment systems in distilled water (DW), raw surface water (SW), tap water (TW) and domestic wastewater treatment plant effluent (WW). Experimental Conditions: TX-45= 2 mg/L; nZVAl=1 g/L; PMS =0.25 mM; pH=3; T=25°C.

Upon comparison of the treatment performances obtained for the investigated nZVAl-mediated treatment systems it is clear that these processes differ appreciably in terms of TX-45 removal rates. TX-45 removal was mostly inhibited in WW for nZVAl/HP and nZVAl/PS treatments, whereas TX-45 removal was most negatively affected in SW for nZVAl/PMS. In the present study, the higher treatment performances obtained for TX-45 degradation with nZVAl/PMS in the SW and WW samples as compared with nZVAl/HP and nZVAl/PS is thought to be a consequence of the differences in water/wastewater characteristics (He et al. 2013; Anipsitakis and Dionysiou, 2004).

Because of their presence in the effluent, the impact of inorganic anions and organic matter on the performance of AOPs needs to be investigated. The variations in inorganic anions and organic matter may further complicate the treatment system by affecting the formation of radicals and their interconversion and consumption. In the related works, it was demonstrated that the presence of inorganic ions such as chloride, sulfate, bicarbonate and carbonate does not always inhibit the degradation rate and efficiency. Moreover, in some studies it was shown that the degradation of organic pollutants can be accelerated in the presence of these anions (Guzman-Duque et al. 2011; Sánchez-Polo et al. 2013; Yang et al. 2016). For example, halides, alkalinity and

organic matter may reduce the process efficiency by scavenging $HO^{\bullet}$ and $SO_4^{\bullet-}$. However, the daughter radicals (eg. $CO_3^{\bullet-}$ and $Cl_2^{\bullet}$) generated by their reactions with reactive oxygen species may act as secondary oxidants, although being more selective than the mother radicals (Yang et al. 2016).

In a recent study, UV/H_2O_2 and UV/$S_2O_8^{2-}$ treatment processes were compared for the degradation of five pharmaceuticals spiked into different water samples containing high salinity (Yang et al. 2016). For the UV/H_2O_2 treatment process, the organic matter present in the effluent scavenged around 75% of the $HO^{\bullet}$, reducing the degradation efficiency of the target contaminants to a similar extent. Cl^-, Br^- and bicarbonate-carbonate scavenging of the associated daughter radicals was less important. For the UV/$S_2O_8^{2-}$ treatment process, anions (mostly Cl^-) scavenged ≈93% of the $SO_4^{\bullet-}$. The reduction in contaminant degradation efficiency was ≈75-80, because daughter radicals of Cl^- contributed to contaminant degradation. The conversion of $SO_4^{\bullet-}$ to more selective halogen and carbonate radicals resulted in changes in degradation efficiencies among the contaminants.

The organic matter content in natural waters may also influence the oxidative efficiency of ZVAl-mediated treatment systems. For instance, humic acid (HA), a main component of dissolved organic matter found in natural water and wastewater, exhibits dual roles in Fenton and Fenton-like reactions (Kang and Choi, 2009; Lindsey and Tarr, 2000); namely as an inhibiting and enhancing agent. HA affects charge transfer reactions of oxidants to form $HO^{\bullet}$ and/or $SO_4^{\bullet-}$. Additionally, HA may compete for reactive sites and $HO^{\bullet}$ and/or $SO_4^{\bullet-}$ during treatment of pollutants by ZVAl (W. Liu et al. 2011; Wu et al. 2010). Sánchez-Polo et al. (2013) reported that the effectiveness of $HO^{\bullet}$, $SO_4^{\bullet-}$ and $CO_3^{\bullet-}$ /$HCO_3^{\bullet}$ radicals in the photodegradation of Bisphenol A (BPA) in aqueous solution was affected by the components of real effluent matrices. In their study, BPA degradation decreased in the following order; wastewater > surface water > ultrapure water. These results suggest that the BPA degradation rate in wastewater might be related to its natural organic matter (NOM) content, which could absorb UV radiation and generate excited triplet states ($^3NOM^*$) and various reactive oxygen species, including additional $HO^{\bullet}$, singlet oxygen ($^1O_2$) and HP which enhance BPA degradation.

Regarding the oxidant consumptions, during nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment of TX-45, the lowest oxidant consumption was obtained for WW. These were 46% for nZVAl/HP, 10% for nZVAl/PS and 9% for nZVAl/PMS treatment combinations in SW. However, a relationship between the TX-45 abatement and oxidant consumption rates could not be established in any case.

