

T.C.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**TREATMENT OF P-AMINOPHENOL PRODUCTION
WASTEWATER BY ELECTROCHEMICAL OXIDATION PROCESS
USING BORON-DOPED DIAMOND ANODES**

MİHRİCAN YURTARSLAN
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF ENVIRONMENTAL ENGINEERING

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PROF. DR. MEHMET KOBYA

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GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

P-AMİNOFENOL ÜRETİM
ATIKSUYUNUN ELEKTROKİMYASAL
OKSİDASYON PROSESİ İLE BOR KATKILI
ELMAS ANOTLAR KULLANILARAK
ARITILMASI

MİHRİCAN YURTARSLAN
YÜKSEK LİSANS TEZİ
ÇEVRE MÜHENDİSLİĞİ ANABİLİM DALI

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GEBZE
2021

GEBZE TEKNİK ÜNİVERSİTESİ	YÜKSEK LİSANS JÜRİ ONAY FORMU
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SUMMARY

Pharmaceutical wastewater has many adverse environmental and health effects. In the drug manufacturing plant, many different kinds of the compound are produced and wastewater composition fluctuates. Therefore, the treatment of this type of wastewater has been a complicated issue to reach discharge standards. Especially, phenol and derivatives are very complex organic pollutants and they are not suitable for conventional biological treatment methods. Thus, advanced electrochemical processes are widely preferred to treat complex substances. The electrochemical oxidation process is very effective to oxidize phenolic wastewater. In this study, treatment of p-aminophenol production wastewater by electrochemical oxidation process using boron-doped diamond anode was investigated. The effects of significant operating parameters such as current density, initial pH, electrolyte concentration, and dilution were researched. According to experiment results, 95% COD and 75.9% TOC removal efficiencies were achieved.

Key Words: Electrochemical Oxidation, p-aminophenol Wastewater, Boron-Doped Diamond Anode, Removal Efficiency.

ÖZET

İlaç üretim atık suyun çevreye ve insan sağlığına birçok olumsuz etkisi vardır. İlaç üretim fabrikasında, farklı türde birçok ürün üretilir ve atık su içeriğinde dalgalanmalar görülür. Dolayısıyla, ilaç üretim atık suyun arıtımı her zaman kompleks bir konu olmuştur ve istenilen deşarj standartlarını sağlamak zordur. Özellikle fenol ve türevleri biyolojik olarak parçalanamayan organik kirleticilerdir ve geleneksel biyolojik arıtma yöntemleriyle arıtıma uygun değildir. Bu yüzden, bu tarz arıtımı zor kirleticilerin giderilmesinde ileri oksidasyon yöntemleri tercih edilir. Elektrokimyasal oksidasyon prosesi fenol içeren atık suların arıtımında oldukça etkilidir. Bu çalışmada p-amino fenol üretim atık suyun bor katkılı elmas anot kullanarak elektrokimyasal oksidasyon prosesi ile arıtılması araştırılmıştır. Akım yoğunluğu, başlangıç pH'ı, elektrolit konsantrasyonu ve seyreltme oranı gibi önemli işletim parametrelerinin etkileri incelendi. Deney sonuçlarına göre, en yüksek %95 KOİ ve %75.9 TOK giderim verimleri elde edildi.

Anahtar Kelimeler: Elektrokimyasal Oksidasyon, p-amino fenol Atıksu, Bor Katkılı Elmas Anot, Giderim Verimi.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms</u>	
A	: Ampere
kWh/m ³	: Kilowatt-hour/Meter cube
mg/L	: Milligram/Liter
mS/cm	: Milli siemens/Centimeter
nm	: Nanometer
AOP	: Advanced Oxidation Process
BDD	: Boron Doped Diamond
BOD	: Biological Oxygen Demand
COD	: Chemical Oxygen Demand
EC	: Electrocoagulation
EF	: Electroflotation
EO	: Electrochemical Oxidation
PAP	: p-aminophenol
SS	: Suspended Solids
TKN	: Total Kjeldahl Nitrogen
TOC	: Total Organic Carbon
TP	: Total Phosphorous

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1. INTRODUCTION

1.1. Background

The importance and necessity of water for living life is indisputable. Water resources are rapidly polluting with industrialization and urbanization. The production and use of chemicals worldwide are very high and as a result, the environmental damage is high. Proper wastewater treatment methods should be chosen [Rajkumar and Palanivelu, 2004].

Many industrial wastewaters include phenol and derivatives that are coming from the production of pesticides, pharmaceuticals, textiles, petrochemicals, pulp, and paper, etc. most of these substances are known as toxic, persistent, corrosive, and non-biodegradable. Pharmaceutical wastewater treatment is always difficult concerning reaching discharge standards [Zhu et al., 2007], [Canizares et al., 2005], [Tekin et al., 2006], [Tewari and Boodhoo, 2005].

Phenolic substances are complex organic compounds that are not suitable for biological degradation. They disrupt the function of the bacterial population. Therefore, conventional biological methods are usually inappropriate for treatment of them. Various advanced oxidation processes (AOPs) such as ozonation, Fenton oxidation, and electrochemical oxidation (EO) were analyzed for the treatment of phenolic wastewater in the literature. Among these, EO appears to be one of the most favorable technologies. EO process is very effective to oxidize toxic substances and the treatment of phenolic wastewater. [Tekin et al., 2006], [Zhu et al., 2007], [Rajkumar and Palanivelu, 2004]. In this study, the treatment of p-aminophenol (PAP) production wastewater with boron-doped diamond (BDD) anodes was studied.

1.2. Purpose and Scope of Research

In this study, PAP production wastewater was treated by using BDD anodes. The experiments were performed by batch processes. PAP wastewater has a high chemical oxygen demand (COD) and it is difficult to treat it. Therefore, the treatment of wastewater containing paracetamol is still being studied. In wastewater treatment,

biological oxygen demand (BOD), total organic carbon (TOC), and COD are generally important parameters. Comprehensive studies examining all parameters for PAP wastewater are very few in the literature.

In previous studies, it was generally studied with synthetically prepared PAP solutions. Since the contaminant parameter concentrations are constant, conducted studies do not fully reflect the truth. This study was aimed at the treatment of real wastewater from the PAP synthesis unit of a pharmaceutical factory and, analyzing different process parameters and their effects.

2. LITERATURE REVIEW

Drugs and medicines are the main sources of pharmaceutical pollution in waters. Pharmaceuticals such as hormones, analgesics, anti-depressants, antibiotics are commonly found in streams, rivers, lakes, and even groundwaters. Drug residues in the water are a critical environmental issue that has to be solved.

Excessive use of medicines to treat diseases contributes to the formation of a new class of potentially hazardous organic contaminants. When medicines are used, they cannot be completely digested in the body. They can convert to metabolites. Many pharmaceutical compounds can be constantly found in the surface waters due to their high concentrations. These compounds in the aquatic environment originate from household sewers, industrial wastewater, hospital, and health centers. Also, these compounds can be leak into the groundwater. Therefore, effective treatment methods should be improved to prevent potential health and environmental effects of pharmaceuticals. It is hard to remove them by conventional biological wastewater treatment methods. Treatment plants are designed to treat municipal and industrial wastewater. In these facilities, various parameters such as particulate matter, nitrogen, phosphate, pathogens, and metal ions are measured. However, parameters related to pharmaceuticals and micro-pollutants are not measured [Dalgic, 2013].

Pharmaceuticals at low concentrations cannot have acute toxic effects on aquatic organisms but they can have chronic effects. Pharmaceuticals can affect the endocrine system of fish and other aquatic creatures.

Wastewater generated in pharmaceuticals facilities is dangerous and toxic. They usually have a dark color and strong odor. Biological treatment systems are not capable to treat wastewater with high COD and low BOD concentration. For these reasons, chemical-physical treatment methods are preferred to remove pharmaceuticals from wastewater [Dalgic, 2013].

The following sections introduce advanced oxidation processes, electrochemical oxidation process in detail, and pharmaceutical treatment methods in the literature.

