ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

ASSESSMENT OF PERSULFATE (PS)/UV-C PROCESS FOR DRINKING WATER TREATMENT

M.Sc. THESIS

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Department of Environmental Engineering

Environmental Science, Engineering and Management Programme

JANUARY 2023

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

İÇME SUYU ARTIMI PERSÜLFAT (PS)/UV-C PROSESİNİN DEĞERLENDİRİLMESİ

YÜKSEK LİSANS TEZİ

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Shahin SHAHKAR, a M.Sc. student of ITU Graduate School student ID 501181729 successfully defended the thesis entitled "ASSESSMENT OF PERSULFATE (PS)/UV-C PROCESS FOR DRINKING WATER TREATMENT", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,
My love,
and my affectionate professor.

FOREWORD

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ABBREVIATIONS

AO7 : Acid Orange 7
AOPs : Advanced Oxidation Processes
BTEX : Benzene, toluene, ethylbenzene, xylenes
COD : Chemical Oxygen Demand
DBPs : Disinfection Byproducts
DOC : Dissolved Organic Carbon
EE/O : Electrical Energy/Order
$HO^{\bullet}$: Hydroxyl Radical
$HO_2^{\bullet}$: Hydroperoxyl Radical
ISCO : In situ chemical oxidation
M.O : Methyl Orange
$O_2^{\bullet-}$: Superoxide Anion Radical
PAHs : Polycyclic Aromatic Hydrocarbons
PCB : Polychlorinated biphenyls
PMS : Peroxymonosulfate
PS : Persulfate
PSD : Particle Size Distribution
$RO^{\bullet}$: Alkoxyl Radical
$ROO^{\bullet}$: Peroxyl Radical
$SO_4^{\bullet-}$: Sulfate Radical
SR-AOPs : Sulfate Radical Based Advanced Oxidation Processes
SUVA : Specific Ultraviolet Absorbance
TDS : Total Dissolved Solid
TOC : Total Organic Carbon
UV_{254} : Ultraviolet absorbance at 254 nm
UV-A : Ultraviolet A
UV-B : Ultraviolet B
UV-C : Ultraviolet C
VUV : Vacuum Ultraviolet

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SUMMARY

In recent years, there has been a significant amount of effort placed on the development of advanced oxidation processes that are based on sulfate radicals. $SO_4^{\bullet-}$ offers several advantages over $OH^{\bullet}$, including a high redox potential (2.5 - 3.1 V), which is significantly higher than the redox potential of $OH^{\bullet}$ (1.8 -2.7 V), excellent selectivity, and a long half-life (30 to 40 s). In addition, $SO_4^{\bullet-}$ is capable of successfully reacting with the contaminants of interest across a broad pH range (ranging from 2 to 8). $SO_4^{\bullet-}$ can break down refractory organic contaminants in water, turning them into carbon dioxide, water, inorganic salt, and other molecules with a smaller molecular compounds. Peroxymonosulfate (PMS) and persulfate (PS) can be converted into these radicals via catalytic, radiation, or thermal activation, among other mechanisms.

The most significant component that determines water quality is the amount of organic matter that is present in the water. Scientists have spent a significant amount of time and effort looking into the effects that organic matter has on conventional drinking water treatment plants over the many years that have passed. The presence of organic matter in water can lead to a variety of unwanted effects, including changes in the color, taste, and odor of drinking water plants; negative variation in the water's overall microbiological quality; the requirement for the installation of additional treatment units; and so on. As a result of this, the removal of organic matter is becoming an increasingly crucial practice with each passing day.

This research focuses primarily on the enhancement of UV-C tertiary treatment using sulfate radical based photochemical Advanced Oxidation Processes (SR-AOPs). This is done in order to treat effectively (mineralize) the organic carbon that is naturally present in raw water, the coagulation-flocculation effluent, the filter effluent and the final effluent.

Within the thesis, experimental research was carried out to investigate the ways in which the initial oxidant concentration influences the effectiveness of the process. Total organic carbon (TOC) removal efficiency, residual oxidant concentration, and UV254 modification were among the data used to establish the procedures' guiding principles. Through the utilization of the PS/UV-C process, a comparison was made on the practicability of using PS oxidant for TOC removal.

In terms of determining the effect of initial concentration of oxidant on the mineralization processes, research was conducted using samples that came from a drinking water treatment plant. Each sample had an initial TOC value, and initial value, and the initial PS concentration ranged from 0.1-1.0 mM. The research was conducted in order to determine the effect that initial concentration of oxidant had on the mineralization processes. During the reaction, evaluations of TOC, PS, pH, and UV254 are carried out on samples that have been taken at predefined time intervals

(the initial, the 15th minute, the 30th minute, and the 60th minute).
As a result of this research, according to the total organic carbon (TOC) removal evaluations, the persulfate/UV-C process is most efficient when used in the raw water coming to the drinking water treatment plant.
In conclusion, it was determined that sulphate radical-based photochemical advanced oxidation techniques, when applied to natural or treated waters under the suitable reaction circumstances, are capable of efficiently removing organic carbon.

İÇME SUYU ARTIMI PERSÜLFAT (PS)/UV-C PROSESİNİN DEĞERLENDİRİLMESİ

ÖZET

Su kalitesini belirleyen en önemli bileşen suda bulunan organik madde miktarıdır. Organik maddenin geleneksel içme suyu arıtma tesisleri üzerindeki etkileri bilim insanları tarafından uzun zamandır araştırılmaktadır. Suda organik madde bulunması, içme suyunun renginde, tadında ve kokusunda istenmeyen etkilere yol açabilir. Bunlar suyun genel mikrobiyolojik kalitesinde azalma, ek arıtma ünitelerinin kurulum gerekliliği, ve benzeridir. Bunun sonucu olarak da organik madde giderimi her geçen gün önemi artan bir uygulama haline gelmektedir.

"Oksidasyon yöntemi" terimi, son derece yüksek oksidasyon potansiyeline sahip serbest radikallerin oluşmasına dayanan prosesleri ifade eder. Bu yöntemler kullanılarak, ilgili kirleticinin bir kısmı, oksidasyon eylemi yoluyla daha az toksik hale getirilir ve/veya kirletici, biyolojik bozunmaya daha yatkın olan oksidasyon ara maddelerine dönüştürülür. Bazı durumlarda, kirletici tamamen oksidasyon son ürünlerine mineralize edilir (CO_2 ve H_2O).

Son yıllarda İOP'lerinin çok çeşitli organik ve inorganik kirleticilerin arıtımında kullanımı derinlemesine araştırılmış ve proseslerin modellenmesi ve optimizasyonu, kirleticilerin giderim mekanizmaları ve prosesin etkinliğini etkileyen faktörlerin tümü incelenmiştir. Bu yenilikler, en yaygın olanı titanyum dioksit (TiO_2) olan metal katalizörlerin veya ultraviyole (UV) radyasyonun hidrojen peroksit, peroksimonosülfat veya persülfat gibi oksidanlarla kombinasyonu olan çok çeşitli fotokatalizörlerin kullanımına dayanmaktadır. Hidroksil radikallerinin üretimine dayanan İOP'ler en yaygın olanlardır.

Son yıllarda, sülfat radikallerine dayanan ileri oksidasyon proseslerinin geliştirilmesi için çalışmalar yapılmaktadır. Bunun nedeni, diğer üçüncül işlemlere (SR-İOP'ler) göre sahip oldukları faydalara ek olarak, bu işlemlerin yüksek oksidasyon potansiyelinden kaynaklanmaktadır. $SO_4^{\bullet-}$, $OH^{\bullet}$'nin redoks potansiyelinden (1,8-2,7 V) önemli ölçüde daha yüksek redoks potansiyeline (2,5-3,1 V), mükemmel seçicilik ve uzun yarı ömüre sahıptir (30 ila 40 s). Ek olarak, $SO_4^{\bullet-}$, geniş bir pH aralığında (2 ila 8 arasında değişen) ilgili kirleticilerle başarılı bir şekilde reaksiyona girebilir. $SO_4^{\bullet-}$ sudaki dirençli organik kirleticileri parçalayarak karbondioksit, su, inorganik tuz ve daha küçük moleküler bileşiklere sahip diğer moleküllere dönüştürebilir. Peroksimonosülfat (PMS) ve persülfat (PS), diğer mekanizmaların yanı sıra katalitik, radyasyon veya termal aktivasyon yoluyla bu radikallere dönüştürülebilir. PS, sodyum ve potasyum tuzları olarak bulunabilen simetrik bir oksidandır. Bu tuzlar, yüksek çözünürlüğe ve kararlılığa sahip beyaz kristaller oluşturur. İlgili bilimsel makaleler incelendiğinde, $SO_4^{\bullet-}$ radikal bazlı İOP'lerin içme sularının arıtımında uygulanabilirliğinin detaylıca araştırılmadığı görülmektedir.

SR-İOP'lerin diğer su arıtma teknolojileriyle kombinasyonu da çok ilgi çekicidir ve iyi

bir gelecek projeksiyonu olan bir alandır. Ultrafiltrasyon işlemleriyle kombinasyonu durumunda, sülfat radikalleri ile bir ön işlemin, membranların ömrünü uzatmanın yanı sıra işlemin etkinliğini iyileştirdiği gösterilmiştir. Maliyet ile ilgili olarak, yapılan az sayıda analiz olmasına rağmen, reaktiflerin fiyatı nedeniyle PS ve PMS ile yapılan işlemlerin diğer ileri oksidasyon işlemlerine göre daha pahalı olduğu bilinmektedir. Öte yandan, SR-İOP'lerin büyük ölçekli uygulaması neredeyse yoktur, bu nedenle gerekli çalışmalardan biri, bu oksidasyon yönteminin uygulanabilirliğinin incelenmesidir. Bu teknolojinin uygulanmasının gerekli reaktiflerin azaltılmasına izin vererek oksidasyonu daha uygulanabilir hale getirmesi beklenmektedir. Mikro kirleticileri ortadan kaldırmanın yanı sıra, sülfat radikalleri dezenfeksiyon için de kullanılabilir.

Sülfat radikallerinin yüksek oksidasyon potansiyelleri nedeniyle, son yıllarda atıksu ve içme sularının arıtılması sürecinde kullanımları ile ilgili çalışmalarda artış gözlemlenmektedir. Bu tezde, sülfat radikali ($SO_4^{\bullet -}$) bazlı persülfat (PS)/UV-C fotokimyasal ileri oksidasyon prosesinin organik karbon gideriminde uygulanması incelenmiştir. İlgili deneyler, optimum çalışma koşulları ve proses mekanizmalarını ortaya çıkarmak için çeşitli oksidan konsantrasyonlarında yürütülmüş ve deney sonuçları, toplam organik karbon (TOC) giderimleri dikkate alınarak değerlendirilmiştir. Bu araştırmanın ilk kısmında, araştırmanın amacı ve kapsamı kısaca anlatılmıştır. Ayrıca araştırma kapsamında incelenen ileri oksidasyon prosesi (PS/UV-C), sülfat ve hidroksil radikalleri hakkında bilgiler sunulmuştur. İkinci kısımda ise, organik maddelerin genel özellikleri, doğal sulardaki kaynakları, içme suyunda yarattığı olumsuz etkiler ve içme suyunda organik karbonun gideriminde kullanılan geleneksel arıtma yöntemleri açıklanmıştır. Ayrıca, araştırma kapsamında yapılan deneysel çalışmalarla ilgili ileri oksidasyon prosesleri kısaca özetlenmiştir. Bunların yanı sıra, PS oksidanın özellikleri ve oksidasyon mekanizmaları anlatılmıştır. Bu tez kapsamında kullanılan en önemli deney parametrelerinden olan UV254 absorbansı ile ilgili bilgilere yer verilmiştir.

Üçüncü bölümde, deneysel çalışmalarda kullanılan malzemeler ve yöntemler detaylıca açıklanmıştır. Uygulanan yöntemin, prosedürü ve kullanılan tüm analiz yöntemleri anlatılmıştır. Dördüncü kısımda ise, bu prosesler kullanılarak yapılan deneylerin sonuçları detaylıca sunulmuştur.

Tezin son kısmında, sayısal veriler özetlenmiş ve tüm sonuçlar kısaca değerlendirilmiştir.

Bu araştırmada PS/UV-C Prosesi, ham suda doğal olarak bulunan organik karbonu, dekantör çıkış suyundan, filtre çıkış suyundan ve genel çıkış suyundan etkili bir şekilde arıtmak (mineralize etmek) için uygulanabilirliği denenmiştir.

Bu çalışmada başlangıçtaki oksidan konsantrasyonunun organik karbon giderim verimliliğini nasıl etkilediğini araştırmak için deneysel araştırmalar yapılmıştır. Toplam organik karbon (TOC) giderme verimliliği, deney sonunda kalan oksidan konsantrasyonu ve UV254 absorbans değişimi, çalışmanın yol gösterici ilkelerini oluşturmak için kullanılan parametreler arasındaydı. PS/UV-C prosesinin kullanılmasıyla, TOC giderimi için PS oksidan kullanımının uygulanabilirliği konusunda bir karşılaştırma yapılmıştır.

Oksidanın başlangıç konsantrasyonunun mineralizasyon süreçlerine etkisinin belirlenmesi açısından içme suyu arıtma tesisinden alınan numuneler kullanılarak araştırma yapılmıştır. Deney boyunca PS konsantrasyonu 0,1-1,0 mM aralığında değiştirilmiştir. Oksidanın başlangıç konsantrasyonunun oksidasyon mekanizması üzerindeki etkisini

belirlemek için başlangıç PS konsantrasyonu değiştirilerek deneyler yürütülmüştür. Reaksiyon sırasında önceden belirlenen zaman aralıklarında (0. dakika, 15. dakika, 30. dakika ve 60. dakika) alınan numuneler üzerinde TOC, PS, pH ve UV254 analizleri yapılmıştır.

pH, deney süresince takip edilen önemli parametrelerden birisidir. PS/UV-C deneylerinde, ilk 15 dakikada daha hızlı olmasının yanı sıra, pH'ın, reaksiyon süresi boyunca azaldığı gözlemlenmektedir.

PS/UV-C yöntemleri, gerçek su numunelerine uygulandığında, suyun başarılı bir şekilde mineralleşmesine yol açtı. Gerçek su numunelerinin fotokimyasal arıtılabilirliği ile ilgili çalışmalarda, toplam organik karbonun tamamen uzaklaştırılması için daha uzun arıtma sürelerinin gerekli olduğu bulunmuştur.

Bu araştırmanın neticesinde, toplam organik karbon (TOC) giderimleri değerlendirmesine göre, persülfat/UV-C prosesi, tesise gelen ham suda kullanılırsa en verimli sonuç elde edilir.

Sonuç olarak, sülfat radikali bazlı fotokimyasal ileri oksidasyon yöntemlerinin, ham veya arıtılmış sulara uygun reaksiyon koşullarında uygulandığında, organik karbonu verimli bir şekilde giderebildiği belirlendi.

1. INTRODUCTION

Both the amount of water that is consumed and the amount that is contaminated has significantly increased over the past few decades due to the simultaneous rise in population and industrialisation. This presupposes a decline in both the water quality and the quantity of hydric resources that are available, and as a result, it is anticipated that the globe will face a 40 % global water deficit by the year 2030 [1]. In some areas, lowering the amount of hydric stress could be accomplished through the regeneration and reuse of wastewater, which is a potential viable solution [2].

In order to accomplish this goal, the quality of the water must conform to the requirements established in the relevant legislation or guidelines, which vary depending on the end use of the reclaimed water. In most wastewater treatment plants (WWTP), the water that is released during the secondary treatment process does not meet these criteria; therefore, the water must undergo advanced treatment, also called as tertiary treatment. There is a large variety of tertiary treatments available, and the one that that is is used will depend on the final quality of water that is desired as well as the specific pollutants required to be removed. some options are sedimentation, coagulation/flocculation, membrane technology, biological filters, ionic exchange, adsorption, chemical oxidation, etc [3].

The term "oxidation method" refers to more recent processes of oxidation that are based on the creation of free radicals that have an extremely high potential for oxidation. Using these methods, a portion of the pollutant of interest is rendered less toxic through the action of oxidation and/or the pollutant is converted into oxidation intermediates that are more readily amenable to biodegradation; in some instances, the pollutant is completely mineralized into oxidation end products ($CO_2$and H_2O).