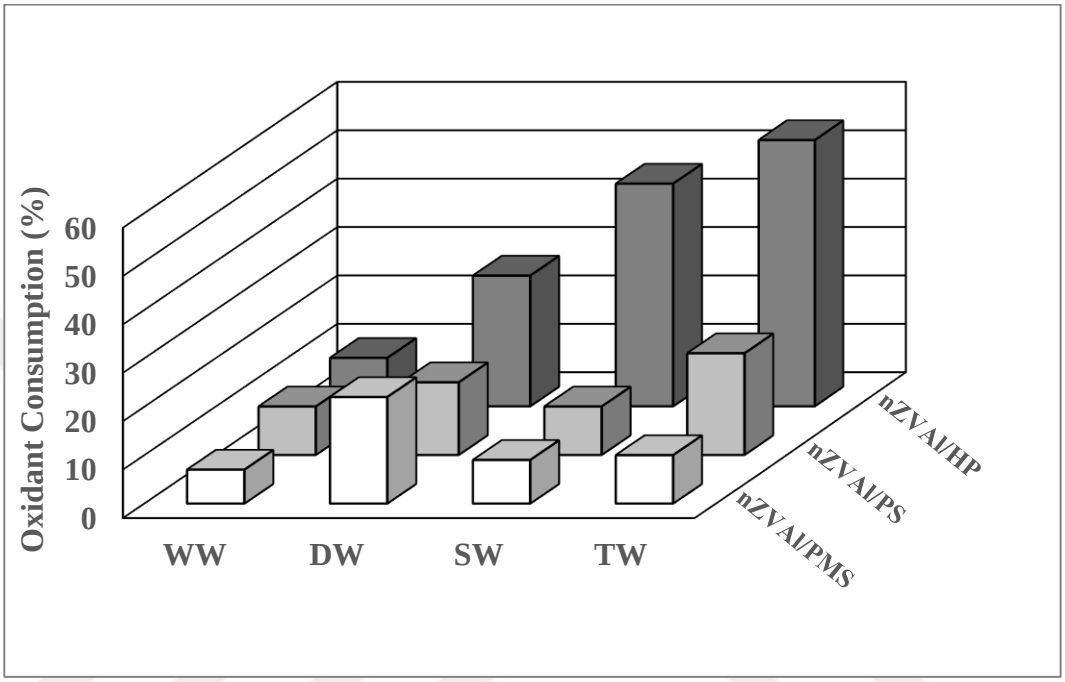


Figure 4.10: Oxidation consumption in percent during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments in DW,SW, TW and WW.

The highest SOE value was determined as 3.2 g TX-45/g oxidant for the nZVAl/HP treatment system in WW, where 58% of TX-45 was removed. The lowest SOE value (0.02 g TX-45/g oxidant) was obtained for the nZVAl/PS treatment system in WW accompanied with only 12% of TX-45 degradation. For nZVAl/PMS treatment in SW and WW, where 93% and 100% TX-45 degradation was achieved, the calculated SOE values were 0.79 g TX-45/g oxidant and 0.68 g TX-45/g oxidant, respectively.

Table 4.3 and **Figure 4.10 and 4.11** showed total results of TX-45 degradation during nZVAl/HP, nZVAl/PS and nZVAl/PMS treatments in different water matrix.

Table 4.3: Summary of the obtained results for TX-45 abatements, oxidant consumptions and SOE values during nZVAl/HP, nZVAl/PS and nZVAl/PMS treatments in different water matrix. Experimental Conditions: TX-45=2 mg/L; HP, PMS=0.25 and PS=0.50 mM; nZVAl=1 g/L; pH=3; T=25℃.

Oxidants Reagent	Type of Water Matrix	TX-45 Removal Efficiency (%)	Oxidant Consumption (%)	SOE value (g TX-45/g oxidant)
nZVAl/HP (0.25mM)	DW	76	27	0.65
	SW	84	46	0.4
	TW	100	55	0.5
	WW	58	10	3.2
nZVAl/PS (0.50mM)	DW	100	15	0.13
	SW	58	10	0.8
	TW	100	21	0.6
	WW	12	10	0.02
nZVAl/PMS (0.25mM)	DW	100	22	0.28
	SW	93	7	0.79
	TW	98	10	1.78
	WW	100	9	0.68

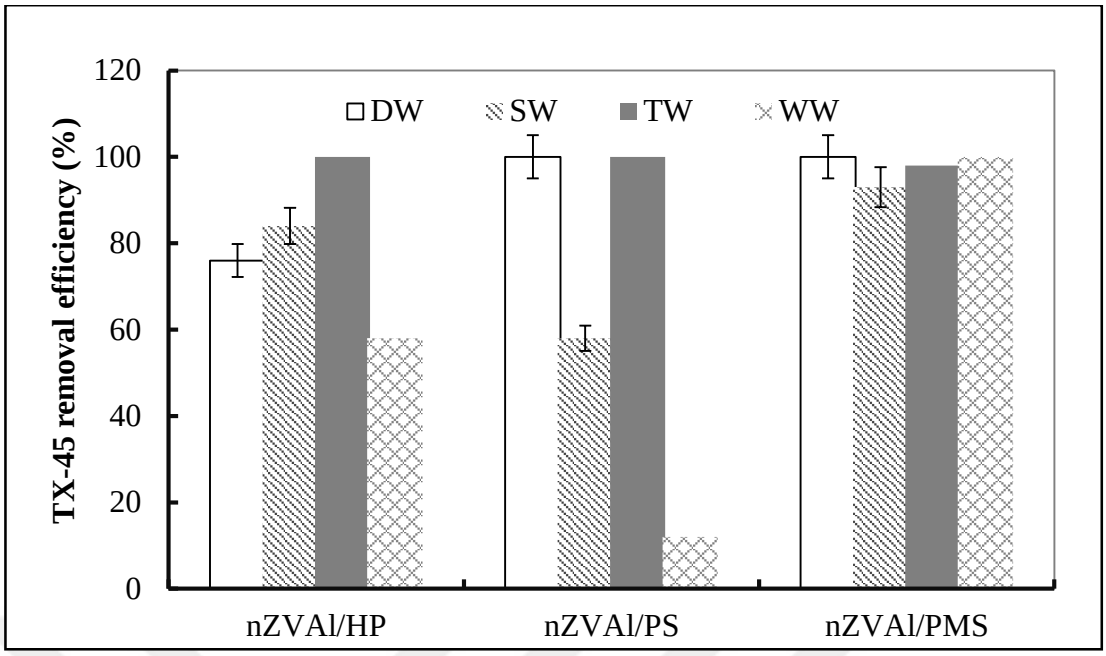


Figure 4.11: Triton X-45 removal efficiency during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments in DW,SW, TW and WW.

In the present study mineralization rates were also followed in terms of the TOC parameter, since TX-45 degradation was also examined in real water and wastewater samples having their own specific natural organic carbon content (see **Table 3.2**). **Table 4.4** summarizes percent overall TOC removal efficiencies obtained during treatment of TX-45 by the nZVAl/oxidant combinations in different water and wastewater matrices. From **Table 4.4** it can be seen that only poor TOC removals were obtained for the nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment combinations. This is not surprising, since TOC removals in complex water/wastewater matrices are usually poor and inefficient as compared to pure water samples. It should be mentioned here that the TOC contribution of the 2 mg/L TX-45 in the SW, TW and WW samples was relatively minor (10-20%) that could not have affected the TOC removal considerably.