2.1. Advanced Oxidation Processes

The presence of toxic and organic substances in wastewater is a problem that has gained importance in the world in recent years. Conventional biological treatment methods are not very effective to biodegrade organic compounds. Although physicochemical methods, such as coagulation-flocculation, activated carbon adsorption, can be effective, they are not preferred due to transferring the pollutant from one phase to another. Advanced oxidation processes convert harmful organic compounds in water to carbon dioxide or other non-toxic end products [Yalabık, 2010]. In AOPs, hydroxyl radicals are the main reactive intermediates that are responsible for organic matter oxidation. Hydroxyl radicals react with organic and inorganic substances in water rapidly. Therefore, they are strong oxidizers for synthetic and natural organic compounds that are resistant to degradation by other processes. They are not very selective in the oxidation processes and their rate constants are large [Akbal and Balkaya, 2002]. Also, these radicals are much stronger than other chemicals used in traditional chemical processes.

AOPs are very effective for many different molecular structures of organic and inorganic pollutants and wastewater with high COD. The efficiency of AOPs depends on some physicochemical parameters like initial oxidant dosage, pH, temperature, and contact time. The advantages of AOPs are; strong oxidant formation, short treatment time, very fast reactions, not creating gas emission or sludge, being effective for many different for many molecular structures. The disadvantages of AOPs are; hydroxyl radicals can oxidize non-target organics due to non-selectivity, the need for control physicochemical parameters, effectiveness in high COD wastewaters, having high operating cost [Yalabık, 2010], [Akbal and Balkaya, 2002].

AOPs technologies include various activation methods as well as oxidant production and can use lots of different methods for destruction. Figure 2.1 gives an overview of the different found AOPs and is classified into five groups that are ozone-based, UV based, catalytic, physical, and electrochemical. But this scheme is not a strict classification because some processes include various technologies and they can be put in different categories [Miklos et al., 2018].

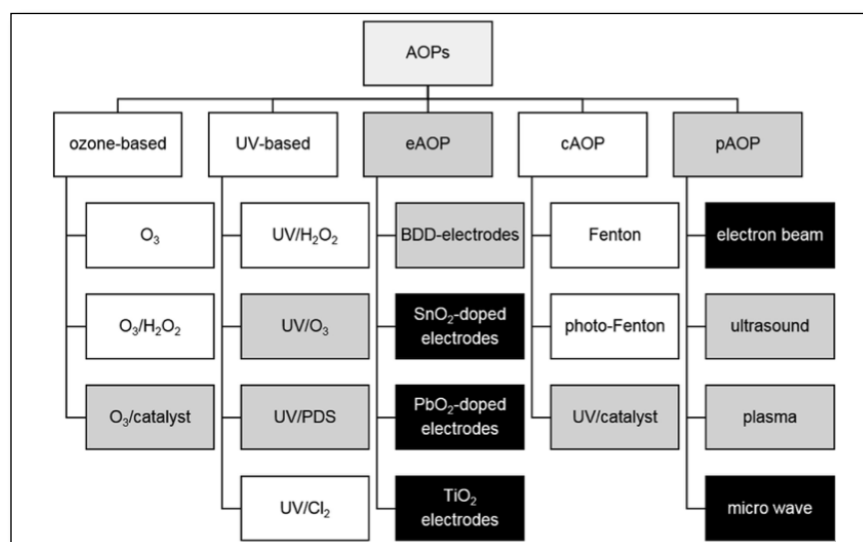


Figure 2.1: Classification of different AOPs.

2.1.1. Ozone Based AOPs

Ozone is a strong oxidizing agent utilized in the treatment of drinking and wastewater [Torun et al., 2015]. Though the main purpose of oxidation with ozonation is disinfection, ozonation can be used for the purification of strong biodegradable compounds and pre-oxidation of wastewater [Yalabik, 2010]. Ozone reactions in water are extremely complicated. Ozone reactions with organic components have different ways, directly (molecular ozone) and indirectly (hydroxyl radical). Direct reactions have more selectivity than indirect reactions [Ikehata and Li, 2018]. These different reactions generate different oxidation products. While the direct mechanism oxidizes at $\text{pH} < 4$, the indirect mechanism oxidizes at $\text{pH} > 9$. At $\text{pH} 4-9$, both mechanisms form radicals [Yalabik, 2010]. Particularly, at $\text{pH} > 9$, ozonation can be thought of as favorable AOP, if the precipitation is not a problem [Miklos et al., 2018].

The $\text{O}_3/\text{H}_2\text{O}_2$ AOP (Peroxone process) is likely best studied and applied to ozone-based AOP for treatment. At a low concentration of H_2O_2 , ozone decomposes very quickly and $\bullet\text{OH}$ concentration rises. Only HO_2^- ion reacts with ozone to start the free radical reactions. The reaction rate constant of this reaction is really large and therefore, ozone decomposes very quickly with the aid of hydrogen peroxide. So, pollutants likely to $\bullet\text{OH}$ reactions can be broken effectively in the peroxone process [Ikehata and Li, 2018], [Miklos et al., 2018].

There are two types of catalytic ozonation relying on the solubility of catalyst in water [Miklos et al., 2018]. Transition metal ions like iron, zinc, cobalt, copper, acted as homogeneous catalysts in the proper medium and the presence of catalyst enhanced the ozone decomposition. On the other hand, dissolved metal ions and some metal oxides like iron oxide, copper oxide played a role in the decomposition of ozone. They are known as heterogeneous catalysts [Ikehata and Li, 2018]. Although both homogenous and heterogeneous catalytic ozonation is functional for high strength wastewaters and landfill leachates, catalyst recovery and understanding of the complex mechanism is an issue [Miklos et al., 2018], [Ikehata and Li, 2018].

2.1.2. UV Based AOPs

UV-based AOPs include the combination of UV light and various radical promoters [Miklos et al., 2018]. UV-based technologies occur either in a homogeneous medium with the addition of suitable oxidants (such as hydrogen peroxide or ozone) or in a heterogeneous medium containing semi-conductor particles [Akbal and Balkaya, 2002]. UV/H₂O₂ combination is the most commonly focused technology. Other radical promoters like chlorine or persulfate are being studied [Miklos et al., 2018].

Hydrogen peroxide is a strong chemical oxidant. The free radicals generated when UV light breaks down an oxidant molecule are more energetic oxidants. Hydrogen peroxide generates hydroxyl radicals in the presence of UV radiation. This process has a synergetic effect to degrade pathogens and organic substances in water and wastewater. Produced hydroxyl radicals play a very important role in the success of the process [Nurazim et al., 2019]. The efficiency of the UV/H₂O₂ process relies on different factors. These factors affect the process degradation ability, light transmittance of the mixture, dosage of hydrogen peroxide, temperature, and pH. The synergetic effect between H₂O₂ and UV radiation has importance for pollutants that need strong oxidation conditions [Nurazim et al., 2019].

For the treatment of organic pollutants, UV/H₂O₂, and UV/O₃ combinations are proper. Combinations of these techniques are almost identical qualitatively but have little differences quantitatively. UV/O₃ process is noticeable for destroying toxic and water refractory organic substances. O₃ irradiation generates H₂O₂ quantitatively.

Generated H_2O_2 is photolyzed in the presence of UV and $\bullet\text{OH}$ radicals are produced [Nurazim et al., 2019], [Covinich et al., 2014]. There are important conditions for the efficiency of the UV/ O_3 process. These are; initial concentration of pollutants, slightly alkaline pH, temperature optimization, the continuous bubbling of ozone, and the existence of radical scavengers [Covinich et al., 2014].