The use of AOPs in the treatment of a wide variety of organic and inorganic pollutants has been investigated in great depth, and the modeling and optimization of processes, the removal mechanisms of pollutants, and the factors that influence the effectiveness of the process have all been reported in great detail. These innovations are based on the

utilization of a wide variety of photocatalysts, the most common of which is titanium dioxide (TiO_2), or the combination of metal catalysts or ultraviolet (UV) radiation with oxidants such as hydrogen peroxide, peroxymonosulfate, or persulfate. AOPs that are based on the production of hydroxyl radicals are the treatments that have recieved the most thought. As seen in Table 1.1, the hydroxyl radical possesses a higher oxidation potential than popular disinfectants such as chlorine, ozone, or permanganate. This is evidenced by the fact that the hydroxyl radical has 2.8 V [4]. Nevertheless, in spite of the fact that SR-AOPs are associated with a number of disadvantages, it is advised that, in order to effectively treatment, SR-AOPs and conventional methods be coupled together [5]. Sulfate radicals have become more the focus of research in recent years. Due to the high oxidation potential of these radicals, it is possible that they will play a key role.

Table 1.1 : Oxidation potential of commonly used oxidants.

Oxidant	Oxidation Potential (V)
Fluorine $[F_2]$	3.0
Hydroxyl radical [HO•]	2.8
Sulfate radical $\left[SO_4 \bullet^{-1}\right]$	2.5-3.1
Ozone $[O_3]$	2.1
Persulfate $\left[S_2O_8{}^{2-}\right]$	2.1
Peroxymonosulfate $\left[HSO_5{}^{-}\right]$	1.8
Hydrogen peroxide $[H_2O_2]$	1.8
Permanganate $\left[MnO_4{}^{-}\right]$	1.7
Chlorine dioxide $[ClO_2]$	3.0
Chlorine $[Cl_2]$	1.4

Using SR-AOPs is more beneficial since the sulfate radical has a longer half-life than the hydroxyl radical and is less impacted by chemicals that induce extension of the reaction time and oxidant consumption. It is clear, after reviewing the relevant scientific articles, that the applicability of SO_4- radical-based AOPs in the treatment of drinking water has not been researched to a great extent.

1.1 Purpose and Inspiration for Study

When all of these factors are taken into consideration, the purpose of the current experimental study, which was motivated by those factors, was to investigate the applicability of AOPs by PS in the treatment of drinking water. It is believed that the present Master of Science thesis is the first of its kind to remove organic carbon from raw water, the coagulation-flocculation effluent, the filter effluent, and the final effluent by applying PS/UV-C treatment combinations.

For the purpose of determining whether or not SR-AOPs are applicable in the process of treating drinking water, a number of oxidation experiments were carried out using raw water, the effluent from coagulation and flocculation, the effluent from the filter, and the final effluent.

1.2 Scope of Thesis

During the research for the thesis, experimental tests were carried out to discover the factors that influence the level of oxidant present at the beginning of the process and how effective it is. Total organic carbon (TOC) removal efficiency, oxidant amount used throughout the operation, and UV_{254} variation were among the variables taken into account when establishing the principles of application for the processes. Other than that, a comparison was made between the influence of PS oxidant on TOC removal efficiency using PS/UV-C procedures [6].

2. LITERATURE REVIEW

2.1 General Characteristics of Organic Substances

The concept "organic matter" is used to refer to a broad category of compounds that comprise one or more of the atoms of hydrogen (H), nitrogen (N), and oxygen (O), with carbon being the most prevalent of these constituents.

While the concept of organic matter initially described compounds that originating from living organisms, currently there is a vast variety of organic matter that is created synthetically and includes components such as fluoride, phosphorus, sulfur, bromine, chlorine, and iodine.

Organic substances can be categorized based on their physical and chemical characteristics. The analysis and treatment of organic substances can be developed by determining their properties. Organic compounds can range widely in molecular size. Simple substances, like chloroform, have molecules that are smaller than 1 nm, but humic acid as a complex compound has molecules that are 1 μm in size. When figuring out the properties of organic substances, determining their Molecular weight and volatility are also incredibly important parameters. The optimal conditions for the removal of organic matter by coagulation or other methods in drinking water treatment can be established with knowledge of the proportions of low and high molecular weight organic components [7]. The low molecular weight hydrophilic fraction is a useful indication of the quantity of dissolved organic carbon that will remain in the water after coagulation since it is almost uncharged and may be removed by coagulation with a lower efficiency than high molecular weight hydrophobic fractions [8]. According to the findings of numerous research, the molecular weight distributions of naturally occurring organic compounds vary from one source to another and with the passage of time. Total organic carbon is a great marker of water contamination when concentrations are compared upstream and downstream of potential pollution sources. Changes in the concentrations of suspended particles in rivers can have an effect on

total organic carbon (TOC), which consists of dissolved organic carbon (DOC) and particulate organic carbon (POC).

2.1.1 Organic matter sources in raw drinking water

Total organic carbon is a measureable component of the organic matter present in most water sources (TOC). In both freshwater and saltwater environments, sources of organic carbon can be broken down into three categories: living matter, waste materials, and effluents. Organic matter can be created either directly, through plant photosynthesis, or indirectly, through terrestrial organic matter.

In natural water, organic matter can be traced back to one of three fundamental sources:

- Organic substances that eventuate to grow naturally in aquatic environment,
- Organic substances produced by industrial and agricultural operations and subsequently dumped into water sources,
- Organic materials created throughout the water treatment process, including water distribution and disinfection.

2.1.2 The effects of organic materials in water supply

The most significant factor influencing water quality is the presence of organic matter in the water. The presence of organic matter has been identified as a major barrier to progress in the study and improvement of water treatment systems [9].

In many instances, the presence of organic matter in water might result in unfavorable Problems :

- Changes in the microbiological quality of treated water can be caused by the decomposition of organic compounds that occur in distribution networks.
- Taste and odor problems can be triggered by organic substances in drinking water systems.
- There is evidence that organic substances in water hinder efficient removal and oxidation of iron and manganese.
- The presence of organic compounds in natural waters results in color problems.
- The existence of organic substances makes it necessary for traditional water treatment systems to incorporate specific treatment parts, such as an anion exchanger,

a membrane, and demineralization processes.

- In drinking water distribution systems, corrosion issues are brought on by the presence of organic material.

Because of these factors, research on organic matter removal has accelerated [9].

2.2 Conventional Drinking Water Treatment Systems and Organic Matter Removal

Safe, plentiful, and sustainable access to drinking water is a basic human right. Protecting people's health requires a worldwide focus on raising standards for potable water. In their natural state, the world's water supplies are inappropriate for human consumption. This is why both traditional and advance treatment methods of water are necessary for use with raw water. Providing the physical and aesthetic quality of the water, removing potentially hazardous and dangerous compounds, and inactivating disease-causing (bacteria, viruses, etc.) microorganisms in water are the three fundamental principles of drinking water treatment plants.

The following are the three primary categories that are used to classify water and wastewater treatment systems:

I. Physical Treatment: It encompasses a variety of treatment methods, including adsorption, filtration, reverse osmosis, air or steam stripping, and combustion.

II. Biological Treatment: Activated sludge, aerated lagoons, anaerobic decomposition, trickling filters, and rotating biological discs are all part of this category of treatment methods.

III. Chemical Treatment: Treatment methods such as chemical precipitation, ion exchange, neutralization, oxidation/reduction and wet air oxidation are included in this process.

A variety of procedures, including aeration, pre-disinfection, coagulation/flocculation, sedimentation, filtration, and final disinfection, are used to treat drinking water. These physical-chemical processes, depicted in Figure 2.1, eliminate turbidity, organic substances, and pathogens. It is possible to improve water quality by using reverse osmosis, in which dissolved solutes are removed from water by the use of membranes [10]. Throughout the pretreatment process, suspended particles that are responsible for

total organic carbon are typically removed by employing a combination of coarse and fine screens, micro-strainers, and/or simple and direct gravity settling.

The process of coagulation and sedimentation is the primary mechanism that is utilized in the elimination of dissolved chemicals such as humic and fulvic acids.

In the pH range of 4 to 6, coagulation is at its most efficient in removing organics. The efficacy of aluminum and iron salts in eliminating organic material ranges from about 55% to over 90%, based on the source water [11]. The ineffectiveness of activated carbon in removing organic compounds can be attributed to early breakthrough problems [12].

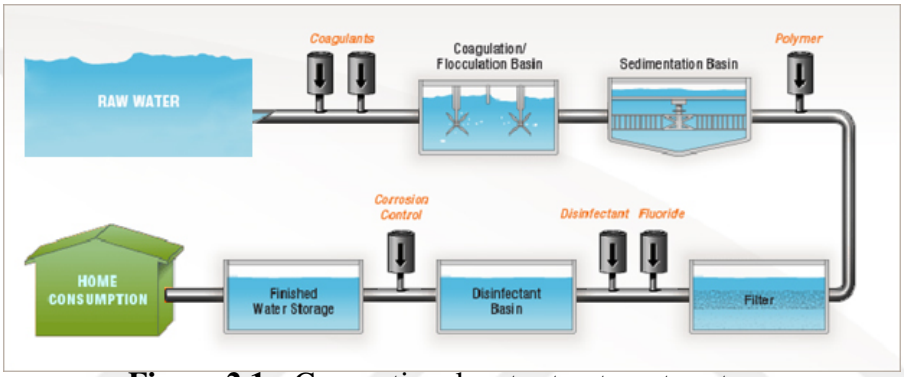


Figure 2.1 : Conventional water treatment system.

Table 2.1, which is a classification of process units, can be used to identify the goals of the treatment process for drinking water. The principal reasons for minimizing the levels of organic carbon in drinking water are to decrease the generation of trihalomethanes (THMs) following chlorination and to prevent an undesirable color from developing in the water if there are significant concentrations of humic and fulvic acids [13].

Table 2.1 : The functions that drinking water treatment plant units are supposed to perform.

Treatment Plant Unit	purpose
Aeration	Elimination of odor and taste caused by volatile chemicals and dissolved gas, elevation of the O2 level in the water, and oxidation.
Pre-Sedimentation	Elimination of sedimentable particles
Chemical Oxidation	Desinfection, taste and odor regulation, oxidation of organic substances, and color removal.
Coagulation-Flocculation	To get rid of turbidity and color, destabilizing colloid and macromolecules and polymerizing settleable particles
Sedimentation	Elimination of flocs that are able to settle.
Filtration	Elimination of particles and improvement of water quality by the utilization of biological and chemical processes
Softening	Magnesium and calcium elimination through sedimentation or ion exchange
Carbon Adsorption	Substances like trihalomethane (THM) and other organic compounds can be filtered out, and the smell, color, and flavor can be managed.

2.3 Advanced Oxidation Processes

The existence of toxic and organic compounds in water and wastewater has become a major global issue in recent years. Conventional procedures are inadequate for treating water and wastewater that contain significant levels of toxic and organic materials [14]. Due to the low biodegradability of insoluble organic contaminants, biological approaches cannot be used [15]. Although physicochemical techniques can be efficient, they aren't recommended due to the pollution's ability to move from one environment to another [14].

Regulations have tightened in recent decades as concerns about the state of the earth

and the wellbeing of its inhabitants have become increasingly well-founded. In particular, businesses have begun searching for innovative water purification methods.

- Reusing water is important in industrial regions.
- The use of traditional techniques is insufficient to meet discharge standards.
- The cost of industrial wastewater removal is relatively expensive.

these are the primary causes of this situation.

In light of these issues, the development of advanced oxidation processes that are both cheaper and more broadly applicable has been a priority [16]. In recent years, the impact of advanced oxidation processes on the manageability of various organic and inorganic pollutants has grown [17]. Several types and quantities of oxidants, including as hydroxyl radicals ($HO^{\bullet}$), sulfate radicals ($SO_4^{\bullet -}$), and superoxide anion radicals ($O_2^{\bullet -}$), have been used in advanced oxidation processes to convert organic contaminants into carbon dioxide (CO_2), water (H_2O), and minor inorganic molecules [15,18].

In order to degrade organic or inorganic contaminants, advanced oxidation processes employ high and strong oxidative radicals. AOPs have a positive effect on treatment duration since they shorten it. Treatment period may range from minutes to hours. The real advantage of AOPs lies in their ability to convert poisonous and persistent organics into nonhazardous end products [17].

Superoxide ($O_2^{\bullet -}$), hydroperoxyl ($HO_2^{\bullet -}$), hydroxyl ($HO^{\bullet}$), peroxyl ($ROO^{\bullet}$), sulfate ($SO_4^{\bullet -}$), and alkoxyl radicals ($RO^{\bullet}$) are the strongest oxidants, although sulfate and hydroxyl radicals have a considerable impact in advanced oxidation processes. The above table displays us the high oxidation potential of sulfate and hydroxyl radicals. Due to their second-order reaction and their rate constant range, hydroxyl radicals react with a wide variety of organic substances ($10^7 - 10^11 s^{-1}$). Since hydroxyl radicals are non-selective, they readily react with nearly all organic substances. Target pollution oxidation becomes more challenging, more oxidant is demanded, and the reaction time increases as a result. At the same time, $HO^{\bullet}$ can also be inadequate for the removal of recalcitrant contaminants such as organic acids (formic acid, oxalic acid etc.) [19].

2.2 illustrates that AOPs can be homogeneous or heterogeneous [20]. Heterogeneous

Table 2.2 : Advantages and disadvantages of AOPs.

Advantages	Disadvantages
High removal efficiency	High treatment cost
Treatment time is short (1-2 hrs)	Hazardous reactive matters (Ozone, H_2O_2)
Not be affected by alterations in water's characteristics.	Non-selective oxidants
Extremely effective on all organic and inorganic compounds, each of which have their own unique molecular structure.	Strong and reliable energy sources (UV, radioactive sources)
Scaled-down equipment.	
extremely efficient for low COD concentrations. (<1000 mg/L)	

Table 2.3 : Oxidation potential of oxidizing species.

Oxidant	Oxidation Potential (V)
Fluorine $[F_2]$	3.0
Hydroxyl radical [HO•]	2.8
Sulfate radical $\left[SO_4 \bullet^{-1}\right]$	2.5-3.1
Ozone $[O_3]$	2.1
Persulfate $\left[S_2O_8{}^{2-}\right]$	2.1
Peroxymonosulfate $[HSO_5{}^{-}]$	1.8
Hydrogen peroxide $[H_2O_2]$	1.8
Permanganate $[MnO_4{}^{-}]$	1.7
Chlorine dioxide $[ClO_2]$	1.5
Chlorine $[Cl_2]$	1.4

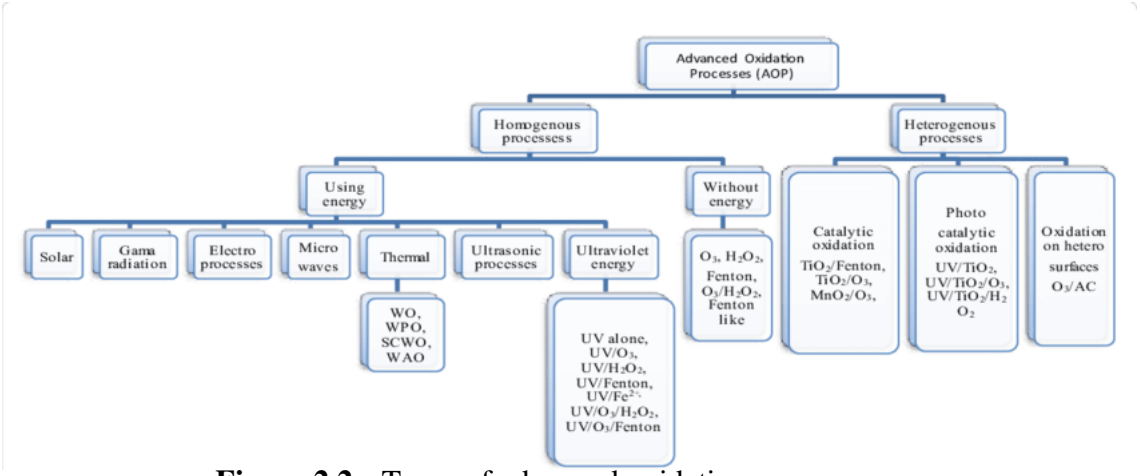


Figure 2.2 : Types of advanced oxidation processes.

advanced oxidation techniques can function throughout a broad pH range, whereas homogeneous advanced oxidation methods are most efficient at acidic pH [21].