Table 4.4: Comparison of percent TOC removals efficiencies obtained after nZVAl/HP, nZVAl/PS and nZVAl/PMS treatment of TX-45 in SW, WW and TW samples. Experimental Conditions: TX-45= 2 mg/L; nZVAl=1 g/L; HP, PMS=0.25 mM; PS=0.50 mM; pH=3; T=25°C.

	TOC Removals (%)		
Treatment System	**SW**	**WW**	**TW**
nZVAl/HP	2	16	-
nZVAl/PS	-	21	-
nZVAl/PMS	22	22	6

4.4 Changes in Acute Toxicity and Genotoxic Activity

The presence of common organic and inorganic components in water and wastewater could affect the performance of AOPs in micropollutant removal Trovó et al. (2009). Particularly the nature and type of degradation products and as a consequence the ecotoxicological behavior during and after treatment might differ. Considering that the degradation and toxicity pattern of TX-45 will be affected by the characteristics of the water/wastewater sample, changes in acute and genotoxicity were examined during its treatment with nZVAl/PS in DW and SW with different battery test using organisms of different trophic levels, such as the photobacteria *V. fischeri* selected as decomposers and freshwater green microalgae *P. subcapitata* selected as producers. Toxicity tests were conducted under following conditions; TX-45=2 mg/L; nZVAl=1 g/L; PS=0.50 mM; pH=3; T=25°C and t=120 min.

Taking into account the direct application of nZVAl in water/wastewater treatment technologies, Al release (into the environment) is inevitable and hence the assessment of its concentration in the reaction medium is very important. In the present study, Al^{3+} dissolution profiles were also followed during nZVAl/PS treatment of TX-45 in DW and SW. Al^{3+} release occurred continuously throughout the treatment period, increasing gradually without evidence of an induction period at any stage of the oxidation reaction. During nZVAl/PS oxidative treatment of TX-45 in DW and SW, Al^{3+} concentration reached a maximum value of approximately 4.0 mg/L at the end of 120 min. The US EPA has listed Al under the secondary drinking water standards with

a maximum contaminant level of 0.2 mg/L and therefore dissolved Al has to be removed from the treated effluent samples by a coagulation + precipitation process (Bokare and Choi, 2009). Considering this limit value, in the present study the final pH of the reaction solutions was increased with NaOH solutions to 6.5-7.0 for Al precipitation and Al ions were removed from aqueous solutions in the form of $Al(OH)_3$ precipitate. The remaining Al concentrations were determined via atomic absorption spectrometry and found to be < 0.02 mg/L. Under these circumstances, the bulk Al concentration was reduced to below the maximum allowable amount of Al in drinking water and its interference with the toxicity and genotoxicity results was entirely eliminated.

It has already been documented that advanced oxidation may result in the formation of some degradation intermediates being more inhibitory/toxic than the original pollutant. Due to progressive shortening of the ethoxylate chain, lower ethoxy chain APEs, carboxylated products and finally complete deethoxylated APs such as NP and OP are formed.

4.5 Acute Toxicity

4.5.1 Biotox (*Vibrio fischeri*) test conducted in DW and SW

Biotox tests were conducted with pure water (data are shown in Table B.1) and raw surface water (data are shown in Table B.2), according to the principles recommended by the (ISO 11348-3:2008). **Figure 4.12** presents percent relative inhibition values before (t=0) and during nZVAl/PS treatment of TX-45 in DW and SW. As shown in **Figure 4.12**, the original TX-45 did not cause substantial inhibition towards *V. fischeri*; however, exerted different toxic behavior in DW and SW. The original relative inhibition values for 2 mg/L TX-45 were obtained as 15% and 6% in DW and SW, respectively. The inhibitory effect of TX-45 towards *V. fischeri* fluctuated during nZVAl/PS treatment in DW ultimately resulting in a slightly higher toxicity value (26% relative inhibition) after 120 min. From **Figure 4.12** it is also evident that in SW, the untreated TX-45 showed an initial increase in relative inhibition from 6% to 20% during first 60 min of nZVAl/PS treatment. At the end of 120 min treatment, the inhibitory effect decreased to practically non-toxic levels (<8%).

The increase in relative inhibition during the treatment might be attributed to the generation of transformation products exerting higher toxicity than TX-45. Karci et al. (2013) evidenced enhancing the relative inhibition at the first stage and then decreasing, on *V. fischeri* test for APEO treatment process with hydroxyl radicals. Also recent study conducted from Olmez-Hanci et al. (2015) display same *V. fischeri* sensitivity results during TX-45 removal by peroxymonosulfate/UV-C process.

According to results, it is found that toxicity of TX-45 in DW is higher than SW. Similarly, Hernando et al. (2007) showed 4-nonylplenol is more toxic in distilled water than seawater on *V. fischeri*.