Another alternative to $\bullet\text{OH}$ based oxidation can be UV/ $\text{SO}_4^{\bullet-}$. This technique principally produces sulfate radicals to oxidize organic pollutants in water. Sulfate radicals are more selective than hydroxyl radicals. And, they are strong oxidants [Miklos et al., 2018]. Sulfate radicals are generally produced from persulfate and peroxymonosulfate. Sulfate radical-based AOPs have many advantages following; sulfate radical has high oxidation potential than $\bullet\text{OH}$, it reacts more selectively to organic substances, it reacts effectively over a wide pH range to organics [Rodriguez et al., 2018]. Therefore, $\text{SO}_4^{\bullet-}$ based AOPs might be a substantial option to $\bullet\text{OH}$ -based processes [Miklos et al., 2018].

The other alternative is UV/ Cl_2 combination. In this technique, activated chlorine generates radicals such as $\text{Cl}\bullet$, $\bullet\text{Cl}_2^-$, and $\bullet\text{OH}$ to oxidize organics. Like sulfate radical, $\text{Cl}\bullet$ is more selective than $\bullet\text{OH}$ because it reacts generally with electron-rich compounds. Chlorine dioxide and hypochlorite are the main oxidants. This technique can be preferred for low pH waters. For now, this technique has been conducted on lab-scale processes [Miklos et al., 2018].

2.1.3. Catalytic AOPs

The Fenton system is one of the effective advanced treatment processes [Dalgic et al., 2017]. Hydrogen peroxide and aqueous ferrous ions react to produce hydroxyl radicals. As known, $\bullet\text{OH}$ can degrade toxic or refractory organic contaminants in wastewater. The main application of Fenton is to purify wastewater by radical oxidation and flocculation. Ferrous ions catalyze H_2O_2 to degrade into $\bullet\text{OH}$ and to start the generation of other radicals in acidic solution. $\bullet\text{OH}$, has a powerful oxidation capacity and it can fully mineralize organic pollutants to CO_2 , inorganic salts, and water [Xu et al., 2020]. The important chemicals of Fenton are iron and H_2O_2 that are inexpensive, safe, and environmentally friendly [Dalgic et al., 2017]. The common Fenton continuous flow process contains acid regulation, catalyst mixing, oxidation

reaction, neutralization, and solid-liquid separation as shown in Figure 2.2 [Xu et al., 2020].

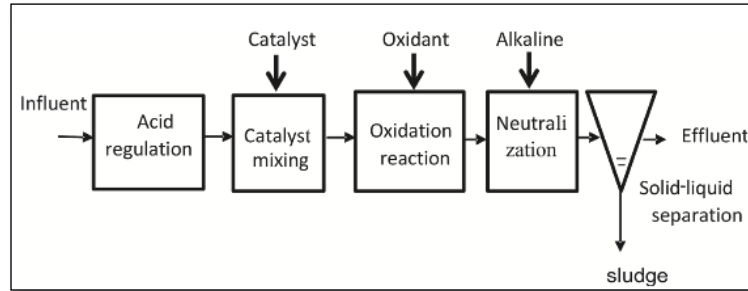
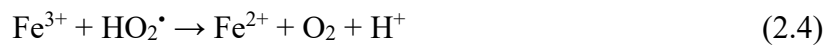


Figure 2.2: Schematic diagram of the Fenton process.

The Fenton process has plenty of advantages following: it has high efficiency and simplicity to oxidize organics, it is a cost-effective and nontoxic process. However, it has some disadvantages, as in every process, such as limited pH range, the formation of more ferric sludge, and high hydrogen peroxide consumption [Dalgic et al., 2017], [Xu et al., 2020]. For defeating these disadvantages, enhanced Fenton processes have been studied broadly in the literature [Xu et al., 2020].

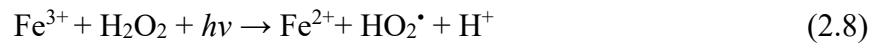
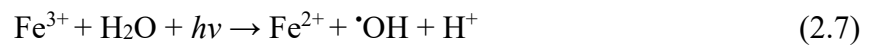
The main mechanism of the Fenton process involves the following reactions [Ameta et al., 2018].



The Fenton process is generally performed at low pH values, under 3. The oxidation performance of $\cdot\text{OH}$ depends on the solution pH. At low pH, the oxidation performance of $\cdot\text{OH}$ is rising and improved [Xu et al., 2020]. Also, coagulation and oxidation stages are mainly affected by the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio [Dalgic et al., 2017]. There

are various types of enhanced Fenton processes, for example, photo-Fenton, electro-Fenton, sono-Fenton, photo-electro-Fenton, and other combinations [Ameta et al., 2018].

The photo-Fenton process is combining the H_2O_2 , UV radiation, and Fe^{2+} or Fe^{3+} ions. This combination generates more hydroxyl radicals. Traditional Fenton reaction collects Fe^{3+} ions in the process. In the Photo-Fenton technique, photochemical reformation of ferrous ions happens. The newly produced ferrous ions react once again with hydrogen peroxide and this process goes like a cycle [Ameta et al., 2018]. Reactions are going like following [Ameta et al., 2018].



The photo-Fenton process works better at pH 3 when the solubility of hydroxy- Fe^{3+} is high. In this process, acidic conditions are more preferable [Ameta et al., 2018]. The advantage of this process is to reduce the dosage of catalyst. And this decreases the production of iron sludge. On the other hand, high energy consumption, high cost, and longtime usage of UV energy are the disadvantages of this process [Xu et al., 2020].

In the literature, there are many different combinations of the Fenton process with other techniques to improve the performance of the process. For example, the electro-Fenton process is combining Fenton processes and electrochemical processes. The sono-Fenton process is combining ultrasound and Fenton reagent to get a synergistic effect on the degradation of organics [Xu et al., 2020]. Every different combination has advantages and disadvantages. Different operational parameters, characteristics of wastewater, and economic limitations decide the proper combination of processes.

2.1.4. Physical AOPs

Electrical discharge technology is one of the newly developed advanced oxidation processes. The main mechanism of this oxidation process is the generation

of non-thermal plasma by electrical discharge [Kaplan Cakmak, 2013]. These strong electrical fields start physical and chemical processes. UV radiation, different types of oxidizing radicals, or shock waves can be generated during discharge and they can also help the oxidation of contaminants [Jiang et al., 2014], [Miklos et al., 2018]. Electrical discharge technology has various advantages for example; it does not need chemical adding, it can oxidize a wide range of pollutants and it is applicable for small treatment systems [Mededovic Thagard and Locke, 2018].

In the ultrasound technique, sonication of water conducts the generation and falling of microbubbles due to acoustical wave-induced compaction and rarefaction. These microbubbles explode wildly after getting critical resonance and form very reactive radicals. Therefore, these reactive radicals destroy the pollutants by their reactions [Miklos et al., 2018]. The disadvantage of this process is to being energy intensive and getting low energy efficiency than other AOP technologies. For this reason, combining ultrasound with other techniques such as UV radiation, oxidants, or catalysts has to gain importance to get high efficiency [Mahamuni and Adewuyi, 2010]. Moreover, another important disadvantage of this process is that a deficient amount of hydroxyl radicals is produced. Also, this is another reason for applying this process with different types of AOPs. Besides, various operational parameters such as ultrasonic frequency and amplitude, the dosage of oxidants, and pH of solution need to be considered for the sonochemical hybrid AOP processes [Oturán and Aaron, 2014].

In addition to electrical discharge and ultrasound, microwaves are also tested to oxidize water pollutants. The microwave technique has been utilized in combinations of other techniques rather than alone. Unfortunately, this process has low electrical energy efficiency similar to the ultrasound technique [Miklos et al., 2018].

2.1.5. Electrocoagulation Process

The electrocoagulation process is another type of advanced oxidation process. Electrocoagulation is used for metal recovery. The electrocoagulation process (EC) is a complex process that involves many chemical and physical processes [Mohammadzadeh Sarabi, 2020]. Electrocoagulation technology is based on the principle of precipitation and purification of pollutants in wastewater, by passing an

electrical current through water, without using coagulants. In the electrochemical reactor, oxidation-reduction reactions take place in the presence of anode and cathode [Yılmaz Nayır, 2016]. Figure 2.3 shows the EC reactor and oxidation-reduction reactions in it.