Numerous advanced oxidation techniques, such as fenton, photo-fenton, photolysis, UV, etc., are employed to decompose refractory organic contaminants in wastewater using strong oxidants. The poor stability of oxidants, which limits their storage and transport, and the system's strict pH requirements ($2 \sim 4$) are some of the limitations of these methods [22].

Table 2.4 : Chemical and photochemical types of AOPs.

Chemical	Photochemical
Ozonation	Vacuum UV (VUV) Photolysis
• O_3/OH^-	UV-C/Oxidation Processes
• O_3/H_2O_2	Direct UV Photolysis
• O_3/Mn^{2+}	Sonication/UV
• O_3/Fe^{2+}	Heterogenous Photocatalysis
• Fenton Process	
• Sonication/H_2O_2, Sonication/O_3	
• Electro-Fenton	
• Wet Air Oxidation	
• Supercritical Water Oxidation	

Table 2.4 shows that there are two primary categories of advanced oxidation processes: chemical and photochemical [23].

Disinfection of drinking water, removal of microorganisms that are resistant to disinfection, treatment of industrial wastewater, treatment of ground water and surface waters, wastewater reuse, oxidation/mineralization of micropollutants, producing of high purity water, minimizing domestic and industrial sludges, and treatment of leachate are some of the general treatment applications that AOPs are used for [23].

2.3.1 Chemical advanced oxidation processes

2.3.1.1 Fenton process

The Fenton reaction, which involves the interaction of Fe^{2+} and H_2O_2 in the dark condition, was firstly used by Fenton in 1894. 40 years later, in 1934, Haber-Weiss proved that the hydroxyl radical was the effective oxidizing agent in the Fenton reaction, thereby validating the mechanism. The formation of hydroxyl radicals under acidic circumstances is the basis of the Fenton process, a homogeneous catalytic

oxidation process [24,25].

In an acidic aqueous solution, the reaction between the ion Fe^{2+} and the radical H_2O_2 generates the extremely reactive hydroxyl radical. This occurs as a result of the oxidation of the Fe^{2+} ion to Fe^{3+}. The process proceeds spontaneously, independent of the effect of light:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \tag{2.1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \tag{2.2}$$

In addition, the radicals react with the organic compounds that are already present in the solution, which results in the formation of oxidized products [26].

The oxidation of toxic and non-biodegradable wastewater can be accomplished in a practical and efficient way through the use of the Oxidation. Also, iron is a non-toxic substance that may be extracted by the coagulation process [27].

2.3.1.2 Ozonation

Ozone has a lot of chemical energy since it's degradability. The degradation of ozone is an intricate process that is dependent on the pH of the atmosphere, the temperature, and the amount of organic and inorganic compounds present [28]. Ozone's principal function is disinfection, but it's also utilized for other things, like pre-oxidizing industrial wastewater and treating chemicals that are resistant to biodegradation [29].

In solutions, ozone reacts directly with organic compounds that have been dissolved or indirectly with free radicals like $HO^{\bullet}$.

Various forms of kinetics are responsible for the management of these reactions, which result in the production of different oxidation products [30].

The following fundamental reactions, which are based on two models, can be used to describe the decomposition of ozone.

$$O_3 + OH^{-} \rightarrow HO_2^{\bullet} + O_2^{-\bullet} \tag{2.3}$$

$$HO_2^{\bullet} \rightarrow O_2^{-\bullet} + H^{+} \tag{2.4}$$

$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \tag{2.5}$$

$$O_3 + H^+ \rightarrow HO_3^{\bullet} \tag{2.6}$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \tag{2.7}$$

$$O_3 + HO^{\bullet} \rightarrow HO_4^{\bullet} \tag{2.8}$$

$$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \tag{2.9}$$

$$HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3 \tag{2.10}$$

$$HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_3 + O_2 \tag{2.11}$$

$$HO^{\bullet} + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet -} \tag{2.12}$$

$$O_3 + CO_3^{\bullet -} \rightarrow products(CO_2 + O_2^{\bullet -} + O_2) \tag{2.13}$$

$$OH^{\bullet} + HCO_3^- \rightarrow OH^- + HCO_3^{\bullet} \tag{2.14}$$

2.3.1.3 H_2O_2/O_3

The production of $HO^{\bullet}$ radicals is enhanced when H_2O_2 interacts with ozone as part of the H_2O_2/O_3 system. When ozone and hydrogen peroxide react, they set off a chain reaction that leads to the creation of $HO^{\bullet}$ radicals (Equation 2.15). Equation 2.16 provides a complete representation of the reaction. The conjugated base, H_2O_2, is responsible for the breakdown of ozone, which results in the generation of hydroxyl radicals [31].

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{-\bullet} \tag{2.15}$$

$$2O_3 + H_2O_2 \rightarrow 2HO^{\bullet} + 3O_2 \tag{2.16}$$

2.3.1.4 Wet air oxidation

Wet air oxidation is the process of oxidizing organic matter while it is in the aqueous phase at high temperatures (100-350 oC) and in the pressure range of 0.5-20 MPa. The oxidant can either be air or pure oxygen. The process of wet air oxidation results in an increased oxidation rate. This, in turn, makes the concentration of dissolved oxygen go up at high temperature and pressure [32].

2.3.1.5 Supercritical water oxidation

Thermal oxidation in an aqueous system occurs at the critical points of mixing; this is known as supercritical water oxidation. Temperature and pressure for pure water are 374 374 °C and 22.1 MPa, respectively. For the reasons given, low polarity describes the behavior of water under these conditions. It has been proven that supercritical water oxidation is an useful method in treatment of a wide variety of industrial wastewaters, like effluent from the textile industry. In this method, the time that is required for a reaction is typically only a few minutes. However, due to the high temperature and pressure requirements, this method is quite costly [33,34]. The most significant disadvantages of using this technique for the treatment of industrial wastewater are corrosion of the reactor and the creation of salt [35].

2.3.2 Photochemical advanced oxidation processes

Light and radicals are one of the most crucial factors to consider while discussing photochemical advanced oxidation processes. UV-C lights provide the optimal conditions for photochemical AOPs because of how well they break down organic pollutants through photolysis [27].

Photochemical AOPs are advantageous for the removal of many persistent organic pollutants due to their straightforward operation, high efficiency, and non-selectivity. The use of strong radicals in photochemical AOPs provides the most effective treatment. Only ultraviolet (UV) light can cause photolysis; however, this process is not employed in water or wastewater treatment [36].

As a rule, photochemistry operates within a wavelength range of 100 to 1000 nm. Longer-wavelength photons (those longer than 1000 nm) have a moderate energy and cannot alter the molecular structure of contaminants. In spite of this, photons, which have a wavelength of fewer than 100 nm and carry a really high energy, are capable of causing the oxidation and ionization of contaminants [37]. Table 2.5 presents the spectral wavelengths of the various kinds of lights that are available [37].

Table 2.5 : Spectral wavelength.

Light Name	Wavelength (nm)
Infrared	>780
Visible Light	400-780
UV-A	315-400
UV-B	280-315
UV-C	200-280
Vacuum-UV	100-200

Table 2.5 presents the spectral wavelengths of the various kinds of lights that are available.

Different wavelengths on the electromagnetic spectrum are utilized in the application of various advanced oxidation processes as a Treatment strategy. In the majority of the AOP investigations, UV-C was applied in order to achieve UV Photolysis by the utilization of an oxidant [38].

2.3.2.1 UV photolysis

Direct ultraviolet photolysis is recognized as the primary photochemical approach that was put into practice for the destruction of contaminants. It is effective in the removal of chlorinated or nitrated aromatics, phenols, halogenated aliphatics, and other possibly hazardous contaminants from the water. While UV photolysis isn't as effective as systems that generate $HO^{\bullet}$ radicals, it still has its uses in situations where radical reactions move at a slower rate.

Direct UV photolysis has a restricted range of applications; photochemical degradation can take place at wavelengths as low as 185 nm (λ<185 nm) for vacuum ultraviolet photolysis or as high as 200 nm (λ>200 nm) for UV light [39].

2.3.2.2 Hydroxyl radical based advanced oxidation processes

This section will provide an explanation of the advanced oxidation processes that make use of UV-C irradiation.

Vacuum UV photolysis

The process of vacuum ultraviolet photolysis involves creating a spectral field of ultraviolet light that incorporates air capable of absorbing powerful radiation [40]. Homolysis of chemical bonds is achieved as a result of the movement in the VUV field.

For the process of VUV photolysis to take place, UV light with a wavelength of less than 190 nanometers is required. The photolysis of water is the basis for the generation of the HO• and H radical ($H^{\bullet}$) in this process [39].

$$H_2O + hv \rightarrow HO^{\bullet} + H^{\bullet} \tag{2.17}$$

At a high humidity level, photolysis of water is carried out by oxidizing pollutants with $HO^{\bullet}$ and reducing them with $H^{\bullet}$. While, there are no commercial applications exist at this time for VUV photolysis [41].

Understanding the significance of UV_{254} analysis in relation to advanced oxidation processes

The determination of UV_{254} is a key metric that is used across the treatment process for drinking water. The quantity of aromatic rings and unsaturated bonds in organic molecules can be determined with the help of UV_{254}. Many naturally occurring complex substances in the environment are recognized to be the primary pioneers of disinfection byproducts such as humic chemicals. UV_{254} is therefore one of the best indications of a water's capacity to form disinfection byproducts (DBPs) the added chlorine should be monitored across the treatment process to make sure that organics are removed. There is a strong relationship between total organic carbon (TOC) and ultraviolet radiation intensity (UV_{254}), suggesting that this method can be used to successfully identify organic matter content [42].

UV photolysis of ozone (O_3/UV-C and and O_3/H_2O_2/UV-C)

Oxygen and hydrogen peroxide are broken down during the UV photolysis of ozone, which requires the presence of water. Next, the H_2O_2 undergoes a reaction with either UV light or ozone to produce hydroxyl radicals. The hydroxyl radicals that organic molecules interact with are necessary for the oxidation process to take place. Ozone, in general, exhibits the highest absorption efficiency at a wavelength of 254 nm. This system consists of three different components in order to generate $HO^{\bullet}$ and oxidize. organic compounds; ultraviolet light; O_3 hydrogen peroxide The initial step in this advanced oxidation process is the photolysis of ozone [43]. The removal efficiency of a system that consists of both ozone and ultraviolet light is greater than the removal efficiency of a system that consists of either ozone or ultraviolet light alone.

$$O_3 + H_2O(aq) + hv \rightarrow H_2O_2 \tag{2.18}$$

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \tag{2.19}$$

The O_3/UV-C method is a form of advanced oxidation process (AOP) that is widely used to remove organic contaminants that cannot be successfully destroyed only by ozone. In contrast to other degradation processes that can create $HO^{\bullet}$ radical, the O_3/UV-C process is capable of oxidizing a wide variety of organic molecules. There is no need for continual observation, and the process can be run in either batch or continuous modes [40]. However, The major drawback of this technique are the limited transportation options for ozone and its low solubility in comparison to H_2O_2.

The effect of UV-C photons is quite substantial during the O3/UV-C process, both in terms of the activation of ozone molecules and the formation of hydroxyl radicals [44]. In order to remove organic materials, this method, which is considered to be one of the advanced oxidation processes, has been utilized for a significant amount of time. Ozone's widespread use in water treatment has helped the O3/UV-C method expand into other fields [39]. The production of hydrogen peroxide (H_2O_2) can occur as a byproduct of the photolysis of ozone in water, or ozone can react with UV radiation to produce the $HO^{\bullet}$ radical. The following is a list of the reactions that occur during this

process:

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{-\bullet} \tag{2.20}$$

$$O_3 + H_2O_{(aq)} + hv \rightarrow 2HO^\bullet \rightarrow O_2 + H_2O_2 \tag{2.21}$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{2.22}$$

$$O_3 + H^+ \rightarrow HO_3^\bullet \tag{2.23}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \tag{2.24}$$

$$O_3^{\bullet-} + H_2O \rightarrow HO^\bullet + OH^- + O_2 \tag{2.25}$$

$$O_3^{\bullet-} + H_2O \rightarrow O_2 + O^{\bullet-} \tag{2.26}$$

$$O^{\bullet-} + H_2O \rightarrow HO^\bullet + OH^- \tag{2.27}$$

$$HO^\bullet + RH(-H_2O) \rightarrow R^\bullet(+O2) + ROO^\bullet \tag{2.28}$$

In contrast to the O_3/UV-C process, the noticeable increase of the HO• radical is caused by adding H_2O_2 to the O_3/H_2O_2 /UV-C system [39,40]. The following is a brief summary of the reaction equations that describe the O_3/H_2O_2/UV-C process:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{2.29}$$

$$O_3^{\bullet-} + H_2O \rightarrow HO^\bullet + OH^- + O_2 \tag{2.30}$$

$$O_3 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet-} + O_2 \tag{2.31}$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \tag{2.32}$$

H_2O_2/UV-C

The H_2O_2/UV-C process, which is one of the oldest known forms of advanced oxidation, possesses a variety of useful properties. The procedure does not result in the production of waste sludge and enables for conduct in a broad pH range. In addition to this, hydrogen peroxide is a chemical that can be purchased and stored commercially, and it is also a source of the $HO^\bullet$ radical that is relatively inexpensive [39,40]. 220 nanometers is the wavelength at which H_2O_2 has the greatest capability for absorption (EPA,).

The H_2O_2/UV-C process results in the formation of two $HO^\bullet$ radicals as a consequence

of the photolysis of H_2O_2 that takes place when H_2O_2 is exposed to UV light with a wavelength that is lower than 280 nm. These free radicals then interact with organic contaminants or cross over into a cycle of H_2O_2 breakdown and formation [45,46]. The subsequent chain reactions that occur are as follows:

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{2.33}$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \tag{2.34}$$

$$H_2O_2 + hv \rightarrow 2HO^\bullet \tag{2.35}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{2.36}$$

$$H_2O_2 + HO_2^\bullet \rightarrow HO^\bullet + H_2O + O_2 \tag{2.37}$$

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O_2 + O_2 \tag{2.38}$$

As can be seen in the reactions, $HO^\bullet$ can sometimes be converted into HO_2, and this creation takes place when an excessive amount of $H_2O_2$is employed. In comparison to the $HO^\bullet$ radical, the reactivity of HO_2 is significantly lower. The effectiveness of the H_2O_2/UV-C process is influenced by the concentration of the pollutant, pH, the amount of time it takes during reactions, and the amount of oxidant (H_2O_2) [47].

Heterogenous photocatalysis reactions (TiO_2/UV-A)

Producing $HO^\bullet$ from semiconductor metal oxides with oxygen as the oxidant and catalyst is at the basis of photocatalytic processes. It is a crucial technique for the breakdown of organic pollutants and toxic materials when UV lights and semiconducter particles are present. A photocatalytic system is made up of semiconductor particles that are dispersed throughout a solvent. The HO• radicals are the most important oxidants in a photocatalytic system [48].

Numerous metal oxides are semiconductors. Fe_2O_3, $SrTiO_3$, In_2O_3, K_4NbO_{17}, WO_3, V_2O_5, MoO_3, MoS_2, SiC, and $ZnFe_2O_4$ have been employed as photocatalysts for the photocatalytic degradation of numerous organic pollutants, especially dyes, insecticides, and herbicides [49]. For this procedure, TiO_2 was shown to be the most cost-effective and stable catalyst. TiO_2 also has excellent photochemical stability across a broad pH range. Aside from that, in contrast to other materials, TiO_2 does not

induce corrosion. The generation of $HO^{\bullet}$ can be boosted with the addition of catalysts such as H_2O_2 [50,51].

Photo-Fenton

Polychlorinated biphenyls (PCB), chlorinated herbicides, phenolic wastes, chlorophenols, perhalogenated alkenes, and dyestuff effluent are just some of the recalcitrant contaminants that the Photo-Fenton method has proven to be efficient at mineralizing [52,53]. In the presence of ultraviolet (UV) light, the Fenton reaction is referred to as the photoFenton reaction. As a result of being exposed to ultraviolet light, the Fenton reaction's oxidizing potential is considerably enhanced [54].
In the photo-Fenton process, $HO^{\bullet}$ is created when H_2O_2 and Fe^{+2} are photolyzed, as well as when Fe^{+2} reacts with H_2O_2. The following is a list of all reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \tag{2.39}$$

$$H_2O_2 + hv \rightarrow Fe^{3+} + 2HO^{\bullet} \tag{2.40}$$

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{+2} + HO^{\bullet} + H^{+} \tag{2.41}$$

The photo-Fenton reaction results in the formation of a greater quantity of $HO^{\bullet}$ as contrasted with the Fenton reaction, radicals are produced. Because the reaction is highly dependent on the pH and the wavelength of the irradiation, an increase in both of these factors results in a reduction in the number of radicals [26]. It has been demonstrated that enhancing the efficiency of $HO^{\bullet}$ formation by employing UV or visible light increases the decomposition rate and degree of mineralization of organic contaminants [26,55,56]. As a result of this, the photo-Fenton process is an efficient method for the oxidation of a wide variety of organic substances, especially dyestuffs.