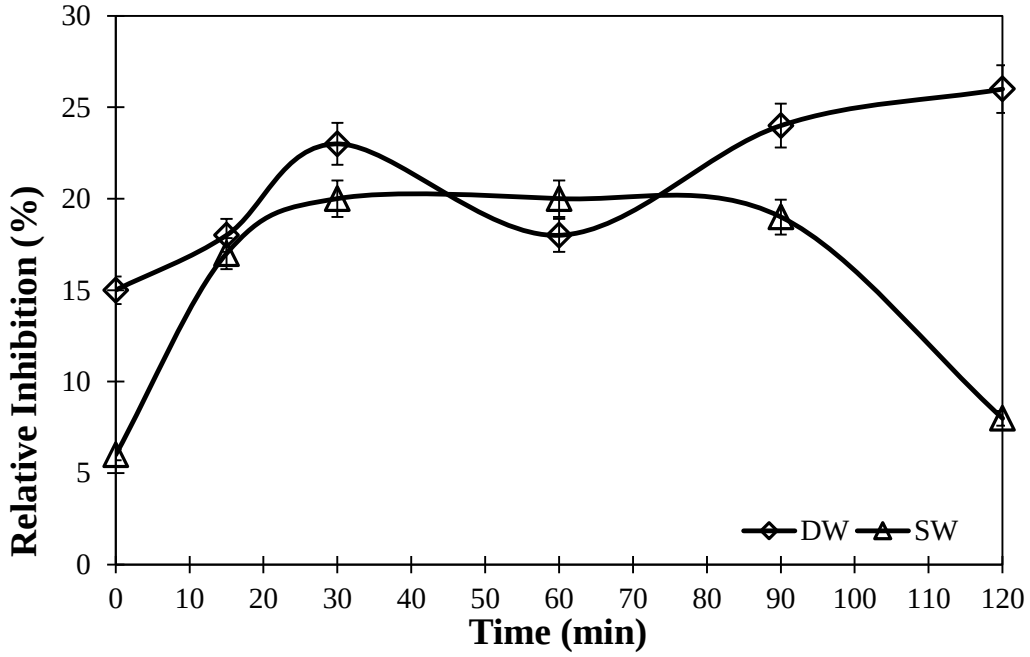


Figure 4.12: Evolution of percent *V. fischeri* relative inhibition rate of the original and nZVAl/PS treated TX-45 samples in distilled water (DW) and raw surface water (SW). Experimental Conditions: TX-45=2 mg/L; nZVAl=1 g/L; PS=0.50 mM (96.0 mg/L); pH=3; T=25°C.

4.5.2 Growth inhibition test with green microalgae *Pseudokirchneriella subcapitata* (formerly known as *Selenastrum capricornutum*)

The algal growth inhibition test using *P. subcapitata* was performed by measuring the fluorescence of biomass of algae at DW (data are shown in Table B.3) and SW (data are shown in Table B.4) samples according to the principles recommended by the (ISO 8692: 2012). The percent relative inhibition values of TX-45-spiked DW and SW samples towards *P. subcapitata* were found to be 35% and 39% for original TX-45,

respectively **(Figure 4.13)**. For nZVAl/PS treatment of TX-45 in DW, the relative inhibition of TX-45 towards *P. subcapitata* originally being 35% increased to 52% after 30 min and continued to increase to 63% after 60 min. Beyond this treatment period, the acute inhibitory effect of the reaction solution decreased down to 40% that is close to that of the original TX-45 solution after 120 min. For nZVAl/PS treatment of TX-45 in SW, an increase in cell growth inhibition from 39% to 52% after 15 min was followed by a decrease to 33% after 60 min. After 120 min treatment, the acute toxic effect towards *P. subcapitata* decreased to 25%. The toxicity profile (increasing and decreasing trend of acute toxicity) observed during nZVAl/PS treatment of TX-45 in DW and SW could speculatively be due to the formation and subsequent disappearance of degradation products being more toxic than TX-45.

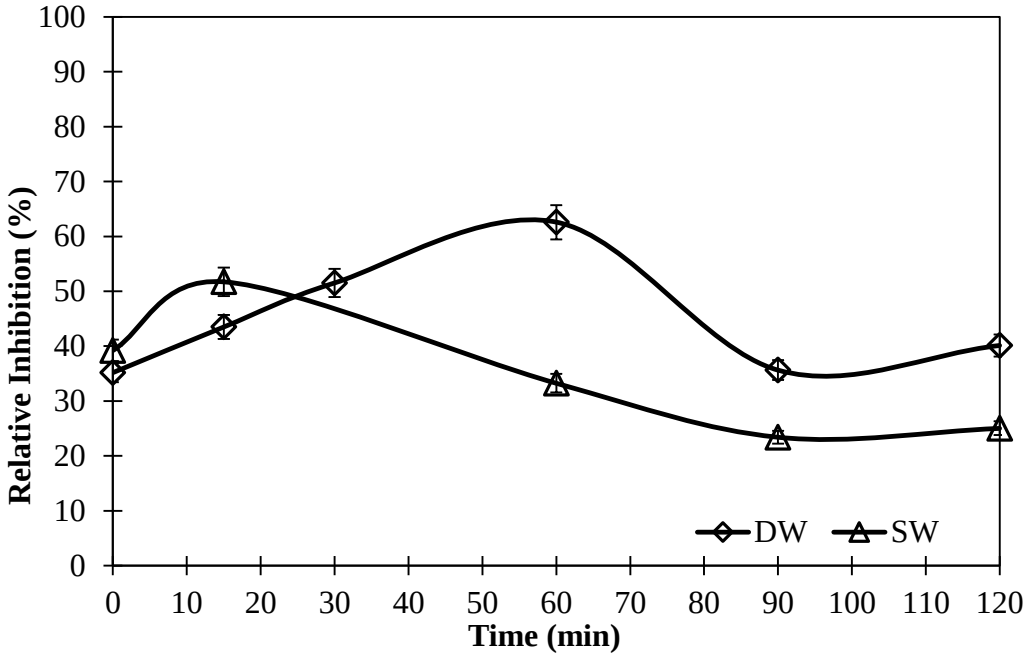


Figure 4.13: Evolution of percent *P.subcapitata* relative inhibition rate of the original and nZVAl/PS treated TX-45 samples in distilled water (DW) and raw surface water (SW). Experimental Conditions: TX-45=2 mg/L; nZVAl=1 g/L; PS=0.50 mM (96.0 mg/L); pH=3; T=25°C.

4.5.3 Comparison of the response of the test organisms and nZVAl/PS treatment process

From the obtained results it could be also concluded that the inhibitory effect induced by TX-45 and its degradation products differed in the DW and SW samples before and throughout nZVAl/PS treatment as well. Moreover, the selected test organisms (*V.*

fischeri, *P. subcapitata*) might exhibit different sensitivities towards TX-45 and its degradation products.