Colloidal pollutants in the wastewater cannot be removed by conventional filtration, sedimentation, or flotation methods due to their stability in the water. For this reason, they should be converted to an unstable state. The mechanisms of breaking the stability of pollutants in the EC process can be summarized as follows [Liu et al., 2010].

- The double-layer around charged particles is compressed by interacting ions that are produced by oxidation of the sacrificial electrode.
- The oppositely charged ions generated by electrochemical dissolution of the sacrificial electrode neutralize the charged compounds in the wastewater. The oppositely charged ions reduce the electrostatic repulsive forces between particles and coagulation happens.
- In this step, floc formation happens. The sludge layer formed in the coagulation also captures the suspended solids in the aqueous phase. And finally, flocs are formed.

The advantages of the EC process are minimizing the sludge, capable of the treat different pollutants, no need for chemicals, low maintenance, low cost, capable of removing suspended solids and complex organics, reaching high removal efficiencies, and providing reliable results.

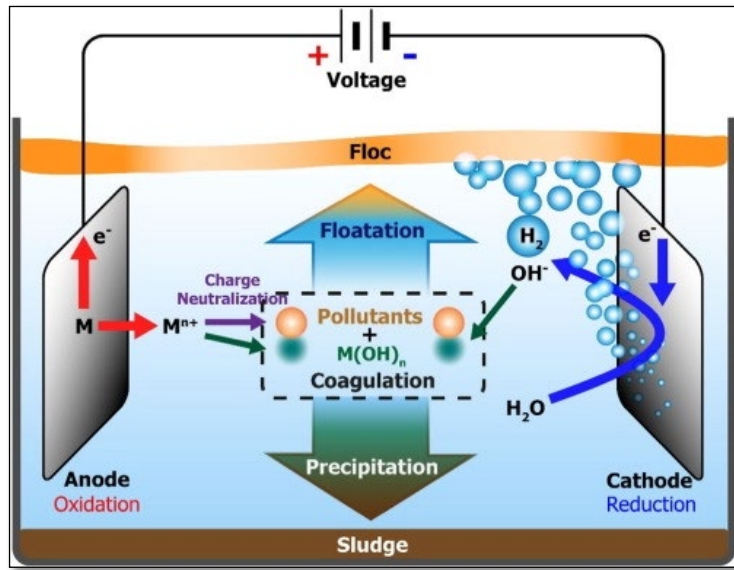


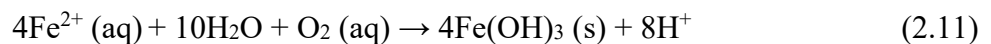
Figure 2.3: Scheme of EC reactor and its reactions.

In the EC process, many reactions take place simultaneously at the cathode and anode. These reactions can be divided into fundamental reactions that break the stability of contaminants and side reactions that produce hydrogen.

The fundamental reactions are formed by dissolving iron and aluminum cations in Al and Fe electrodes. The fundamental reactions are presented below [Vepsalainen, 2012], [Yılmaz Nayır, 2016].



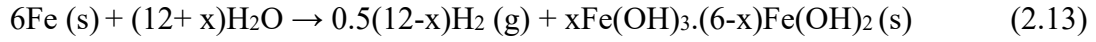
While aluminum dissolves only as Al^{3+} in the wastewater, iron can dissolve as Fe^{2+} and Fe^{3+} depending on its oxidation-reduction potential and pH conditions. The following reaction happens at neutral pH and alkaline pH.



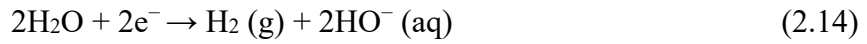
At high pH, aluminum dissolves as aluminate, like in the following reaction.



When iron electrodes are used, green rust that contains Fe (II) and Fe (III), Cl^- , CO_3^{2-} , SO_4^{2-} are formed.



In addition to fundamental electrochemical reactions, side reactions that form hydrogen are observed in the system. At the end of these reactions, pH increases due to the production of hydroxyl ions.



Moreover, precipitation reactions of carbonate salts occur on the cathode surface, as shown in the following equations.



In the EC process, hydrogen gas is released during the side reactions that occur in the cathode. And this gas causes flotation in the system. Therefore, flocs rise to the surface and they can be removed from the surface [Vepsalainen, 2012].

The efficiency of the EC process depends on the applied current efficiency, operation time, electrode material, pH of the wastewater, and distance between electrodes.

2.1.6. Electroflotation Process

Electroflotation process is one of the electrochemical treatment processes. Electroflotation is mainly used in mineral recovery and it is a gravity separation process. It is the most effective process for the separation of oil and low-density solids in water and wastewater treatment. In the EF process, hydrogen and oxygen bubbles are generated in the reactor and these bubbles carry the suspended solids to the surface of the water. EF principle is based on operating the water electrolysis on electrodes. During the water electrolysis, oxygen and hydrogen are formed at anode and cathode. EF process has the following steps: electrochemical production of hydrogen and oxygen bubbles, the interaction of suspended particles with bubbles and generation of particle-gas complexes, and flotation of these complexes to the water surface and froth layer formation. EF is mostly preferred for the treatment of suspended solids, grease, minerals, metal ions, and emulsified substances [Web 1, 2019]. Figure 2.4 represents the EF reactor and its reactions [Web 2, 2015].

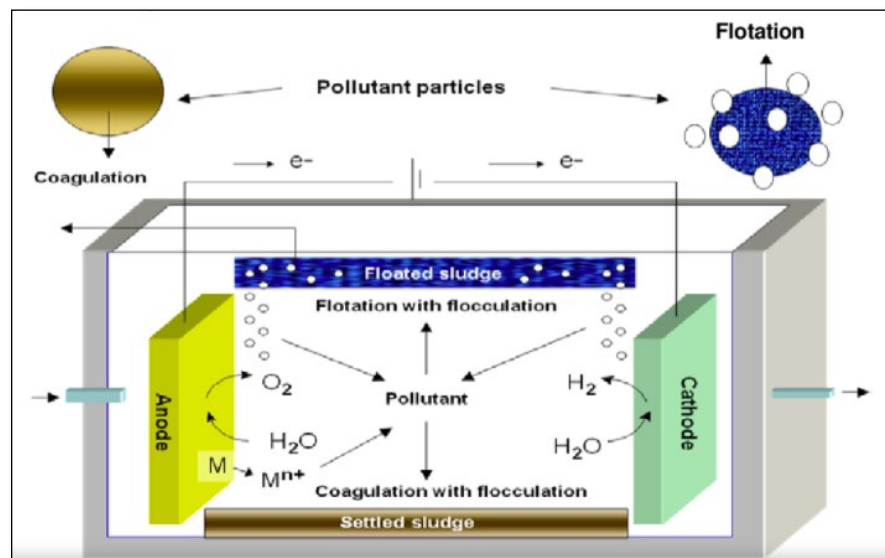
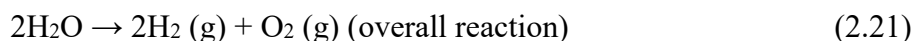
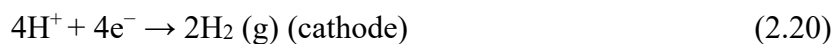


Figure 2.4: Scheme of EF process.

The reactions of the EF process in the reactor are following [Web 1, 2019].





EF reactors have been developed according to industrial and technological investments. In the EF process, the design of the reactor, the type of electrodes, electrolyte concentration, current density, pH of wastewater, arrangements of the electrodes, and bubble size are the important parameters [Web 1, 2019].

2.2. Electrochemical Oxidation Process

Traditional processes for water treatment can be ineffective to toxic and refractory organic contaminants when compared with electrochemical methods. These methods offer direct or indirect production of hydroxyl radicals [Radha and Sirisha, 2018], [Martinez-Huitle and Ferro, 2006]. In the water medium, organic substances such as pesticides and persistent organic pollutants have been discovered at high concentrations. And they cause a rise in the toxicity level in the water environment [Radha and Sirisha, 2018]. For this reason, traditional methods are not enough to solve this problem efficiently. Therefore, electrochemical processes have been truly promising alternatives to solve major problems [Ratiu et al., 2010].