2.3.2.3 Sulfate radical based advanced oxidation processes

Scientific investigations have shown that effective ways to create highly reactive sulfate radicals $SO_4^{\bullet -}$ can be accomplished by activating peroxymonosulfate (PMS)

or peroxydisulfate (PS) in sulfate radical-based AOPs by exposing them to ultraviolet (UV) light [17].

Persulfate and peroxymonosulfate oxidants

Both peroxydisulfate (PS) and peroxymonosulfate (PMS) are becoming more widely used in the treatment of wastewater and water. Peroxydisulfuric acid, often known as $H_2S_2O_8$, was first discovered in 1878 by the French chemist Marcelin Berthelot [57]. The electrolysis of sulfate salt is the process that gives rise to its production. There are three distinct salt forms that PS can be found in: ammonia, potassium, and sodium. Potassium PS has minimal solubility, making it ideal for in situ treatment, while ammonium PS can produce residual ammonia, leading to secondary contamination. For this reason, in-situ chemical oxidation using sodium PS salt $Na_2S_2O_8$ is the method of choice for treatment (ISCO).

Because the bond length of PMS is shorter than that of PS, there is a greater rise in the bond dissociation energy, which is 377 kJ/mol. To phrase it another way, more energy is needed to create sulfate radicals from PMS than it does from PS [58].

One of the advantages of using peroxydisulfate and peroxymonosulfate as an ISCO reagent is that they have a significantly higher stability than the other ISCO reagents that are usually employed, which are hydrogen peroxide and ozone [59]. Two of the most strong oxidants employed in water and wastewater treatment are peroxydisulfate and peroxymonosulfate. The activation of PS and PMS oxidants is described below, along with several processes that result in the production of sulfate radicals.

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \tag{2.42}$$

$$HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O \tag{2.43}$$

In the case of persulfates, which are employed for the decomposition of pollutants, the radicals that are created as a result of the breakdown of the peroxide bond are the most important. Photochemical or thermal breaking of the peroxide bond, as well as chemical reduction, are all possible sources of radical formation. Sulfate radicals are often the consequence of PS degradation. Alternatively, PMS can decompose into sulfate and hydroxyl radicals [60].

Advantages and disadvantages of Sulfate radical-AOPs

Table 2.6 provides a summary of the advantages and disadvantages of sulfate radical based AOPs. [61]

Table 2.6 : Advantages and disadvantages of Sulfate radical-AOPs.

Advantages	disadvantages
High oxidation potential from $SO_4^{\bullet-}$ and $HO^{\bullet}$	High selectivity for oxidation due to $SO_4^{\bullet-}$
The long half life of SO_4	Costly
The pH range in which it is effective is quite large.	Potential for the production of poisonous by-products in the presence of Cl_ and Br
large-scale, secure oxidant storage	

Activation mechanisms of peroxydisulfate and peroxymonsulfate

Table 2.7 : PS activation methods.

Method	Mechanism	Predominant Radical Species
Heat	Homolysis of peroxide bond	Sulfate radical/Hydroxyl radical
UV Radiation	Homolysis of peroxide bond	Sulfate radical
Transition Metals	One electron transfer	Sulfate radical
Alkaline pH	Base-catalysed hydrolysis of PS to hydroperoxide, which later initiates radical formation	Sulfate radical/Hydroxyl radical

PS and PMS-based oxidation rely heavily on the formation of highly reactive species, which can assist in reducing pollution [62]–[64]. It is possible to generate sulfate and hydroxyl radicals via homolysis of preoxide bond using heat and Ultraviolet irradiation. Furthermore, PMS and PS can be oxidized chemically with low valent transition metals, leading to the production of sulfate radicals.

Another process for activating persulfate that is frequently used in situ is called alkaline activation. This method involves dosing solutions of sodium hydroxide (NaOH) or

Table 2.8 : PMS activation methods.

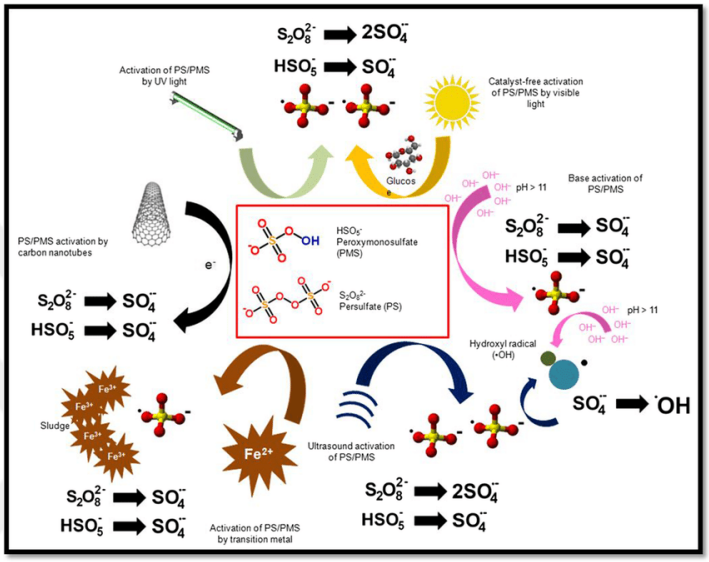
Method	Mechanism	Predominant Radical Species
Heat	Homolysis of peroxide bond	Sulfate radical/Hydroxyl radical
UV Radiation	Homolysis of peroxide bond	Sulfate radical/ Hydroxyl radical
Transition Metals	One electron transfer	Sulfate radical
Alkaline pH	Base-catalysed hydrolysis of PMS to hydrogen peroxide	Superoxide radical
Ozone	Formation of an $-O_3SO_5-$ adduct that decomposes into radicals	Sulfate radical/ Hydroxyl radical

potassium hydroxide (KOH) in order to elevate the pH to a value that is normally higher than 11 [59]. Activated PS was able to reduce the levels of BTEX chemicals, which include benzene, toluene, ethylbenzene, and xylenes, as well as PAHs, which are polycyclic aromatic hydrocarbons. Hydrolysis of PS to hydrogen peroxide anion (HO_2^-) and reduction of PS by this anion, leading to the production of sulfate and superoxide radicals (O_2^-), is proposed as the mechanism for alkaline activation of PS [65].

Hydrolysis of PMS to H_2O_2 can also take place at high pH via base catalyzed, revealing a similar activating tendency for PMS. Scientists have identified O_2^- as the most abundant radical species in this system [66]. Numerous organic contaminants have been eliminated through the use of UV irradiation for PS and PMS activation in recent years. UV irradiation has two main effects on organic contaminants, both of which lead to their degradation. One, The pollution's chemical bonds are broken when exposed to UV radiation. Second, when exposed to UV light, PS and PMS become activated, releasing active radicals that can destroy the chemical bonds holding contaminants together.

Many techniques have been developed for the production of $SO_4^{\bullet}$ for the activation of peroxymonosulfate (PMS) or persulfate, including the use of heat [67], transition metals [68], ultrasonic waves [69], and light radiations [6]. Between all these

activation techniques, photo-activation is insufficient as a therapeutic option. Under ideal circumstances, PS/PMS photo-activation can accelerate the mineralization and decomposition of organic matter. Direct UV irradiation is the most effective method for photo activation of PS/PMS due to the high energy of UV. Consequently, the elimination of organic contaminants made possible by PS/PMS photo-activation results in a greater conservation of energy.



[70]

Figure 2.3 : PS/PMS activation mechanism.

In order to activate PS/PMS, UV irradiation is utilized, which results in the production of $SO_4^{\bullet}$ and OH radicals. Due to the fact that PS is a symmetrical oxidant, Eq. 2.44 results in the formation of two $SO_4^{\bullet}$. On the other hand, PMS is an asymmetrical oxidant, which means that the reaction results in the production of one $SO_4^{\bullet}$ and one OH radical, as shown in Equation 2.45. According to equation 2.46, the partial $SO_4^{\bullet}$ can spontaneously transform to OH in an aqueous solution. This conversion is related to the solution's pH. At alkaline pH values, there is a greater potential for conversion to take place as equation 2.47.

$$S_2O_8^{2-} + h\nu \rightarrow 2HSO_4^- \tag{2.44}$$

$$HSO_5^- + h\nu \rightarrow HSO_4^- + OH^- \tag{2.45}$$

$$HSO_4^{\bullet -} + H_2O \rightarrow HSO_4^{2-} + OH^- \tag{2.46}$$

$$HSO_4^{\bullet -} + OH^- \rightarrow HSO_4^{2-} + OH^- \tag{2.47}$$

[71] investigated the effect of Ultraviolet light on the activation performance of three common oxidants—PS, PMS, and H_2O_2—on the decomposition of Acid Orange 7 (AO7) in terms of the azo dye. They discovered that AO7 could be decomposed when subjected to Ultraviolet irradiation; nevertheless, the rate of AO7's degradation could be sped up by roughly 40% when only these oxidants were present. They ranked the effectiveness of these oxidants in order of degradation as follows: PS > H_2O_2 > PMS. In addition to this, the oxidation efficiency of UV/PS and UV/PMS systems commonly varies when it comes to the various organic contaminants. According to the findings of a series of studies, the potential of UV/PS to oxidize organic pollutants was greater than that of UV/PMS [71]. It is possible that the quantum yield of radical generation is the basis for it.

Electrical energy/order (EE/O, kWh/m3) was employed as an important feature in relation to relative absorbance by Anipsitakis et al. In order to measure the efficacy of AOPs, it is necessary to calculate the amount of electrical energy required to remove pollutants from one cubic meter of polluted water or air. As can be seen in Table 2.9, the relative absorbance of PS at UV254 is noticeably higher than that of PMS and H_2O_2. According to the findings of this research, Anipsitakis and Dionysiou concluded that the process will be more effective and Cost-effective to the extent that its EE/O ratio is lower [72]. The following is how the rate of EE/O was obtained for UV-activated peroxides:

UV/PMS (0.125P) > UV/PS (0.183P) > UV/H2O2 (0.250P).

The Value of p was expected to be the same for each and every one of individuals.

Table 2.9 : Bond distances in PS, PMS, H_2O_2, and quantum yield of radical formation and relative absorbance of PS, PMS, H_2O_2 at UV_{254}.

Types of uxidants	0-0 bond distance	Quantum yield of radical formation	Relative absorbance
Persulfate (PS)	1.497	1.8	0.044
Peroxymonosulfate (PMS)	1.460	0.52	0.024
Hydrogen Peroxide H_2O_2	1.453	1.0	0.022

In the same study that This to researcher carried out, the rate of degradation of 2, 4-dichlorophenol (2, 4-DCP) in the UV/PSM system was shown to be significantly faster than the rate of degradation in other oxidations/UV systems. During the decomposition of 2, 4-DCP, chlorideion (Cl-) is produced, and this is what they believe caused the problem. According to Eq. 2.48, Cl- could react with PMS to produce OCl-, which has the ability to break down organic substances [72]. According to the findings, UV-activated SR-AOPs are superior to OH- based AOPs in terms of both effectiveness and cost-effectiveness in the process of organic pollutant degradation.

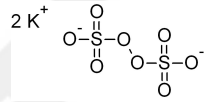
$$CL^{-} + HSO_5^{-} \rightarrow SO_4^{2-} + HOCL \tag{2.48}$$

3. MATERIALS AND METHODS

3.1 Chemicals and Materials

Potassium persulfate ($PS, K_2S_2O_8, > 99.5\%$) was used in persulfate/UV-C experiment conducted with advanced oxidation processes. Physicochemical parameters of PS oxidant is shown in Table 3.1.

Table 3.1 : Properties of PS.

Physicochemical Parameters	Potassium Persulfate
IUPAC Name	Potassium peroxydisulfate
Molecular Structure	
CAS No.	7727-21-1
Molecular Formula	$K_2S_2O_8$
Molecular Weight	270.322 g/mol
Water Solubility	1.75 g/100 mL (0 °C) 4.49 g/100 mL (20 °C)
Appearance (Color and Odor)	White and Odorless
Appearance (Form)	Powder
Density	2.477 g/cm3
Flash Point	Non-flammable

3.1.1 Drinking water sample

In this thesis, tests have been done with 4 samples which are raw water, the coagulation-flocculation effluent, the filter effluent, and the final effluent that used in all experimental studies was supplied by drinking water treatment plant in İstanbul. The samples were transferred to the laboratory in a cooler at 4 degrees Celsius and kept refrigerated until usage. The sample's characterisation will be described in the following section.

3.1.2 Residual persulfate measurements

3.1.2.1 Determination of Persulfate by Colorimetry

At the end of PS/UV-C reactions, the calorimetric Alcian Blue method was applied to determine the amount of persulfate oxidant that remained. 50 mg of Alcian Blue was dissolved in 160 ml of distilled water. The pH of Alcian Blue solution was adjusted with HCl acid (pH=2.5), and the volume of the solution was brought to 200 mL. 5 ml of various sample concentrations and five ml of alcian blue solution were placed in test tubes for one hour. At the end of the waiting period, 20 mL of distilled water was added to the sample for further mixing. At 615 nm, a calibration curve was developed with this sample by using a spectrophotometer. Persulfate concentrations between 5 and 30 mg/L (0.02 and 0.1 mM) were appropriate for measurement. Residual PS was

Figure 3.1 : Jenway 6300 spectrophotometer.

measured in the same manner with the creation of a calibration curve. In test tubes, 5 mL of sample and 5 mL of alcian blue solution were placed. within one hour After this period, 20 mL of distilled water was added to the test tubes. At 615 nm, the sample was evaluated with a spectrophotometer.

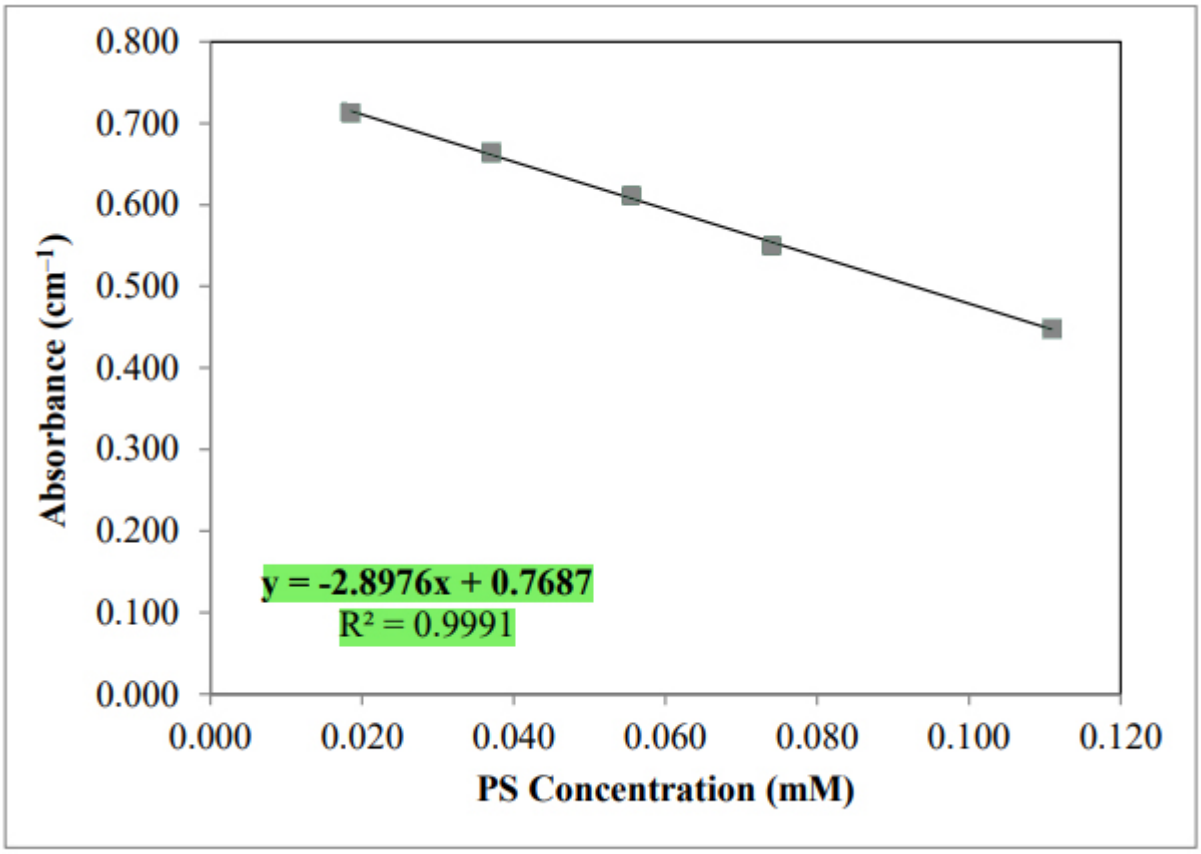


Figure 3.2 : Calibration curve for residual PS concentration.