Figure 4.14 displays comparison of the two toxicity test results. It could be mention that the most sensitive organism to TX-45 and its degradation products was *P. subcapitata*, which showed inhibition between 35-63% in DW and 23-52% in SW during 120 min treatment. However, non-toxic levels (<8%) was achieved for *V. fischeri* after 120 min treatment in SW and max 26% in DW.

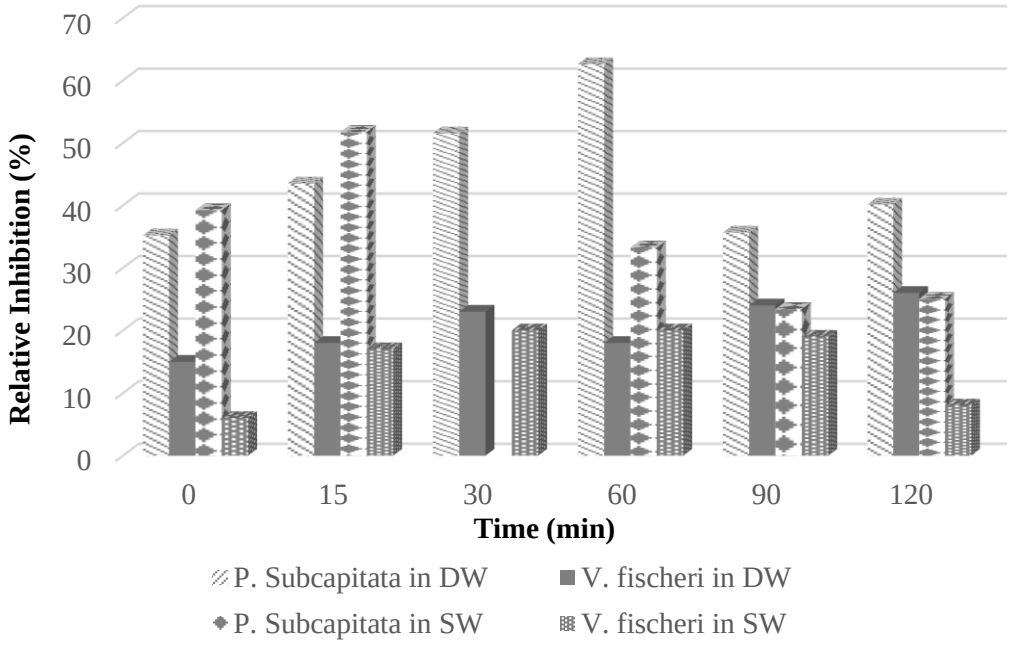


Figure 4.14: Comparison of the percent changes in inhibition rate of the *P.Subcapitata* and *V.fischeri* organisms and nZVAl/PS treated TX-45 samples in distilled water (DW) and raw surface water (SW). Experimental Conditions: TX-45= 2 mg/L; nZVAl=1 g/L; PS=0.50 mM (96.0 mg/L); pH=3; T=25°C.

4.6 Genotoxic Toxicity

The umuC assay responds specifically to genotoxic compounds that cause DNA damages. For the detection of genotoxic effects caused by metabolites, the test is also performed in presence of a rat liver extract that can transform indirect genotoxicants to metabolites that are DNA damaging compounds (Karci et al. 2014; Frassinetti et al. 2011). In the present study, the umuC assay was only conducted in the absence of the rat liver extract.

Figure 4.15 presents the induction ratios obtained for the raw and nZVAl/PS-treated TX-45 solutions in DW under the above mentioned reaction conditions (data are shown in Tables C.1-C.3). As is evident in **Figure 4.14**, both raw and nZVAl/PS-treated TX-45 solutions had no genotoxic activity according to the umuC test results without S-9 activation, since the induction ratio of 1.5 defined by the International Standard Organization (ISO) guideline as the threshold of genotoxic effect (ISO 13829). Only for the 1:1.5 dilution ratio of the nZVAl/PS-treated TX-45 an induction ratio being close to 1.5 was calculated. As mentioned in the genotoxicity test procedure, a growth factor <0.5 that represents 50% inhibition of biomass growth, was considered to be indicative of samples being cytotoxic. The growth factors calculated in the present study demonstrated that neither the original TX-45 nor the effluent after nZVAl/PS treatment were cytotoxic. Considering the inhibitory and estrogenic effect of biotransformation products of APEOs, determination of genotoxicity, that is known to correlate well with carcinogenesis, is of vital importance in order to ensure the ecotoxicological safety of the proposed AOPs.

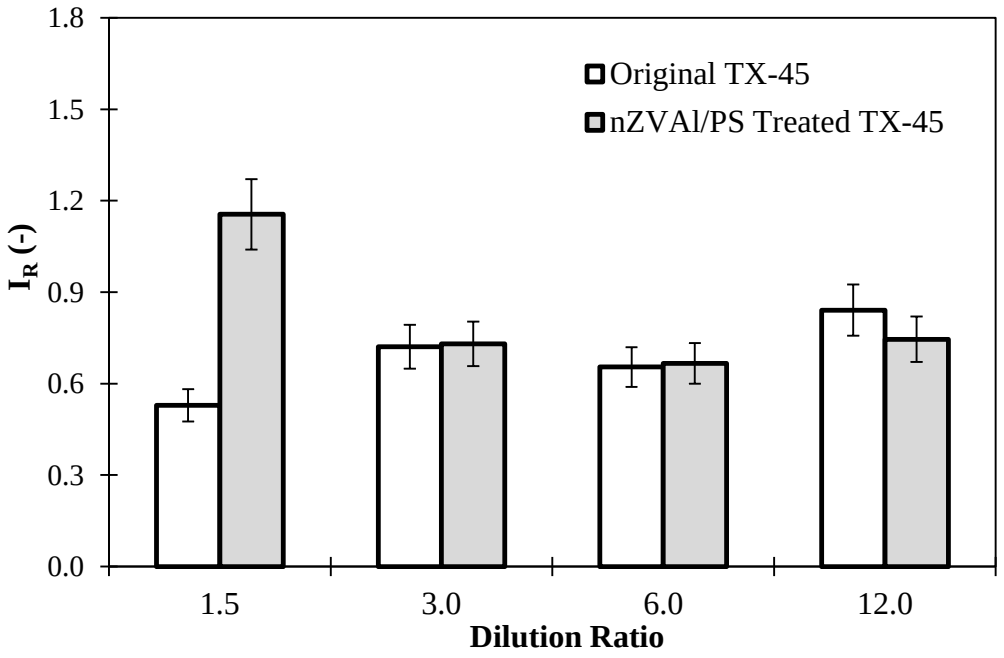


Figure 4.15: Genotoxic effects of original and nZVAl/PS treated TX-45 samples in distilled water (DW) and raw surface water (SW). Experimental Conditions: TX-45= 2 mg/L; nZVAl=1 g/L; PS=0.50 mM (96.0 mg/L); pH=3; T=25°C.