In this study, treatment of p-aminophenol production wastewater by electrochemical oxidation process was studied. In this section, the EO process and its principles will be explained in detail. Pharmaceutical wastewater treatment methods and best processes to treat paracetamol production wastewater will be clarified regarding literature research in the next section.

Electrochemistry has a significant role in different fields of science and technology [Martinez-Huitle and Ferro, 2006]. Electrochemistry proposes promising advances for the treatment of industrial wastewater [Polcaro et al., 2010]. Electrochemistry aims treatment of discharges and waste and improving different processes without harmful effects. It has many promising advantages such as energy efficiency, sophistication, cost-effectiveness, proper automation, and compatibility. For these reasons, it can be regarded as an alternative to solve environmental problems.

It has a broad range of studied processes, technologies, and applications in the literature [Martinez-Huitle and Ferro, 2006].

Electrochemical processes have significance for various industries to treat their process wastewaters and waste. Electrochemical technologies for wastewater and water treatment include different processes like electrocoagulation, electrodeposition, electro-flocculation, and electrooxidation [Martinez-Huitle and Ferro, 2006]. Research on EO for wastewater treatment dates back to the 19th century when the electrochemical decomposition of cyanide was studied. Throughout the last two decades, studies have been concentrated on the electrochemical solidity of electrode substances, the effectiveness of various electrodes to oxidize different contaminants, different process parameters, explaining mechanisms of contaminant degradation [Chen, 2004].

In this study, the EO process was used for p-aminophenol production wastewater treatment. Because, it has many advantages such as high removal efficiency, minimum need for chemical use, simplicity in operation, the versatility of process, and cost-effectiveness [Mohammadzadeh Sarabi, 2020]. Despite its perfect advantages, practical use of the EO process for wastewater treatment has been restricted and it demonstrates a niche process [Polcaro et al., 2010].

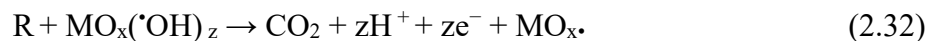
Wastewater treatment by the EO process can oxidize directly on the surface of the electrode or strong oxidants are produced electrochemically [Kaur, 2014]. EO process can generally divide into two categories. Anodic oxidation happens the whole mineralization of organic pollutants while cathodic reduction is applied to transform organic contaminants into nontoxic substances [Randazzo, 2010]. Besides, the EO process has two procedures according to utilizing non-sacrificial electrodes [Liu et al., 2019].

In the indirect electrooxidation procedure, strong oxidizing agents, for example, hypochlorous acid, chlorine, hydrogen peroxide, hypochlorite, and ozone are generated on the surface of electrodes. And then these produced reagents destroy contaminants in wastewater [Gengec, 2017]. In the indirect system, these oxidizing reagents are produced by the following reactions [Liu et al., 2019].



At high chloride concentrations, the indirect system can oxidize organic and inorganic contaminants successfully. In the process, generated strong reagents destroy the contaminants in wastewater by oxidation reactions. All of the reagents are produced in-situ and are used immediately. Production of hypochlorite is easy because most of the discharges have some portion of chloride [Kaur, 2014].

The second procedure of electrooxidation of contaminants is anodic or direct oxidation. In a direct system, oxidation happens directly on the surface of anodes by producing chemisorbed active oxygen or physically adsorbed active oxygen ($\bullet\text{OH}$). The physically adsorbed active oxygen results in the combustion of organics (R) completely. Chemisorbed active oxygen (MO_{x+1}) involves the generation of selective oxidation products. The reactions of this process are the following [Chen, 2004].



Usually, $\bullet\text{OH}$ is a more effective oxidant for the oxidation of contaminants than O in MO_{x+1} . This system does not need the addition of a high amount of chemicals to

wastewater without the tendency of generating secondary pollution. Therefore, anodic oxidation becomes a more effective process than other EO processes [Gengec, 2017], [Chen, 2004]. Figure 2.5 shows the indirect and direct oxidation processes [Chen, 2004].

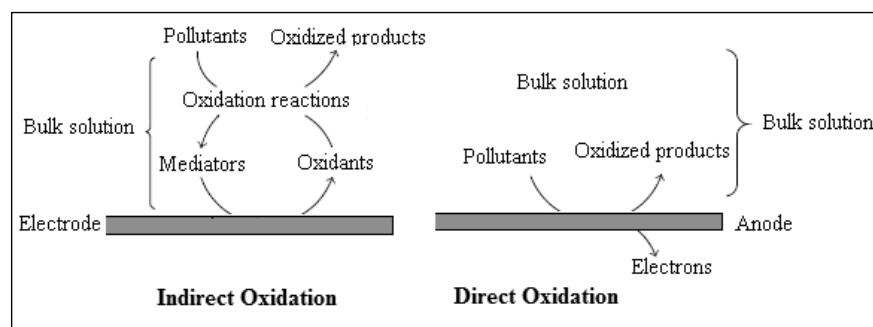


Figure 2.5: Scheme of indirect and direct processes.

Electrochemical oxidation experiments are generally carried in cylindrical containers with a DC power supply, as shown in Figure 2.6 [Liu et al., 2019].

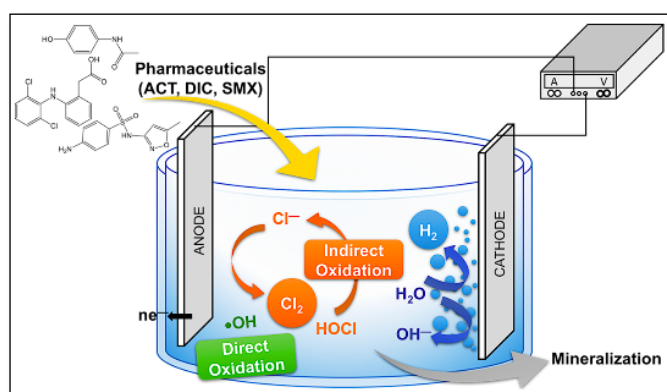


Figure 2.6: Diagram of the electrochemical reactor.

Both indirect and direct processes have various advantages compared to other processes. EO process can treat toxic and refractory organics. Its operation is simple, at room temperature and atmospheric pressure. It generally does not need the addition of chemical reagents. It does not generate process sludge. The main disadvantage of this process can be high energy consumption that depends on the COD of water. Moreover, the destabilization of the electrode material should be considered by avoiding the improper selection of pairs. Electrode fouling may be another concern

due to the deposition of substance on the electrode surface [Kaur, 2014], [Web 3, 2011].

Table 2.1 summarizes the principal characteristics of the electrochemical processes [Martinez-Huitle et al., 2008].

Table 2.1: Principal characteristics of direct and indirect oxidation processes.

	Direct oxidation	Indirect oxidation
Objective	The complete oxidation of organics to CO ₂ .	Complete pollutants conversion to CO ₂ , H ₂ O, and other inorganic components.
Method	Water is passed through cathodic and anodic compartments of one or more electrochemical cells with specific features.	Anodically formed oxidants react with organic substrates.
Factors	Current, pH, temperature, anodic material.	Current, pH, nature of oxidants.
Results	Elimination of organic pollutants from water.	Elimination of organic pollutants from water, good current efficiencies, no formation of chlorinated products.

2.2.1. Parameters Affecting the EO Process

Different types of parameters affect the removal efficiency of the EO process and energy consumption of the system. Critical operating parameters are applied current, wastewater pH, the type of electrolyte, electrode material, and organic concentration [Klavarioti et al., 2009]. These parameters can be listed as follows [Kaygusuz, 2013].