3.1.3 Determination of total organic carbon

The TOC Shimadzu VCPN analyzer was calibrated utilizing standard solutions of potassium hydrogen phthalate for total carbon and sodium hydrogen carbonate and sodium carbonate for inorganic carbon. To measure inorganic carbon and total carbon with concentration values of 0–20 mg/L, 20–100 mg/L, and 100–300 mg/L separately, the TOC device was calibrated.

The organic carbon parameter required for the investigation was produced by deducting the inorganic carbon value from the total carbon parameter. Concentrated standards of total carbon and inorganic carbon were produced for the 0-20 mg/L range, including 0, 2.5, 5, 7.5, 10, 15, and 20 mg/L; for the 20-100 mg/L range, including 20, 30, 40, 50, 60, 70, 80, and 100 mg/L; and for the 100-300 mg/L range, including 100, 150, 200, 250, and 300 m/L. The TOC device was used to look at how the standards worked.

Calibration curves were generated by recording the area sizes that corresponded to the concentrations of the standard solutions.

3.2 Experimental Procedure

Samples from a drinking water treatment facility in Istanbul were utilized to determine the ideal condition using advanced oxidation techniques based on sulfate radicals (persulfate (PS)/UV-C). Parameters such as pH, UV254, particle size distribution (PSD), and residual PS concentrations were monitored alongside total organic carbon (TOC) and dissolved organic carbon (DOC) removal efficiencies during all experiments.. A 500 mL three-neck quartz flask with room temperature (25±2 °C) was used for each experiment. To maintain homogeneity throughout the experiment, the sample was mixed. First, 2, 6, and 10 lamps in the UV-C reactor were tested to see how changing the number of lamps affected the overall efficiency of the operation. In this control experiment, the best condition was set at 10 lights. A power meter was used to detect radiation fluxes in the UV reactor at the start and end of the experiment. In the optimization experiments, the initial concentrations of PS was changed to be 0.0 mM, 0.1 mM, 0.2 mM, 0.5 mM, and 1 mM. This was done to find out how the changes affected the efficiency of the process.

The samples were treated with PS/UV-C after all of the optimisation trials had been run. In these tests, samples were obtained from the reactor at predetermined intervals to assess TOC, and then filtered through 0.45 μm Millipore membranes to analyze DOC, UV254, residual PS concentrations and pH.

After collecting samples, pure sulphuric acid was used to acidify them, and the mixture was then stirred overnight on a magnetic stirrer so that the TOC and DOC concentrations could be accurately measured. The impact of reaction time on process efficiency was studied, and the trials were run for a full 60 minutes. By sampling samples at various periods, the treatability of the drinking water sample was investigated (0, 15, 30 and 60 minutes).

Figure 3.3 : UV-C photoreactor.

3.3 Analytical Procedure

3.3.1 pH measurement

Thermo Orion's 720A+ pH meter and 9165BNWP pH probe were used to detect pH during all of the advanced oxidation processes studies. Prior to each experiment, pH meters were calibrated using buffer solutions .

Figure 3.4 : Thermo Orion 720A+ pH meter and Thermo Orion 9165BNWP pH probe.

3.3.2 Distilled water

With the assistance of an Arium 611UV water purification system, ultrapure water for the chromatographic experiments was successfully produced (Sartorius AG, Germany).

Figure 3.5 : Sartorius Stedim distilled water device.

3.3.3 UV254 analysis

Throughout all of the advanced oxidation processes tests, UV254 measurements were carried out using a Schimadzu UV-1800 spectrophotometer at a wavelength of 254 nm with a 1 cm quartz cell. Measurements were made using samples that had been filtered via a 0.45 µm membrane filter to eliminate turbidity, and distilled water was used to calibrate the spectrophotometer.

3.3.4 TOC analysis

The Shimadzu V_{CPN} (Japan) analyzer determined the total organic carbon (TOC) content of the sample. Autosamplers and infrared (IR) detectors were built into the devices that made up the instruments. Before anything else, acidified samples were

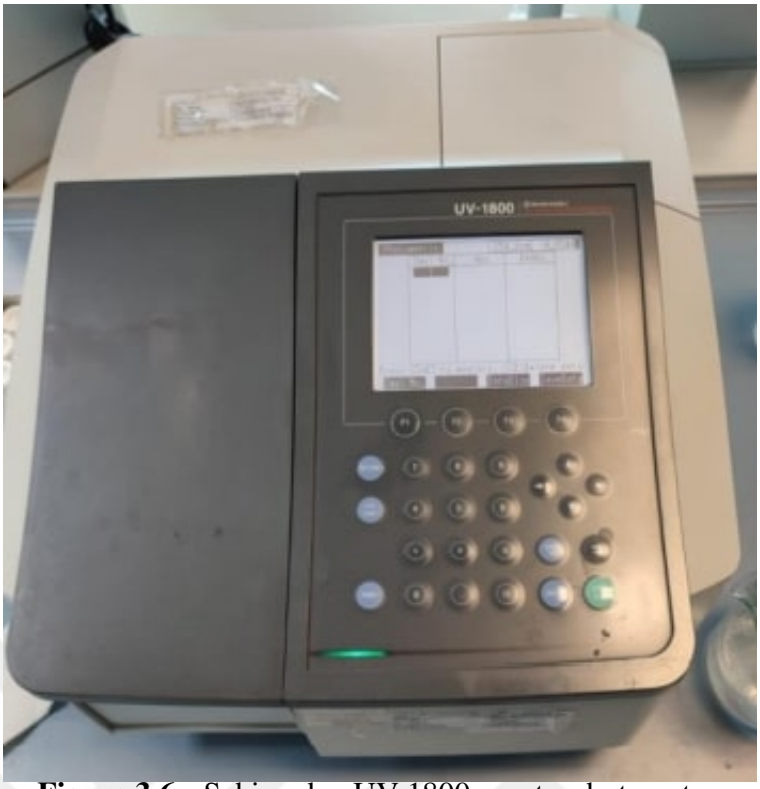


Figure 3.6 : Schimadzu UV-1800 spectrophotometer.

collected in 25 mL vials for the purpose of analyzing the degree of mineralization of organic matter during and after photochemical oxidation processes. The principle of "Determination of CO_2 by utilizing Non-Dispersive Infrared Following Oxidation" was applied to determine the levels of TOC and DOC.

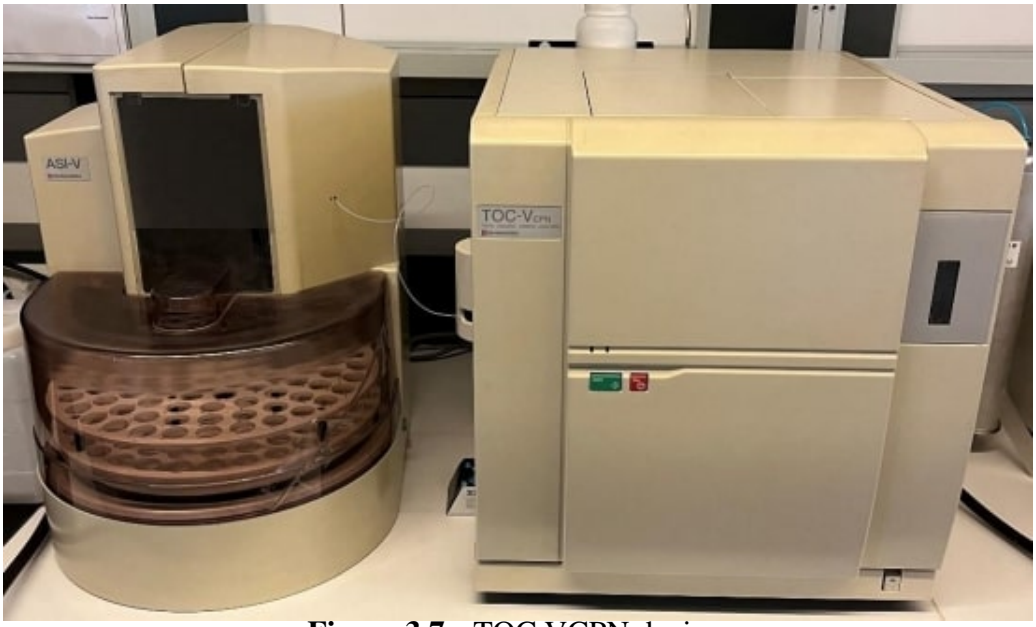


Figure 3.7 : TOC VCPN device.

4. RESULTS AND DISCUSSION

4.1 The Capability of Treating Organic Carbon Using the PS/UV-C Process Application

Initial oxidant concentration is regarded a major process parameter due to the impact it has on the organic carbon removal efficiency for PS/UV-C processes. Because of this, the initial oxidant concentration that is found to be the most effective should be chosen. To this end, we conducted experiments to measure the impact of initial PS concentration on the PS/UV-C process for removing organic carbon in our samples at the original TOC concentration of raw water, the coagulation-flocculation effluent, the filter effluent, and the final effluent.

We have analyzed our samples with their initial TOC concentration, at their initial pH of the solutions, and with their initial PS content ranging from 0.10 to 1.00 mM. Experiments with only direct UV-C photolysis (PS = 0 mM) and only PS (1 mM) were run as controls at the original pH values in order to investigate the influence that PS concentration has on the breakdown of total organic carbon (TOC). During the course of the process, measurements of TOC, PS, pH, and UV254 are carried out on samples taken at certain times. Every outcome is broken down in detail in the following sections.

4.1.1 Raw Water and final efflunet Characterization and Statistical Data of Pollutants

Tables 4.1 and 4.2, respectively, provide a description of the characteristics of the raw water and the final efflunet that are collected from a drinking water treatment plant. This drinking water treatment facility utilizes the more common types of water purification techniques. The following are the process units that are included:

- Structure for the intake of untreated water
- Aeration

- Coagulation and Flocculation
- Sedimentation
- Sand Filter
- Disinfection
- Sludge thickening and dewatering

Table 4.1 : Raw water characterization.

Parameter	Unit	Raw Water
pH	-	8.19
TOC	mg/L	4.70
DOC	mg/L	4.30
UV254	cm^{-1}	0.079
Turbidity	NTU	3.68
Free Chlorine	mg/L	<0.20
Conductivity	$25^{\bullet}C\mu S/cm$	584
Color	mg/LPt-Co	5.2
Total Alkalinity (M.O)	mgCaCO/L	149
Total Hardness	mgCaCO/L	202
Ammonium	mg/L	<0.05
TDS	mg/L	297
Bicarbonate	mg/L	181.8
Calcium	mg/L	60.9
Magnesium	mg/L	12.20
Sodium	mg/L	62.07
Potassium	mg/L	5.15
Sulfate	mg/L	68.9
Nitrate	mg/L	0.76
Nitrite	mg/L	<0.02

Table 4.2 : Final effluent characterization.

Parameter	Unit	Final effluent
pH	-	7.18
TOC	mg/L	3.95
DOC	mg/L	4.30
UV254	cm^{-1}	0.04
Turbidity	NTU	0.24
Free Chlorine	mg/L	1.36
Conductivity	$25^{\bullet}C\mu S/cm$	587
Color	mg/LPt-Co	<2.0
Total Alkalinity (M.O)	mgCaCO/L	116
Total Hardness	mgCaCO/L	206
Ammonium	mg/L	<0.05
TDS	mg/L	298
Bicarbonate	mg/L	141.5
Calcium	mg/L	58.5
Magnesium	mg/L	14.60
Sodium	mg/L	62.7
Potassium	mg/L	5.17
Sulfate	mg/L	96.5
Nitrate	mg/L	0.88
Nitrite	mg/L	<0.02

4.1.2 TOC Removal

Figures 4.1 to 4.4 reveal, for each sample, the impact that the initial PS concentration has on the removal efficiency of total organic carbon (TOC). As it is clear from the figures, when there is a greater concentration of initial PS, there is a corresponding increase in the TOC removal efficiency. Experiments serving as control experiment were carried out on each sample by employing only PS (1.00 mM) and not subjecting it to UV-C irradiation. It is not possible to determine whether or not there was a decrease in TOC concentration as a result of this control experiment. On the other hand, an additional control experiment was carried out on each sample by only irradiating them with UV-C light. The findings of the control experiment indicate that the concentration of TOC has decreased. As can be observed from the figures, the combination of UV-C and PS has a very substantial effect, which leads to an increase in the efficiency of toal organic carbon removal. Removal of TOC was not seen in the control experiments

carried out with only 1 mM PS, but it was achieved with a removal efficiency of 68% in a reaction time of 60 minutes when using 1 mM PS/UV-C under the identical experimental conditions. correspondingly, a rise in PS concentration has a positive impact on the amount of TOC that can be removed using the PS/UV-C process. For instance, after 60 minutes of reaction time, 0.1 mM PS/UV-C removed just 25% of TOC from the coagulation-flocculation effluent sample. Under the same experimental conditions, however, the treatment efficiency increased to 36%, 64%, and 68% with 0.2 mM, 0.5 mM, and 1 mM PS/UV-C, respectively.

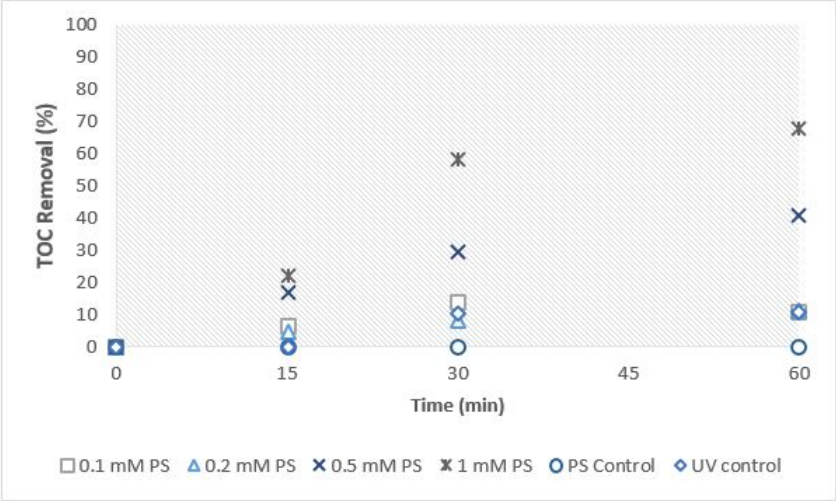


Figure 4.1 : The effect of initial PS concentration on TOC removal efficiency (%) in the raw water sample.

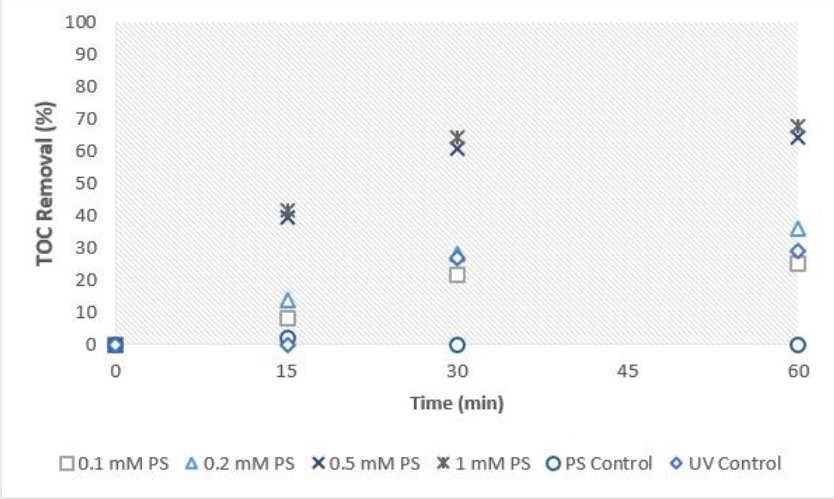


Figure 4.2 : The effect of initial PS concentration on TOC removal efficiency (%) in the coagulation-flocculation effluent sample.