5. CONCLUSIONS AND RECOMMENDATIONS

In the present study, activation of hydrogen peroxide (HP), persulfate (PS) and peroxymonosulfate (PMS) with nanoscale zero valent aluminum (nZVAl; 1 g/L) particles was comparatively investigated for the treatment of a commercially important octylphenol polyethoxylate type nonionic surfactant, namely Triton™ X-45 (TX-45; 2 mg/L), at pH 3 for 120 min. TX-45 abatement was examined in distilled water (DW) as well as in various real water and wastewater matrices including raw surface water (SW), treated domestic wastewater (WW) and tap water (TW). The conclusions of this work are given below;

1. TX-45 treatment without HP, PS and PMS activation -in the absence of nZVAl- resulted in TX-45 removals in the range of 5-38%.
2. Only 22% TX-45 removal was achieved for the nZVAl/O_2/H^+ treatment system in the absence of oxidant.
3. HP, PS and PMS activation with nZVAl greatly enhanced the degradation rates of TX-45 resulting in complete TX-45 removal with nZVAl/PMS and nZVAl/PS combinations in 60 min and 90 min treatment, respectively. For the nZVAl/HP treatment combination 76% TX-45 removal could be achieved (TX-45=2 mg/L; nZVAl=1g/L; HP and PMS=0.25 mM; PS=0.50 mM; pH 3).
4. The environmental characteristics of the water/wastewater matrix (its inorganic and organic matter content) affected the obtained TX-45 removals considerably. The treatment efficiencies of the nZVAl/oxidant combinations followed the decreasing order of nZVAl/PMS ≈ nZVAl/PS > nZVAl/HP in DW, whereas the most efficient system was nZVAl/PMS followed by nZVAl/HP and nZVAl/PS in SW and WW samples.
5. No correlation between the TX-45 removals and oxidant consumption rates was evident.
6. The inhibitory effect of TX-45 towards *V. fischeri* fluctuated during nZVAl/PS treatment in the DW sample ultimately resulting in a slightly higher toxicity value (26% relative inhibition) than that of the original (untreated) TX-45 (%15 relative inhibition) sample at the end of treatment. On the other hand, in the

SW sample, the original inhibitory effect was decreased to practically non-toxic levels (<8%) after 120 min treatment.

7. The inhibitory effect towards *P. Subcapitata* observed in the DW and SW samples after the nZVAl/PS treatment of TX-45 was not practically different from that of the untreated TX-45.
8. All acute toxicity results showed that the only factor causing toxicity was not TX-45, but could be formation and subsequent disappearance of some oxidation products.
9. According to the UMU-Chromo test results, the original and nZVAl/PS-treated TX-45 samples neither exhibit cytotoxic nor genotoxic effects.

It was observed that nZVAl/PS, nZVAl/PMS and nZVAl/HP process can be recommended as effective treatment system in reducing TX-45 from aqueous solution also could lead to completely removal from water matrixes.

Overall speaking, the toxicity test results revealed that the most sensitive organism to TX-45 and its degradation products was *P. Subcapitata*, whereas *V. fischeri* was the least sensitive organism so, this study has highlighted that the use of a battery of tests involving representatives from different trophic levels together with genotoxicity test is very crucial to decide whether the application of nZVAl/oxidant treatment systems are ecotoxicologically safe.

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APPENDICES

APPENDIX A: Effect of HP, PS and PMS oxidation and nZVAl/PH, NZVAl/PS and nZVAl/PMS treatment process on aqueous TX-45 removal.

Table A.1: Triton X-45 removals observed during mere HP, PS and PMS oxidation experiments. Experimental Conditions: TX-45= 2 mg/L; HP, PS, PMS =0.25 and 0.50 mM; pH=3; T=25℃.

Time	HP		PS		PMS	
	0.25	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**
0	1.93	2.00	1.92	2.00	1.98	2.00
5	1.83	1.84	1.93	1.67	1.92	1.97
10	1.84	1.84	1.94	1.69	1.9	1.92
15	1.83	1.85	1.94	1.66	1.86	1.85
20	1.83	1.90	1.95	-	1.86	1.83
25	1.89	-	1.89	1.58	1.87	1.79
30	1.83	1.90	1.9	1.6	1.77	1.74
40	1.82	-	1.85	1.52	1.7	1.72
50	1.82	-	1.92	-	1.64	1.72
60	1.79	1.90	1.93	1.54	1.57	1.68
90	1.76	1.90	1.75	1.59	1.33	1.66
120	1.72	1.90	1.72	1.6	1.23	1.45

Table A.2: pH changing during mere HP, PS and PMS oxidation experiments.

Time	Oxidant Consumption (mM)						pH Changing					
	HP		PS		PMS		HP		PS		PMS	
	0.25	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**
0	0.26	0.47	0.21	0.47	0.28	0.51	3.06	3.1	3.04	3.13	3.14	3.12
120	0.25	0.46	0.20	0.44	0.27	0.48	3.01	3.08	3.03	3.13	3.15	3.12

Table A.3: Triton X-45 removals observed during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments. Experimental Conditions: TX-45= 2 mg/L; HP, PS, PMS =0.25 and 0.50 mM; nZVAl=1 g/L; pH=3; T=25°C.