Current density: Current density controls the rate of reaction in the EO processes. The effect of the current density on the efficiency of the treatment depends on the characteristics of wastewater. However, conducting the experiments with higher current densities generally requires higher energy consumption, and as a result cost increases [Kaygusuz, 2013]. Moreas and Bertazzoli [2005] indicated that color removal from leachate strongly depends on the current density. Although the high

current application can be shortening the treatment time, this does not always mean high treatment efficiency [Drogui et al., 2007].

Temperature: Direct oxidation processes are usually considered not affected by temperature. They can operate at lower temperatures than other EO processes. However, usually ambient temperature is preferred when conducting experiments [Kaygusuz, 2013].

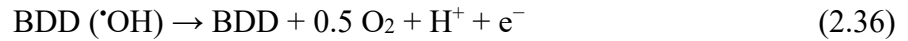
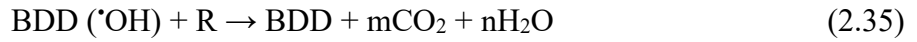
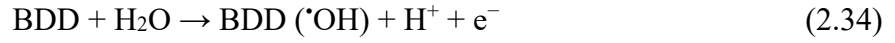
pH: pH is effective for the formation of hydroxyl ions in the EO process. In the literature, the effect of pH on removal efficiency is a controversial issue [Kaygusuz, 2013].

Electrolyte: The addition of electrolyte to the EO system aims to increase the conductivity of the solution, ensure that more current passes through the system and support the indirect oxidation process. It affects COD removal from wastewater. Different types of electrolytes such as NaCl, hydrogen peroxide, and sulfate can be preferred to add the system [Kaygusuz, 2013].

Electrode material: Anode electrode plays an active role in the electrochemical oxidation process. The selection of electrode material affects the efficiency of the EO process. The electrode material should have the next features: high electrical conductivity, catalytic selectivity, long physical and chemical stability, resistance to corrosion, composed of inexpensive materials, and durable for long usage. There are various electrode types, for example, PbO₂ electrodes, doped SnO₂ electrodes, doped TiO₂ electrodes, and boron-doped diamond electrodes [Kaur, 2014]. And these electrodes are divided into two categories. Carbon and graphite, platinum anodes, iridium oxides, and ruthenium oxides are known as active anodes. Antimony doped tin oxide, lead oxides, and boron-doped diamond oxides are known as passive anodes [Yılmaz Nayır, 2016]. In this study, BDD electrodes were preferred for the treatment of p-aminophenol production wastewater.

BDD as an electrode material has many outstanding features than other conventional carbon electrodes. BDD has low capacitance, dimensional stability, a broad range of operating potential windows, and high chemical inertness [Kapalka et al., 2009]. During recent years, BDD anodes have gotten increasing attention for the oxidation of contaminants as they present important electrochemical stability, good conductivity, and accomplished increased mineralization rates with very good current efficiencies [Klavarioti et al., 2009]. Besides, BDD anodes have higher O₂ overvoltage than traditional anodes. Because of higher O₂ overvoltage, the anode can produce large

quantities of hydroxyl radicals physisorbed on the surface of the anode. Therefore, formed heterogenous $\bullet\text{OH}$ reagents undergo indirect and direct oxidation of organic contaminants [Oturán and Aaron, 2014]. The reaction at the surface of the anode is following [Radjenovic and Sedlak, 2015], [Yılmaz Nayır, 2016].



Concerning the direct oxidation, $\text{BDD}(\bullet\text{OH})$ conducts the destruction of contaminants efficiently and rapidly. The great advantage of $\text{BDD}(\bullet\text{OH})$ action is to yield complete mineralization of wastewater [Oturán and Aaron, 2014].

Table 2.2 gives examples of electrochemical oxidation of different wastewaters and pollutants by using BDD anode from the literature [Martinez-Huitle and Panizza, 2018], [Lan et al., 2017], [Candia-Onfray et al., 2018], [Zou et al., 2017], [He et al., 2016], [Zhang et al., 2017].

Table 2.2: EO examples by using BDD anode.

Pollutants	Anode	Concluding remarks
Pharmaceuticals	BDD	The complete removal of ciprofloxacin, sulfamethoxazole, and salbutamol was observed. A theoretical model was proposed.
Winery wastewater	BDD	The effective removal of organics from real winery wastewater was obtained by anodic oxidation. The COD removal efficiency was 63.6%.
Real textile wastewater	BDD	The oxidation rate increased linearly with applied current and exponentially with NaCl concentration. Complete mineralization was obtained in low energy consumption and short electrolysis time.
Triphenylmethane dye	BDD	The presence of Cl^- in the solution promoted an efficient removal of COD and color.
Creatinine	BDD	Creatinine and TOC removals were faster in NaCl than in Na_2SO_4 . A maximum mineralization percentage, 80%, was achieved within 120 min. electrolysis.

2.3. Pharmaceuticals Treatment Methods from Wastewater

Large quantities of pharmaceutical substances such as analgesics, chemotherapy reagents, antibiotics, drugs, and antidepressants are introduced into the environment. Some important pollutants, for example, personal care products, flame retardants, and illegal drugs cause environmental damaging due to their endocrine-disrupting features. Unfortunately, these pollutants can have toxic effects on algae, create genotoxicity, and endocrine system damage [Wang and Xu, 2018]. In pharmaceutical operations, water is an important raw material. In the various stages like production, substance processing, and cooling, water is used extensively. The wastewater from different categories needs proper treatment. The wastewater produced from pharmaceutical units varies in concentration and content [Gadipelly et al., 2014]. Table 2.3. summarizes some parameters of pharmaceutical wastewaters [Gadipelly et al., 2014], [Li and Li, 2015], [Peng et al., 2004], [Chen et al., 2011], [Boroski et al., 2009], [Zheng, 2011].

Table 2.3: Composition of pharmaceutical wastewater.

Parameter	Minimum and maximum value
COD, mg/L	375 - 32500
BOD ₅ , mg/L	200 – 6000
TOC, mg/L	860 - 4940
TKN, mg/L	165 - 770
TP, mg/L	50 – 250
SS, mg/L	200 – 500
SO ₄ ²⁻ , mg/L	890 - 1500
pH	3 - 9

After the use of pharmaceuticals, personal care products, and disinfectants, they can enter the environment commonly [Olvera-Vargas, 2014]. These pharmaceutical chemicals usually move into streams, aquifers, and groundwater. Also, everyday used chemicals such as human and veterinary drugs, detergents, insecticides, and hormones can get into the environment in wastewater [Gadipelly et al., 2014]. Moreover,

pharmaceuticals can occur in the soil. For example, veterinary drugs pollute the soil directly by manure or surface runoff. Pharmaceutical chemicals are not eliminated in sewage treatment plants due to their persistence. Discharges of sewage treatment plants can include not-degradable pharmaceutical residues [Sires and Brillas, 2012], [Olvera-Vargas, 2014]. Figure 2.7 summarizes the pathways of pharmaceutical residues in the environment [Heberer, 2002].

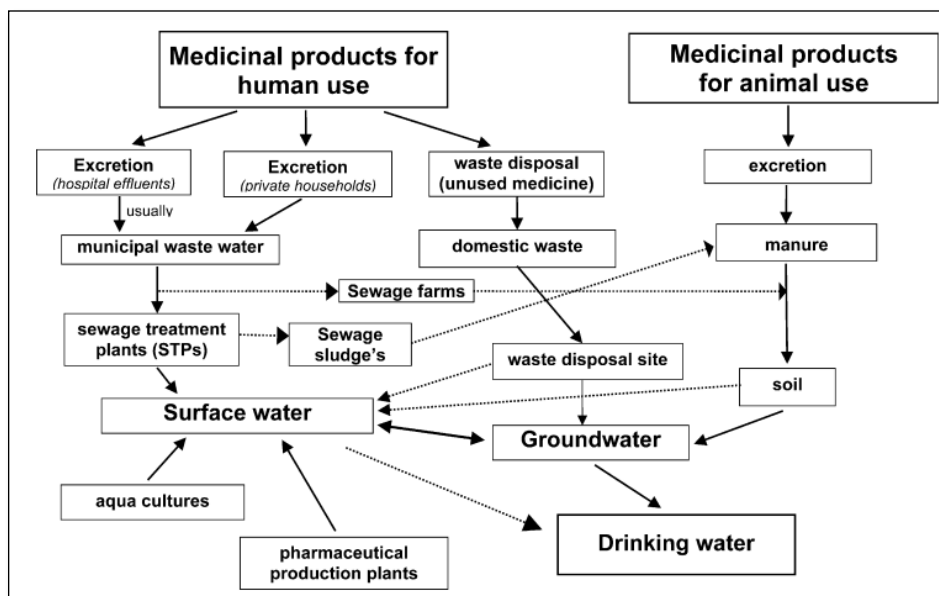


Figure 2.7: Possible pathways for pharmaceutical residues in the environment.