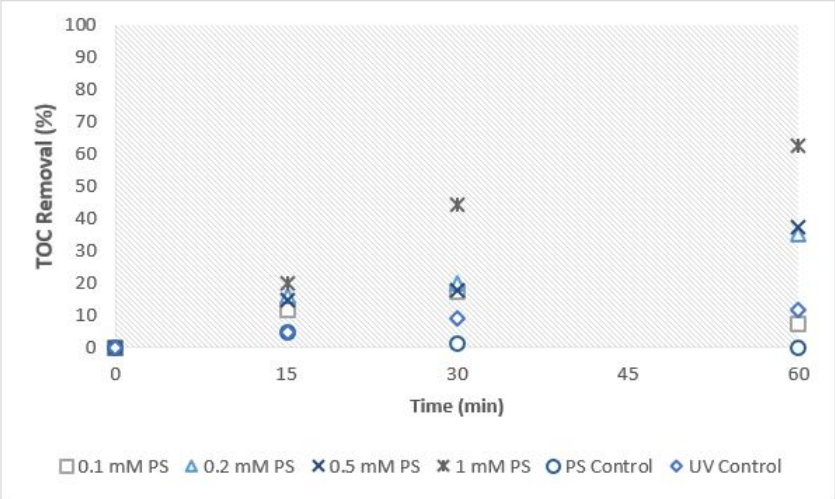


Figure 4.3 : The effect of initial PS concentration on TOC removal efficiency (%) in the filter effluent sample.

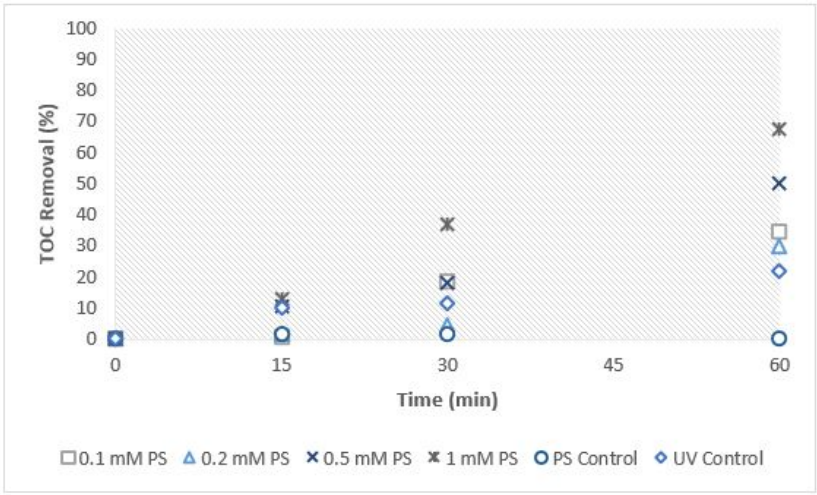


Figure 4.4 : The effect of initial PS concentration on TOC removal efficiency (%) in the final effluent sample.

4.1.3 PS Consumption

The subsequent figures illustrate how the various initial PS concentrations in each of the samples affected the amount of PS consumption at the PS/UV-C process. As can be observed from Figures 4.5 to 4.8, after the reaction period of 60 minutes, all of the PS that was present in the samples with an initial concentration of 0.1, 0.2, and 1 mM was entirely consumed. However, by the completion of the 1 hour, approximately half of the 0.5 mM PS that was originally present could be consumed because it had dropped to that level. The initial PS concentration was maintained at around the same

level throughout all of the control experiments, which were carried out with 1 mM PS.

Figure 4.5 : The effect of initial PS concentration on the PS consumption in the raw water sample.

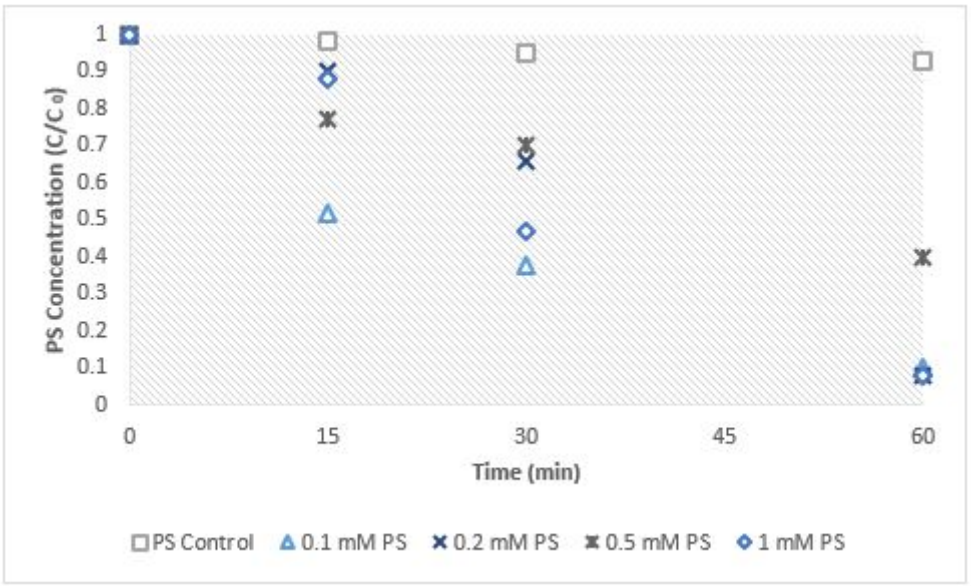


Figure 4.6 : The effect of initial PS concentration on the PS consumption in the coagulation-flocculation effluent sample.

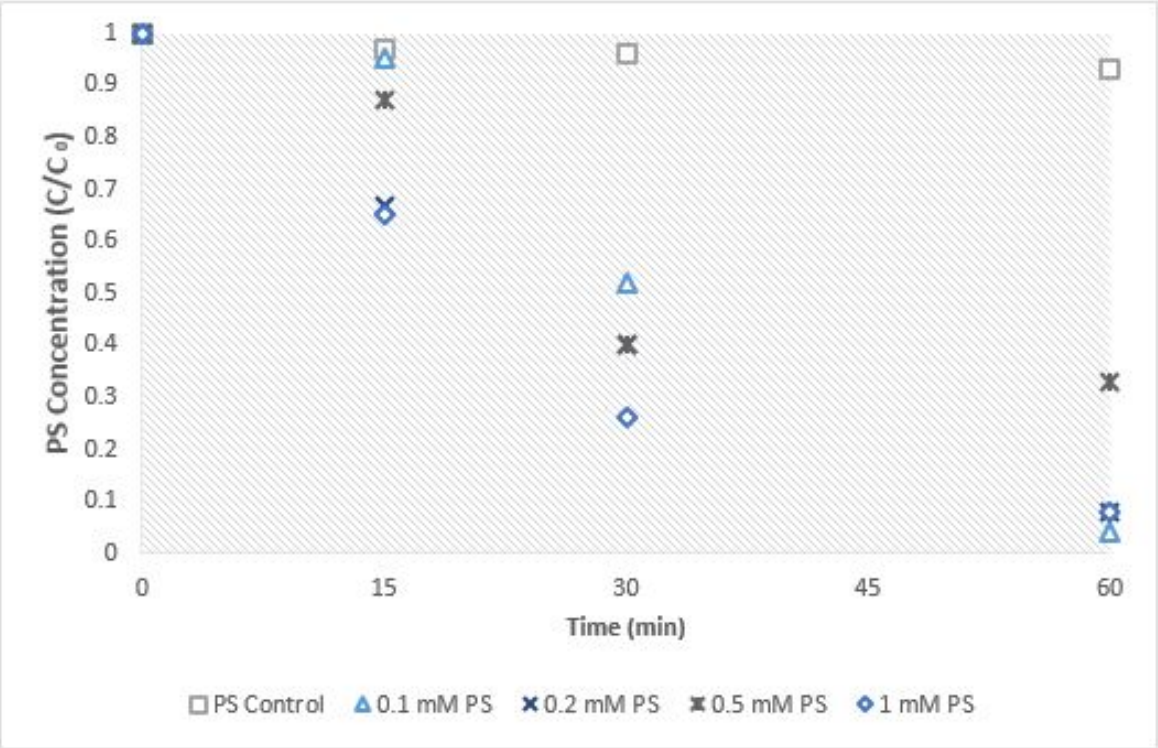


Figure 4.7 : The effect of initial PS concentration on the PS consumption in the filter effluent sample.

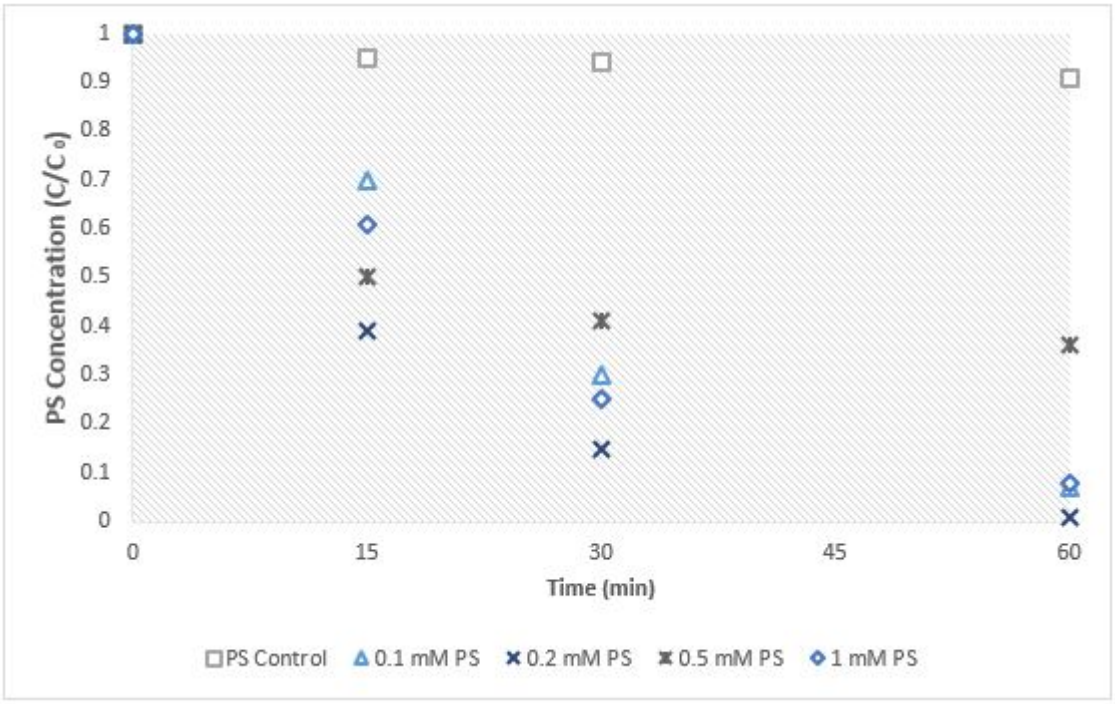


Figure 4.8 : The effect of initial PS concentration on the PS consumption in the final effluent sample.

4.1.4 Change of pH

According to the published research, the pH of the solution drops as the reaction proceeds in the PS/UV-C method for the elimination of organic contaminants [73]. As the subsequent figures illustrates, within the scope of this thesis, substantial drops in pH were seen during the reaction time in the oxidation procedures that were conducted at various initial concentrations of PS.

Except for the control experiment, dramatic reductions in pH was observed to take place during the first 15 minutes of the reaction when high PS dosages were used. In the experiments that served as a control experiments, the pH stayed unchanged. The pH continued to drop in the following times, albeit at a slower rate, and then stayed the same for the last 30 minutes. According to the figure 4.10 The coagulation-flocculation effluent sample experienced the greatest substantial decreases in pH at PS values of 1 mM and 0.5 mM, respectively. During the course of the experiment that was carried out using a coagulation-flocculation effluent sample and 1 mM PS/UV-C, the pH value dropped from 7.8 to 3.6 in the first 15 minutes, and then it decreased to 3.2 at the end of the 30 minutes. After that, it maintained at 3 across the reaction.

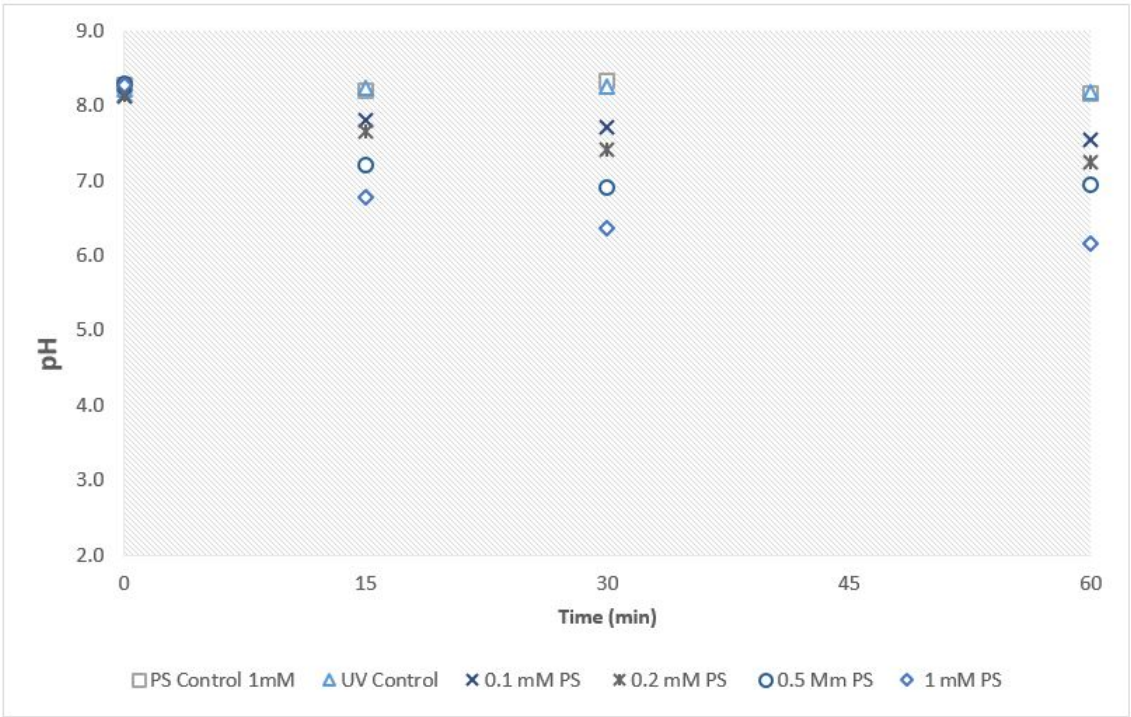


Figure 4.9 : Changes in pH levels during the reaction at various initial concentrations of PS in the raw water sample used in the photochemical treatment of organic carbon using the PS/UV-C process.