Time	nZVAl/HP		nZVAl/PS		nZVAl/PMS		nZVAl (1g/L)
	0.25	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	
0	2.00	1.88	2.00	1.92	2	1.92	2.00
5	1.98	1.83	-	1.38	1.61	1.73	1.93
10	1.98	-	1.92	1.35	1.51	1.66	1.95
15	1.97	1.76	1.94	1.30	1.33	1.66	1.83
20	1.96	-	1.93	1.24	1.32	1.63	1.84
25	1.95	1.74	1.99	1.22	1.32	1.61	1.90
30	1.94	1.72	1.98	1.15	1.29	1.45	1.89
40	1.97	1.70	1.96	0.89	0.9	0.9	1.86
50	1.94	1.39	1.94	0.54	0.5	0.74	1.82
60	1.24	1.45	1.67	0.09	0	0.644	1.89
90	1.08	1.20	1.06	0.00	0	0	1.84
120	0.49	0.90	0.29	0.00	0	0	1.56

Table A.4: pH changing during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments.

Time	Oxidant Consumption (mM)						pH Changing					
	HP		PS		PMS		HP		PS		PMS	
	0.25	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**	**0.25**	**0.50**
0	0.25	0.54	0.22	0.48	0.28	0.51	3.163	2.90	3.14	3.09	3.20	3.17
120	0.18	0.01	0.15	0.41	0.22	0.45	3.480	2.978	3.95	3.15	3.46	3.32

Table A.5: Triton X-45 removals observed during nZVAl/HP, nZVAl/PS and nZVAl/PMS oxidation experiments in SW, TW and WW. Experimental Conditions: TX-45=2 mg/L; HP and PMS =0.25 and PS=0.50 mM; nZVAl=1 g/L; pH=3; T=25℃.

Time	nZVAl/HP			nZVAl/PS			nZVAl/PMS		
	SW	WW	TW	SW	WW	TW	SW	WW	TW
0	1.9	1.9	1.9	1.93	1.98	1.9	1.83	1.97	1.85
5	-	-	1.29	-	1.98	1.75	1.25	1.61	1.57
10	1.56	1.55	1.22	1.93	1.97	1.77	1	1.31	1.5
15	-	-	-	-	-	-	0.95	1.23	1.49
20	1.43	1.56	1.06	1.83	1.97	1.64	0.93	1.21	1.47
25	-	-	-	-	-	-	0.79	1.12	1.44
30	1.19	1.53	1.1	1.85	1.79	1.57	0.69	0.99	1.4
40	1.09	1.16	0.9	1.67	1.78	0.8	0.59	0.25	1.07
50	-	-	-	-	-	-	0.45	0.1	0.96
60	1.06	1.16	0.6	1.6	1.82	0.5	0.26	0.03	0.71
90	0.01	1.1	0.00	1.18	1.85	0.3	0.27	0	0.29
120	0.3	0.8	0.00	0.8	1.74	0	0.12	0	0.03

APPENDIX B: Acute toxicity test results data.

- ✓ **Acute toxicity test with photobacteria *V. fischeri.***

Table B.1: Luminescence intensity of *V. fischeri* after 120 min treatment process in distilled water.

Time (min)	T= 0' min	T= 0 min	T= 15 min
Control(DW)	132982	107817	71770
Control(DW)	131246	105730	71610
Control(DW+TS)	135957	106499	69188
Control(DW+TS)	127276	100764	64592
0	134154	104331	61681
0	126182	102016	59711
15	125894	97816	56990
15	125424	99171	60477
30	125390	98744	55930
30	127687	98759	54801
60	124658	98371	58344
60	124664	95782	58685
90	120142	92439	54618
90	123269	92548	54442
120	123338	92506	53201
120	122017	90379	52609

Table B.2: Luminescence intensity of *V. fischeri* after 120 min treatment process in raw surface water.

Time (min)	T= 0' min	T= 0 min	T= 15 min
Control(DW)	104636	91338	65289
Control(DW)	103621	91839	65651
Control(DW+TS)	105495	83501	54636
Control(DW+TS)	103337	81463	56814
0	107048	89555	60500
0	104776	86135	62471
15	101465	81236	54610
15	102926	81217	54247
30	102098	87406	51078
30	104373	70849	54203
60	102499	80806	51888
60	103109	80802	53431

Table B.2 (continued): Luminescence intensity of *V. fischeri* after 120 min treatment process in raw surface water.

90	99011	75732	53391
90	99327	70501	52332
120	104668	83903	60810
120	106330	84212	59164

✓ **Acute toxicity test with freshwater green microalgae *P. Subcapitata***

Table B.3: Biomass readings of the test samples for 72 h incubation period after 120 min treatment in distilled water.

Time (min)	Day 0 Biomass reading	Day 1 Biomass reading	Day 2 Biomass reading	Day 3 Biomass reading	Day 3 Growth Rate (μ)	Day 3 Average (μ)	Day 3 Inhibition Iμi (%)
Control (culturing)	0.001	0.015	0.021	0.068	0.058604274	0.045954187	0
Control (culturing)	0	0.016	0.014	0.055	-		
Control (culturing)	0.006	0.011	0.027	0.066	0.033304101		
Control (culturing+TS)	0	0.012	0.018	0.058	-	-	-
Control (culturing+TS)	0	0.054	0.042	0.061	-		
Control (DW)	0	0.007	0.014	0.015	-	0.003995584	0
Control (DW)	0.003	0.017	0.02	0.004	0.003995584		
Control (DW)	0	0.049	0.014	0	-		
Control (DW+TS)	0.015	0.01	0.029	0	-	0	0
Control (DW+TS)	0.078	0.044	0.039	0.015	-		
Control (DW+TS)	0.015	0.011	0.012	0	-		
0	0.058	0.076	0.063	0.081	0.004638974	0.002589208	35
0	0.101	0.125	0.102	0.105	0.000539442		
15	0.074	0.09	0.081	0.084	0.00176044	0.002258352	43
15	0.082	0.115	0.095	0.1	0.002756263		
15	0.076	0.134	0.131	0.128	-		
30	0.214	0.212	0.183	0.183	-	0.001937022	51
30	0.222	0.24	0.232	0.223	6.24221E-05		
30	0.076	0.071	0.091	0.1	0.003811623		

Table B.3 (continued): Biomass readings of the test samples for 72 h incubation period after 120 min treatment in distilled water.