Traditional treatment methods that are principally utilized from microbes are not efficient to destroy pharmaceutical chemicals because of their low concentration and complex structure. So, biological treatment systems have a limited ability to remove persistent chemicals [Olvera-Vargas, 2014]. Therefore, the advanced treatment of pharmaceutical wastewater needs physicochemical technology. This technology includes different processes such as coagulation and sedimentation, activated carbon adsorption, membrane separation, flotation, and advanced oxidation processes [Guo et al., 2017]. Table 2.4 gives examples for the treatment of pharmaceutical wastewaters with different processes and technologies from the literature [Gadipelly et al., 2014], [LaPara et al., 2001], [Chang and Chang, 2008], [Tekin et al., 2006], [Dominguez et al., 2012], [Adishkumar and Kanmani, 2010], [Cokgor et al., 2004], [Wang and Xu, 2018].

Table 2.4: Pharmaceutical wastewater treatment processes.

Technology or process	Matrix	Concluding remarks
Aerobic biological treatment with variable temperature study	COD: 8150-7170 mg/L, BOD: 3800-7900 mg/L, ammonia: 220-750 mg/L	COD removal in a given batch reactor decreased as temperature raised.
Membrane bioreactor technology (hollow fiber membrane)	COD: 800-11800 mg/L, BOD: 100-6350 mg/L, SS: 60-360 mg/L, pH: 6.6-9.4	The membrane system can remove 95% and 99% of COD and BOD respectively.
Fenton (pretreatment) followed by aerobic and biological degradation	COD: 900-6800 mg/L, BOD: 85-3600 mg/L	Fenton treatment removed 45-50% of COD, and the biological treatment reduced the COD by 98%.
EO with BDD anodes	COD: 12000 mg/L, TOC: 1600 mg/L, pH: 8.5	Depending on current density and operation time, more than 90% of TOC removal observed.
Photocatalysis + H ₂ O ₂	COD: 1082 mg/L, BOD: 170 mg/L, phenol: 380 mg/L, pH: 8.2	The phenol removal rate was enhanced from 40% to 45%.
Ozonation (pretreatment), biological activated sludge treatment	COD: 710 mg/L, BOD: 200 mg/L, pH: 6.85	Ozonation removed 34% COD and 24% TOC and then water showed efficient COD removal by activated sludge.

Pharmaceutical wastewater treatment processes are improved according to high concentrations of well-known and most used compounds in different fields of the sector. These processes are used commonly as a pre-biological treatment step in the wastewater treatment plant. However, they are sometimes used as post-treatment processes. Physical-chemical treatment methods that are suitable for the treatment of pharmaceutical wastewater can be listed following [Li and Li, 2015].

- Flotation: This method is used to stick wastewater contaminants to bubbles in the water. This method is useful for the wastewaters with high suspended solid concentration as pretreatment. This process is simple and easy to control.
- Adsorption: This method is used for the purification of wastewater. Soot or carbon is mostly preferred as adsorption material for the removal of pharmaceuticals. Also, this method helps the removal of color and odor of wastewater.
- Fenton method: Fenton's oxidation technique is efficient to treat dangerous organic contaminants in wastewater. It is also efficient to reduce the toxicity of wastewater and to convert contaminants to by-products.
- Coagulation and sedimentation: In this method, some chemicals are needed as coagulants. Coagulants provide the cohesion of colloidal particles and form large flocks. This method can increase the biodegradability of wastewater [Li and Li, 2015].

Table 2.5 compares some physical-chemical treatment methods [Li and Li, 2015].

Table 2.5: Comparison of some physical-chemical removal methods.

Methods	Efficiency	Processing	Cost
Coagulation and flocculation	50-80%	Pretreatment	Low
Fenton	60-95%	Secondary	Low
Flotation	70-85%	Pretreatment	Low
Photo-catalytic	85-99%	Advanced treatment	High
Adsorption	80%	Pretreatment	Low

2.3.1. Paracetamol Treatment

Paracetamol is a nonsteroidal anti-inflammatory drug. It has a pain reliever and antipyretic properties. It is widely used for cold, headache, and other similar pains. Figure 2.8 displays the structure of paracetamol. Paracetamol is usually found in odorless, bitter, and white crystalline powder. A saturated solution of paracetamol shows weak acidic properties. It is hardly soluble in ether and benzene, however; it can dissolve in organic solvents and water [Dalgic, 2013].

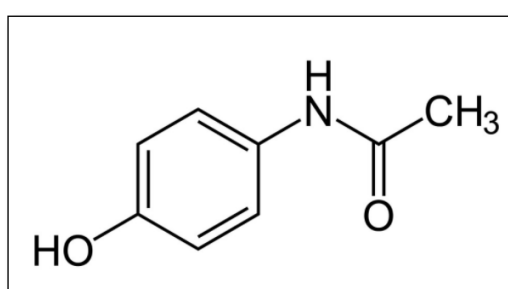


Figure 2.8: Structure of paracetamol.

Paracetamol is also known as acetaminophen. It is an extensively used analgesic. Acetaminophen production includes three steps. Firstly, phenol is altered to nitrophenol by the electrophilic aromatic exchange. Then, the nitro part of para-substituted nitrophenol is turned into an amine. Lastly, the para-aminophenol is

transformed into acetaminophen by an acetic anhydride reaction, as shown in Figure 2.9 [Ogemdi, 2019].

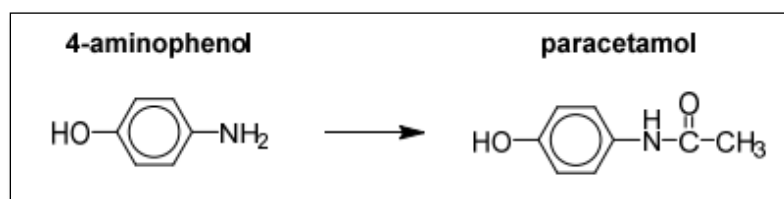


Figure 2.9: Structural representation of the conversion of 4-aminophenol.

Paracetamol removal has been studied by many different methods in the literature. Balci et al. [2012] studied the treatment of paracetamol from synthetic wastewater in a batch activated sludge system. The effects of different initial paracetamol concentrations were studied on different biomass concentrations. The activated sludge adapted to new conditions in 11 days after adding paracetamol to the system. After that, removal rates of paracetamol were high. High biomass concentrations were effective to treat paracetamol. Jorda et al. [2011] used the photo-Fenton process to generate intermediate products that can be removed by biological treatment. The biodegradation rate of paracetamol was increased by the photo-Fenton process. This study was conducted on a laboratory scale. About 157,5 mg/L paracetamol from synthetic wastewater was treated by the photo-Fenton process within 25 minutes. Valdez et al. [2012] investigated the photochemical, electrochemical, photo-electrochemical degradation of synthetic paracetamol wastewater. Photochemical processes, electrolysis, and photo-electrolysis processes have been used in the presence of hydrogen peroxide. And, the high TOC removal efficiencies were achieved in these processes. Andreozzi et al. [2003] studied the oxidation of synthetic paracetamol wastewater by ozonation and H₂O₂ photolysis processes. Ozonation and H₂O₂ photolysis processes were obtained 30% and 40% mineralization rates of paracetamol, respectively.