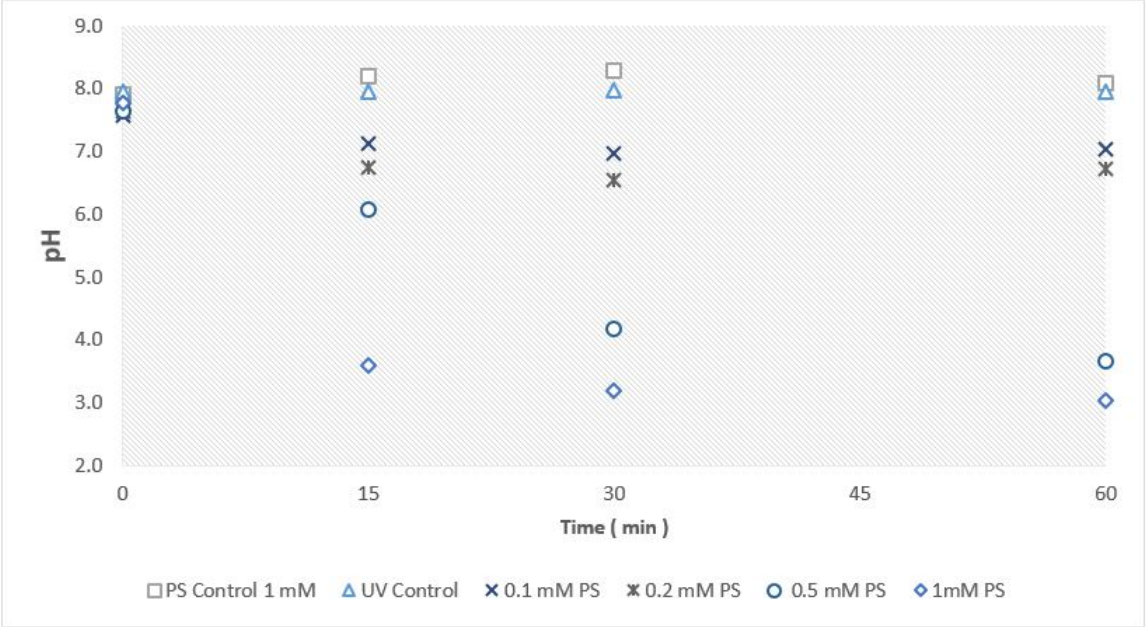


Figure 4.10 : Changes in pH levels during the reaction at various initial concentrations of PS in the coagulation-flocculation effluent sample used in the photochemical treatment of organic carbon using the PS/UV-C process.

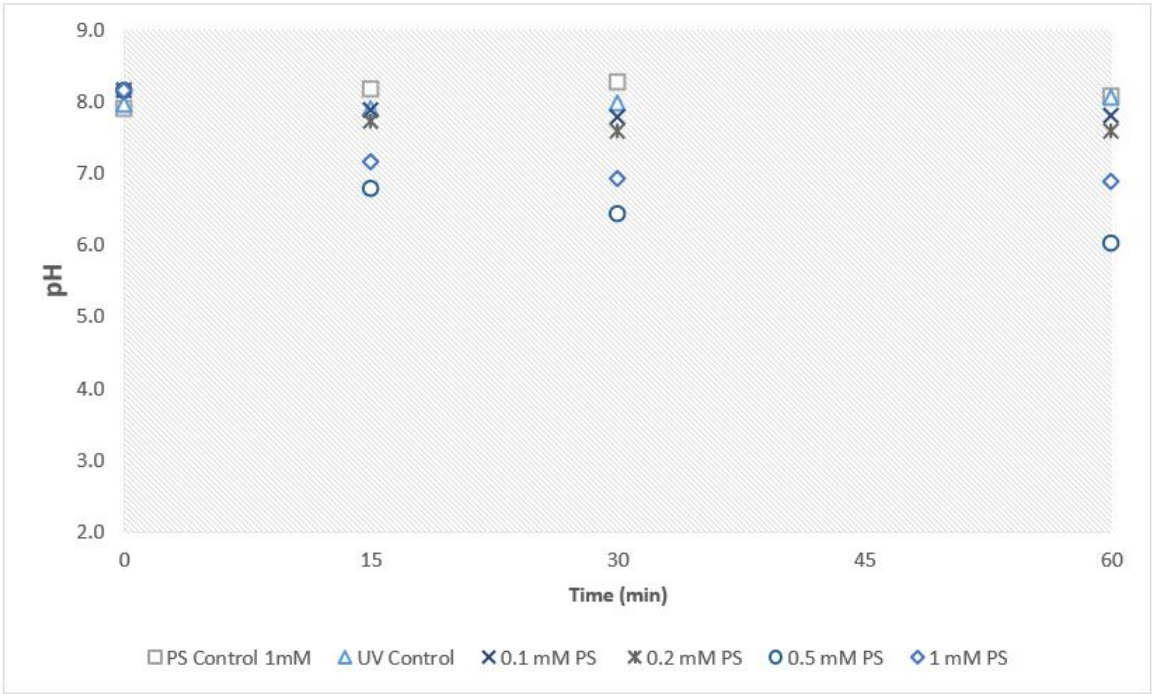


Figure 4.11 : Changes in pH levels during the reaction at various initial concentrations of PS in the Filter effluent sample used in the photochemical treatment of organic carbon using the PS/UV-C process.

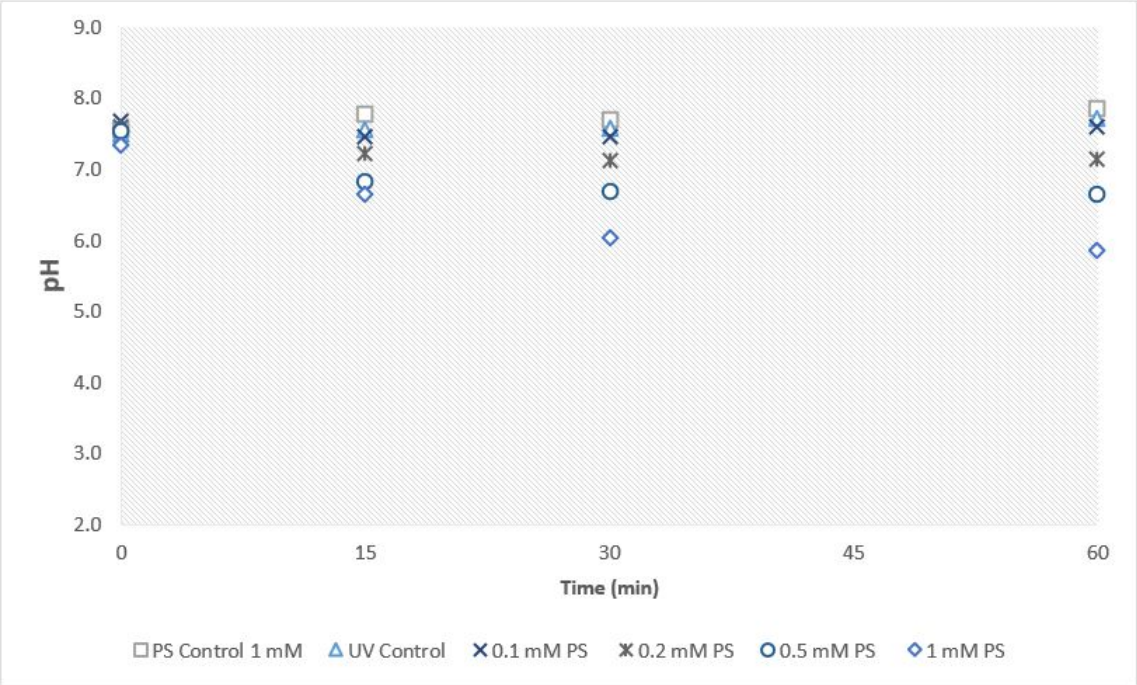


Figure 4.12 : Changes in pH levels during the reaction at various initial concentrations of PS in the Final effluent sample used in the photochemical treatment of organic carbon using the PS/UV-C process.

4.1.5 Change of UV254 and calculations for SUVA

The elimination of organic matter, particularly that which has an aromatic structure, can be indicated by the parameter UV254, which is of great significance in this regard. The drop in UV254 that can be seen in Figures 4.13 to 4.16 occurred during the PS/UV-C procedure after a period of 60 minutes. In light of this, it can be deduced that the removal of organic carbon occurred effectively. Although there is a clear declining trend of UV254 in 1 mM PS/UV-C processes in each sample within the first 30 minutes, it did not change much at the end of the 60th minute and stayed practically the same. In addition to this, the concentration of PS had an effect on the decrease in UV254.

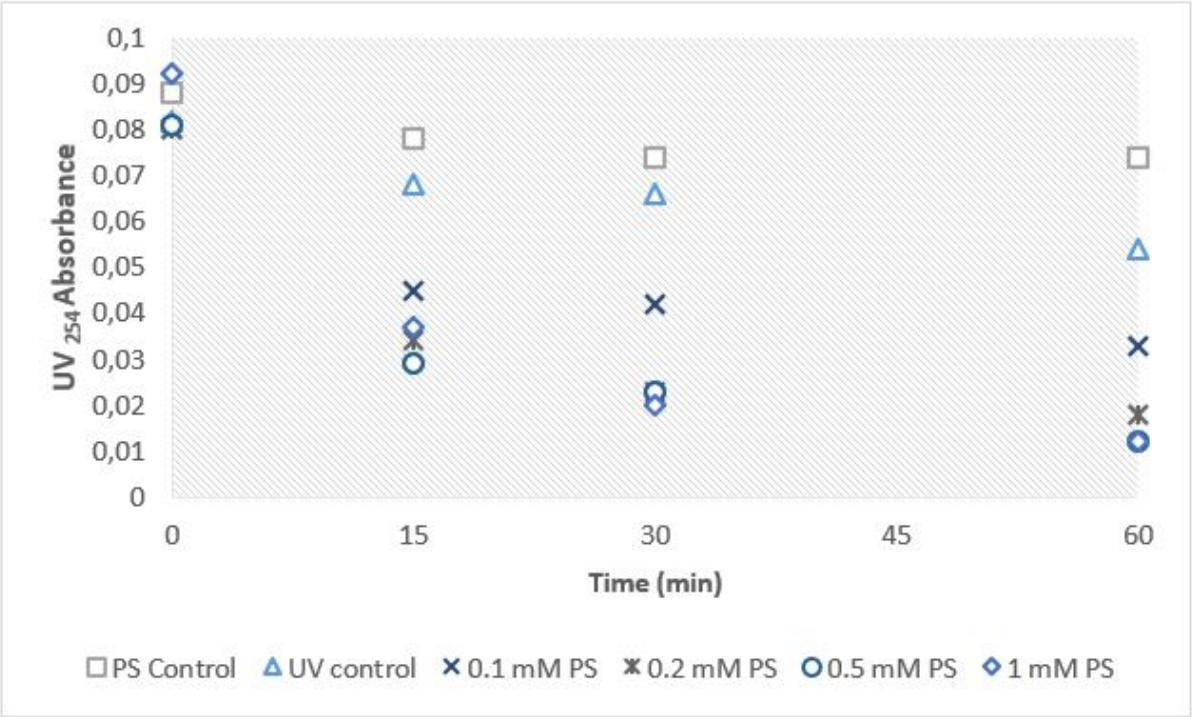


Figure 4.13 : Alterations in UV254 profiles observed during the reaction at various initial concentrations of PS in the photochemical treatment of organic carbon utilizing the PS/UV-C process in the raw water.

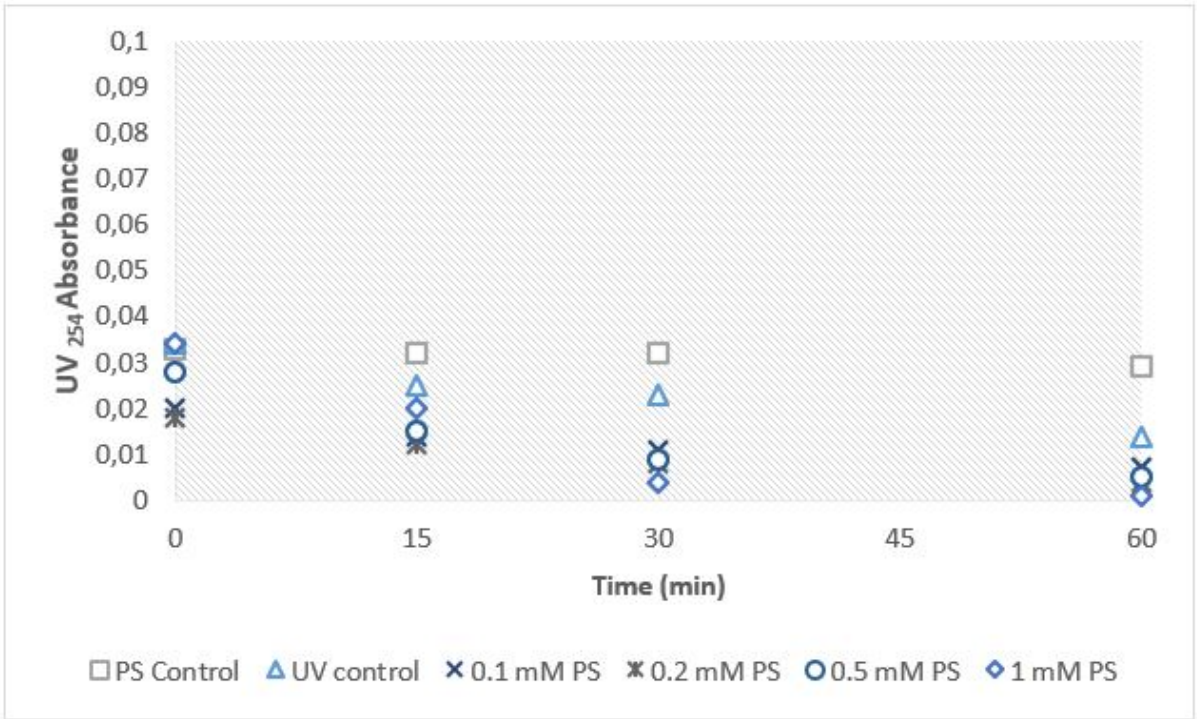


Figure 4.14 : Alterations in UV254 profiles observed during the reaction at various initial concentrations of PS in the photochemical treatment of organic carbon utilizing the PS/UV-C process in the coagulation-flocculation effluent.

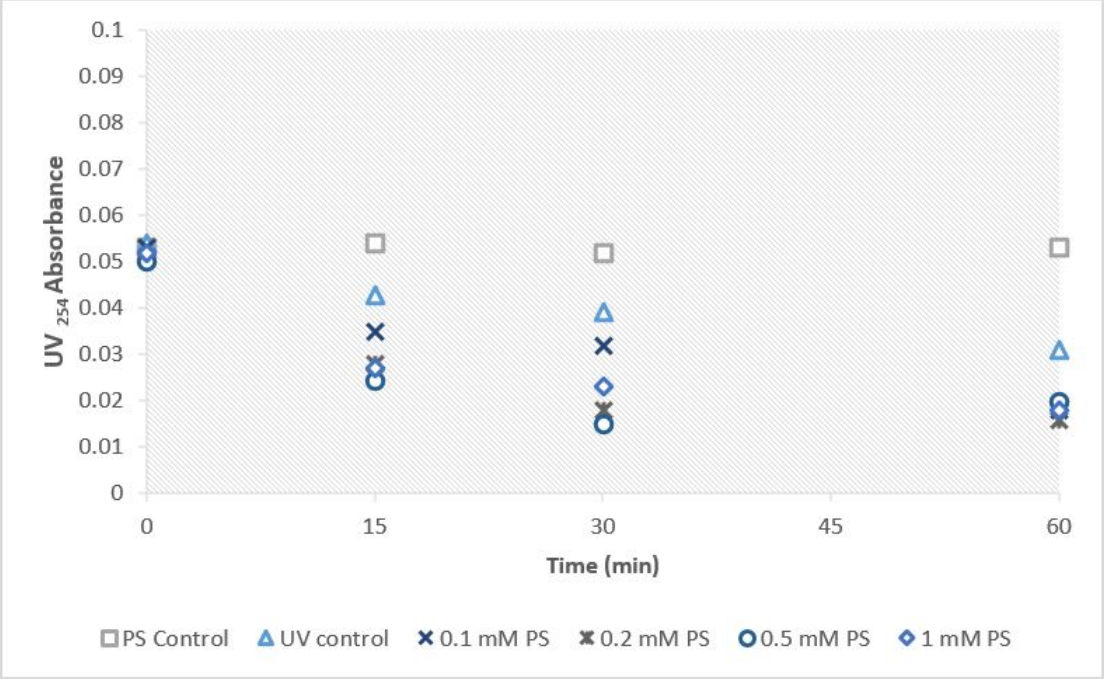


Figure 4.15 : Alterations in UV254 profiles observed during the reaction at various initial concentrations of PS in the photochemical treatment of organic carbon utilizing the PS/UV-C process in the filter effluent.