60	0.146	0.146	0.166	0.162	0.001444302		
60	0.146	0.139	0.164	0.147	-	0.001494551	63
60	0.17	0.184	0.217	0.19	0.0015448		
90	0.062	0.082	0.091	0.081	0.003712705		
90	0.154	0.219	0.178	0.165	-	0.002571005	36
90	0.286	0.322	0.32	0.317	0.001429305		
120	0.165	0.196	0.204	0.196	0.002391239		
120	0.118	0.147	0.152	0.141	0.002473268	0.00239183	40
120	0.116	0.146	0.141	0.137	0.002310982		

Table B.4: Biomass readings of the test samples for 72 h incubation period after 120 min treatment in raw surface water.

Time (min)	Day 0 Biomass reading	Day 1 Biomass reading	Day 2 Biomass reading	Day 3 Biomass reading	Day 3 Growth Rate (μ)	Day 3 Average (μ)	Day 3 Inhibition Iμi (%)
Control (culturing)	0.001	0.014	0.013	0.013	0.035624297	0.0246234	0
Control (culturing)	0.015	0.023	0.037	0.04	0.013622629		
Control (culturing)	0	0	0.01	0.019	-		
Control (culturing+TS)	0.006	0.012	0.02	0.028	0.02139507	0.0213950	0
Control (culturing+TS)	0	0.013	0.006	0.011	-		
Control (DW)	0.064	0.073	0.078	0.09	0.004735091	0.0100544	0
Control (DW)	0.013	0.024	0.033	0.038	0.014897733		
Control (DW)	0.032	0.04	0.044	0.046	0.005040354		
Control (DW+TS)	0.03	0.047	0.045	0.064	0.010523413	0.0067685	0
Control (DW+TS)	0.068	0.072	0.075	0.102	0.00563146		
Control (DW+TS)	0.089	0.066	0.107	0.12	0.004150769		
0	0.024	0.029	0.048	0.038	0.006382393	0.0130012	39
0	0.042	0.056	0.072	0.066	0.006277571		
0	0.029	0.045	0.055	0.029	-		
15	0.032	0.05	0.045	0.037	0.002016417	0.0103248	52
15	0.042	0.061	0.073	0.054	0.003490478		
15	0.042	0.065	0.076	0.063	0.00563146		
30	0.008	0.021	0.04	0.05	0.02545252	0.0238083	-
30	0.028	0.048	0.057	0.071	0.0129232		
30	0.005	0.027	0.033	0.054	0.0330492		

Table B.4 (continued): Biomass readings of the test samples for 72 h incubation period after 120 min treatment in raw surface water.

60	0.019	0.027	0.06	0.063	0.0166485		
60	0.063	0.129	0.088	0.094	0.0055577	0.014278894	33
60	0.012	0.022	0.039	0.053	0.0206303		
90	0.061	0.081	0.105	0.132	0.0107212		
90	0.026	0.045	0.059	0.085	0.0164521	0.016383759	23
90	0.015	0.037	0.052	0.073	0.0219779		
120	0.027	0.057	0.064	0.104	0.0187299		
120	0.051	0.067	0.095	0.124	0.0123396	0.016038146	25
120	0.034	0.048	0.094	0.116	0.0170448		

APPENDIX C: Genotoxicity test results data.

Table C.1: Genotoxicity results first reading in Plate B in 600nm wavelength.

Time	**1:1.5**				**1:3**				**1:6**			
Original	0.061	0.058	0.055	0.062	0.061	0.06	0.061	0.06	0.061	0.064	0.063	0.056
120	0.081	0.08	0.078	0.083	0.089	0.096	0.086	0.087	0.089	0.088	0.1	0.089

	Negative Control											
Control Samples	0.09	0.074	0.073	0.066	0.068	0.067	0.068	0.07	0.067	0.063	0.068	0.066
	0.058	0.066	0.073	0.063	0.073	0.056	0.042	0.043	0.041	0.042	0.044	0.042
	Positive Control		**Solvent Control**				**Blank**					

Table C.2: Genotoxicity results second reading in Plate B in 600nm wavelength.

Time	**1:1.5**				**1:3**				**1:6**			
Original	0.096	0.09	0.09	0.1	0.096	0.093	0.094	0.097	0.087	0.1	0.097	0.082
120	0.081	0.08	0.078	0.083	0.089	0.096	0.086	0.087	0.089	0.088	0.1	0.089

	Negative Control											
Control Samples	0.208	0.148	0.143	0.106	0.105	0.101	0.104	0.108	0.1	0.09	0.105	0.093
	0.051	0.098	0.142	0.093	0.146	0.087	0.042	0.043	0.043	0.041	0.043	0.04
	Positive Control		**Solvent Control**				**Blank**					

Table C.3: Genotoxicity results first reading in Plate C in 420nm wavelength.

Time	1:1.5				1:3		1:6			1:12		
Original	0.088	0.086	0.086	0.097	0.092	0.092	0.099	0.086	0.086	0.099	0.094	0.093
120	0.099	0.094	0.095	0.09	0.09	0.093	0.09	0.088	0.088	0.088	0.095	0.095

	Negative Control											
Control Samples	0.132	0.147	0.168	0.114	0.104	0.098	0.098	0.125	0.098	0.11	0.114	0.101
	0.11	0.14	0.165	0.103	0.1	0.103	0.071	0.074	0.071	0.104	0.072	0.073
	Positive Control		**Solvent Control**				**Blank**					

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