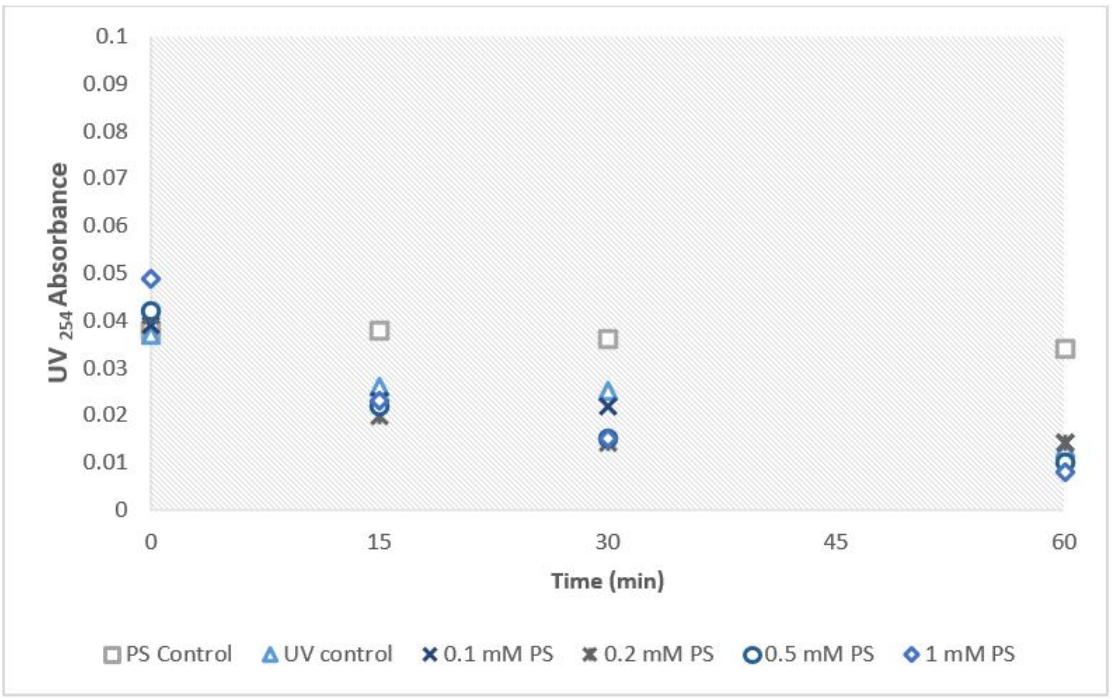


Figure 4.16 : Alterations in UV254 profiles observed during the reaction at various initial concentrations of PS in the photochemical treatment of organic carbon utilizing the PS/UV-C process in the final effluent.

The specific ultraviolet absorbance (SUVA) values that were determined based on the measurements of UV254 and DOC are listed in Table 4.3 to 4.6 below. As can be

seen from the UV254 readings and the declining SUVA levels, the organic carbon was successfully removed in all samples.

$$SUVA(\frac{L}{mgM}) = \frac{UVA(cm^{-1})}{DOC(mg/L)} \times 100(\frac{cm}{M}) \tag{4.1}$$

$$UVA(cm^{-1}) = \frac{UVAbsorbanceat254nm}{Thequartzcellpathlength(cm)} \tag{4.2}$$

Table 4.3 : SUVA calculations of PS/UV-C process for the final effluent sample.

Time (min)	Control (1 mM)	0.1 mM	0.2 mM	0.5 mM	1 mM
0	1.10	0.85	0.88	0.84	1.10
60	0.86	0.38	0.40	0.38	0.49

Table 4.4 : SUVA calculations of PS/UV-C process for the coagulation-flocculation effluent sample.

Time (min)	Control (1 mM)	0.1 mM	0.2 mM	0.5 mM	1 mM
0	1.39	0.76	1.25	1.82	2.22
60	1.34	0.41	0.33	1.28	0.14

Table 4.5 : SUVA calculations of PS/UV-C process for the filter effluent sample.

Time (min)	Control (1 mM)	0.1 mM	0.2 mM	0.5 mM	1 mM
0	1.46	1.51	1.25	1.57	1.40
60	1.37	0.56	0.50	0.88	1.30

Table 4.6 : SUVA calculations of PS/UV-C process for the raw water sample.

Time (min)	Control (1 mM)	0.1 mM	0.2 mM	0.5 mM	1 mM
0	1.72	1.80	1.46	1.67	1.56
60	1.42	0.83	0.37	0.37	0.49

4.2 Comparison of TOC Removal in Various Samples

Figure 4.17 reveals, for each sample, the impact of 1 mM PS on the removal efficiency of total organic carbon (TOC). As is obvious, when we apply 1 mM PS in the PS/UV-C process, we achieve the most significant TOC removal efficiency in our samples.

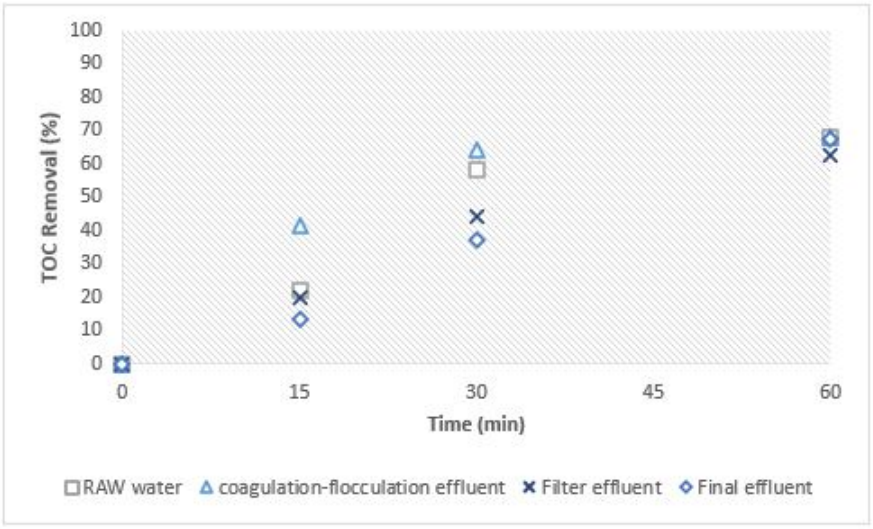


Figure 4.17 : Comparison of the effect of an initial PS concentration of 1 mM on TOC removal efficiency (%) in all samples.

Figure 4.18 shows the effect that 0.5 mM PS has on the effectiveness of removing total organic carbon for each sample.

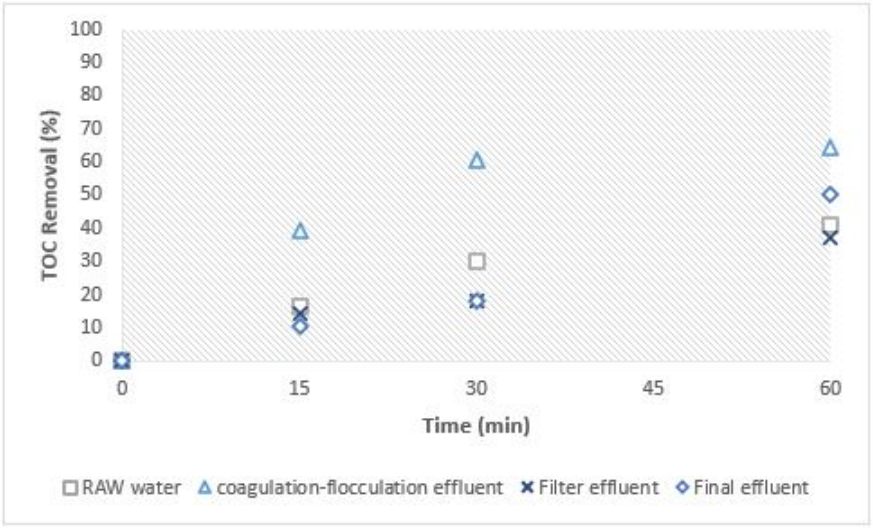


Figure 4.18 : Comparison of the effect of an initial PS concentration of 0.5 mM on TOC removal efficiency (%) in all samples.

Figure 4.19 reveals, for each sample, the impact of 0.2 mM PS on the removal efficiency of total organic carbon (TOC).

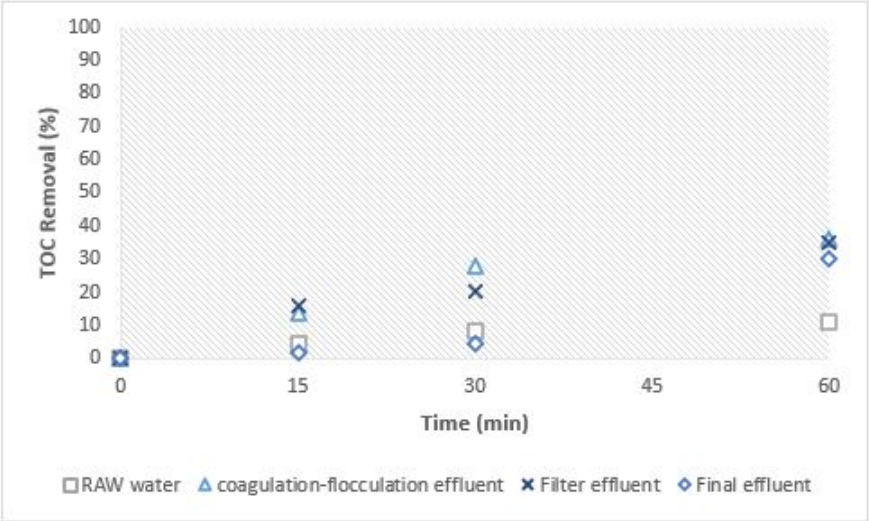


Figure 4.19 : Comparison of the effect of an initial PS concentration of 0.2 mM on TOC removal efficiency (%) in all samples.

Figure 4.20 shows the effect that 0.1 mM PS has on the effectiveness of removing total organic carbon for each sample. As is clear, an initial PS concentration of 0.1 mM has a small effect on the efficiency of TOC removal in all samples.

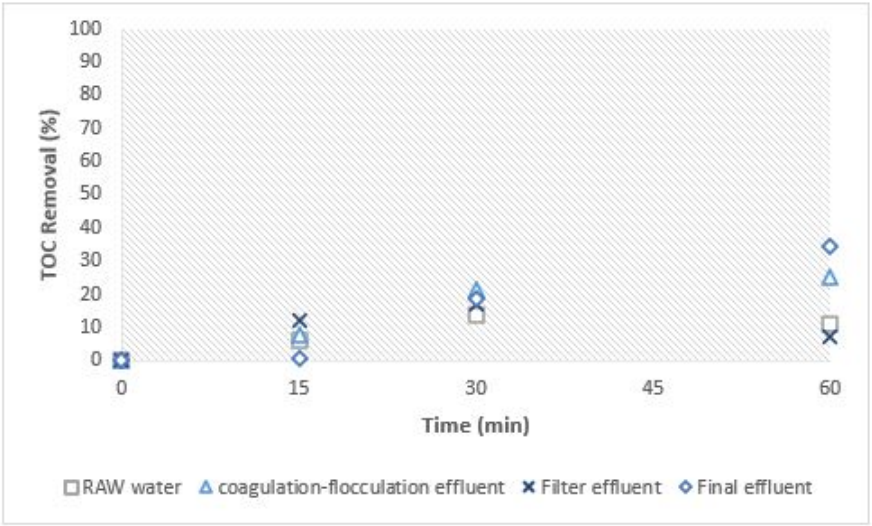


Figure 4.20 : Comparison of the effect of an initial PS concentration of 0.1 mM on TOC removal efficiency (%) in all samples.

According to figures 4.17 to 4.20, for each initial concentration of PS, the impact that it has on the removal efficiency of total organic carbon (TOC) in our samples. As is clear from the figures, the most significant TOC removal efficiency (68.21%) occurred when we applied the process with 1 mM initial PS in the coagulation-flocculation effluent sample. But, because of the great drop in PH value at the end of the process, we do not prefer to apply this method after the coagulation-flocculation step. According to results, it seems applying the PS/UV-C process with an initial PS concentration of 1 mM for raw water is the best choice to achieve the most efficiency in a drinking water treatment plant for the removal of total organic carbon.

5. CONCLUSIONS AND PERSPECTIVES

Due to the high oxidation potential of sulfate radicals, there has been an increase in recent years in the amount of interest that has been generated by their use in the process of treating wastewater and drinking water. In this thesis, the application of sulfate radical ($SO_4^{\bullet -}$) based persulfate (PS)/UV-C photochemical advanced oxidation procedures in organic carbon removal was investigated. The processes in concern were investigated at a variety of oxidant concentrations in order to find the optimal operating conditions and process mechanisms andThe achievements of the processes were assessed by taking into consideration the total organic carbon (TOC) removals. These are the experimental outcomes we observed:

1. The PS/UV-C methods, when applied to real water samples, led to successful mineralization of the water. In studies of the photochemical treatability of real water samples, it was found that longer treatment durations were necessary for the complete removal of total organic carbon.
2. According to the results of control experiments, when the control experiments were carried out with only 1 mM PS and no UV-C irradiation, the treatment efficiency of TOC was found to be negligible; on the other hand, application of only UV-C irradiation was shown to be slightly effective in the removal of TOC.
3. In the experiments conducted by utilizing 1 mM PS/UV-C in the raw water sample, the total organic carbon removal efficiency was found to be 22%, 58%, and 68% for the duration of the experiment (first 15 minutes, 30 minutes, and 60 minutes, respectively). Then, the total organic carbon removal efficiency was determined to be 42%, 64%, and 68% in the first 15 minutes, 30 minutes, and 60 minutes, respectively, in the experiments using 1 mM PS/UV-C in the coagulation-flocculation effluent sample.
4. The total organic carbon removal efficiency in the experiments using 0.1 mM, 0.2 mM, and 0.5 mM PS/UV-C in the raw water sample was found to be 11%, 11%, and

41%, respectively, at the completion of the reaction time (60 minutes). Similar to that, The total organic carbon removal efficiency in the experiments using 0.1 mM, 0.2 mM, and 0.5 mM PS/UV-C in the the coagulation-flocculation effluent sample was determined to be 25%, 36%, and 64%, respectively, at the completion of the reaction time.

5. After that, In the experiments conducted by utilizing 1 mM PS/UV-C in the filter effluent sample, the total organic carbon removal efficiency was found to be 20%, 44%, and 63% for the duration of the experiment (first 15 minutes, 30 minutes, and 60 minutes, respectively). Then, the total organic carbon removal efficiency was determined to be 13%, 37%, and 68% in the first 15 minutes, 30 minutes, and 60 minutes, respectively, in the experiments using 1 mM PS/UV-C in the final effluent sample.

6. The total organic carbon removal efficiency in the experiments using 0.1 mM, 0.2 mM, and 0.5 mM PS/UV-C in the filter effluent sample was found to be 7%, 35%, and 37%, respectively, at the completion of the reaction time (60 minutes). Similar to that, The total organic carbon removal efficiency in the experiments using 0.1 mM, 0.2 mM, and 0.5 mM PS/UV-C in the the final effluent sample was determined to be 35%, 30%, and 50%, respectively, at the completion of the reaction time.

7. The formation of carboxylic acid during the reaction caused a considerable reduction in pH in all of the PS/UV-C experiments. During the phase of the experiment in which the coagulation-flocculation effluent sample was subjected to 1 mM PS/UV-C, the level of reduction that was measured was found to be the most significant.

8. At all concentrations except 0.5 mM, approximately all of the PS was consumed in each sample, and just about half of the 0.5 mM PS that was originally present could be consumed.

9. In all of our samples, the reduction in UV254 value that occurred during the PS/UV-C procedure after a period of 60 minutes shows that the removal of organic carbon occurred effectively.

As a consequence of the study carried out for the thesis, it was discovered that sulfate radical-based photochemical advanced oxidation processes can be utilized in order to efficiently remove the organic matter that is present in the water. It is hypothesized that

the mechanisms of advanced oxidation that have been researched can also be utilized successfully in the treatment of drinking water. However, in order to discover the ecotoxicological effects of these pollutants and oxidation products, it is necessary and important to evaluate the biotoxic impacts of intermediate and end product generated during the treatment of organic pollutants by advanced oxidation processes. This research should be conducted in conjunction with toxicity testing.

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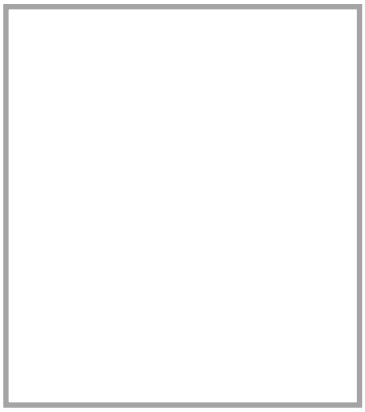

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