Phenols and derivatives are widely found in industrial wastes. Several industries such as food industries, pulp, and paper industries, petrochemical refineries, and coke plants produce common wastewater containing phenolic substances [Polcaro et al., 2010]. These substances are known as toxic and carcinogenic even at low concentrations so they have a priority for treatment [Polcaro et al., 2010], [Web 3,

2011]. The solubility of phenol in water is very high. More than 70% of phenol will end up in the water, and about 25% of it can be found in the air. A very little portion of it can be detected in the soil [Web 3, 2011].

Treatment of phenolic substances from wastewaters was studied with various technologies in the literature due to their devastating environmental impact [Polcaro et al., 2010]. For example, Beltran et al. [2005] compared photocatalytic ozonation, ozonation, catalytic ozonation, ozone photolysis, photocatalysis, and photolysis processes for the removal of phenolic substances. They studied mineralization rates of substances and kinetics in the aqueous treatment. Rate constants of these processes were calculated. Among all processes, photocatalytic ozonation exhibited the highest rate of mineralization of phenols. Also, electrochemical oxidation of phenols was investigated broadly in the literature [Polcaro et al., 2010]. For instance, Comninellis and Pulgarin [1993] studied the electrochemical oxidation of phenolic wastewater using Pt and SnO₂ anodes. Also, the behavior of anodes was explained.

For the anodic oxidation of phenolic wastewater, the most favorable anode was BDD. If the current density is applied enough high, BDD works very fast. BDD is a more common electrode material and it has a very good performance to oxidize phenolic substances [Polcaro et al., 2010]. Therefore, in this study, the EO process was used for p-aminophenol production wastewater treatment. BDD was preferred to oxidize p-aminophenol.

3. EXPERIMENTAL MATERIAL AND METHODS

3.1. Characterization of Produced Wastewater

The wastewater used in this study was taken from a pharmaceutical factory producing paracetamol in the region of Gebze. Produced paracetamol is used in the production of the drug. Figure 3.1 summarizes the process flow chart of paracetamol production [Dalgic, 2013].

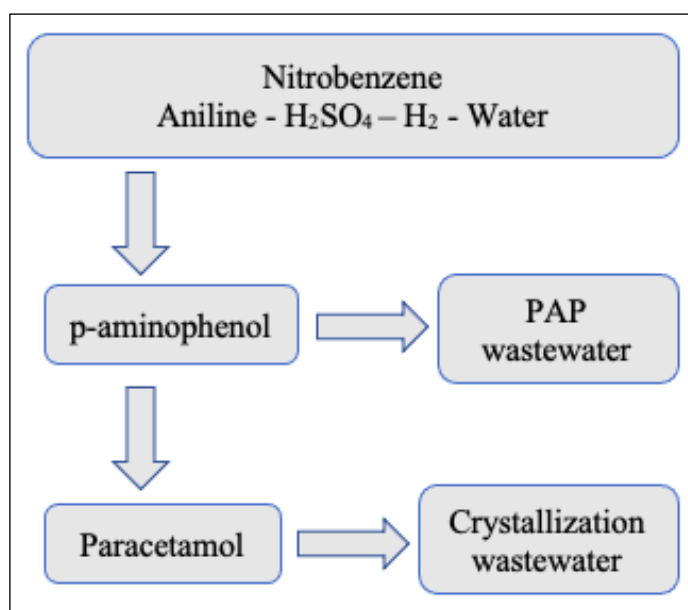


Figure 3.1: Process flow chart of paracetamol production.

As seen in Figure 3.1, firstly PAP molecule is synthesized as an intermediate product. In this synthesis, aniline, sulfuric acid, hydrogen, and water is used. When synthesizing the PAP molecule, PAP wastewater is generated. This wastewater was the subject of this study. The treatment of this wastewater has been studied. Secondly, PAP reacts with acetic anhydride to crystallize and then a paracetamol molecule is formed [Dalgic, 2013]. Figure 3.2 shows the synthesis mechanism of acetaminophen.

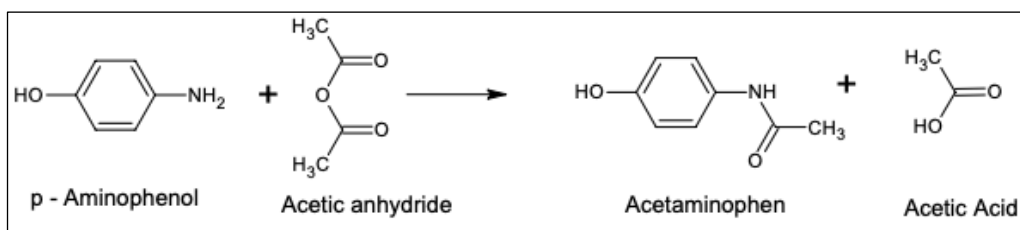


Figure 3.2: The synthesis mechanism of acetaminophen.

4-aminophenol or p-aminophenol or para-aminophenol has the formula of $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$. It is an organic compound and being as a white powder. It is an intermediate product of paracetamol and has a commercial value. Table 3.1 represents the properties of p-aminophenol [Web 4, 2020].

Table 3.1: Properties of p-aminophenol.

Properties	
Chemical formula	$\text{C}_6\text{H}_7\text{NO}$
Molar mass	109.128 g/mol
Appearance	Colorless to brown-yellow
Density	1.13 g/cm ³
Melting point	187.5 °C
Boiling point	284 °C
Solubility in water	1.5 g/100 mL
Solubility	Very soluble in dimethylsulfoxide Soluble in acetonitrile, ethyl acetate, and acetone Slightly soluble in toluene, diethyl ether, and ethanol Negligible solubility in benzene and chloroform

In this study, p-aminophenol production wastewater is used. Pollutant parameter concentrations in wastewater can change depending on processes monthly and seasonally. PAP wastewater has a dark color and bad smell and it consists of organic, inorganic, and suspended compounds. Characteristics of raw PAP wastewater are presented in Table 3.2.

Table 3.2: Characteristics of raw PAP wastewater.

Parameter	Value
COD, mg/L	50000 - 70000
TOC, mg/L	18000 - 21000
pH	5.5 – 6.5
Conductivity, mS/cm	119.7

As seen in Table 3.2, pollutant parameter concentrations in wastewater are very high and the treatment of this wastewater is hard work. High COD value comes from aniline, and PAP. So, conventional treatment methods are not sufficient to treat this wastewater due to the high and strong chemical compounds in it. And biological treatment methods cannot remove these strong chemicals effectively. Therefore, chemical treatment methods should be considered. Tekin et al. [2006] also indicated that pharmaceutical wastewater is resistant to biological degradation and conventional treatment methods are not suitable due to the presence of complex organic chemicals in their structure. And they stated that advanced oxidation treatment methods can remove complex organic pollutants.

It is aimed to reduce COD and TOC values that are important pollutant parameters of wastewater by using the electrochemical oxidation method in this study.

3.2. Used Devices and Chemicals in the Study

In this study, for the experiments, different types of devices and chemicals were needed. The list of them is presented below.

- For the pH measurement: Mettler Toledo Seven Compact pH/ion.
- For the conductivity measurement: Mettler Toledo Seven Go pro conductivity.
- For COD measurement: WTW Thermoreactor CR3000.
- For TOC measurement: Shimadzu TOC-L.
- Magnetic stirrer: Heilodp MR 3000D.
- Precision balance: Precisa XB 220A.
- DC digital power source: Agilent 6675A.

- Sulfuric acid, H_2SO_4 .
- Sodium hydroxide, NaOH .
- Phosphoric acid, H_3PO_4 .
- Sodium chloride, NaCl .
- Filter paper.

3.3. Experimental Set-up and Procedure

In the experiments, BDD anode and stainless-steel cathode was used to treat PAP wastewater. The experiments were conducted by batch processes. Before the experiments, first of all, the wastewater was filtered by using a rough filter so that suspended solids can remove. Then, filtered wastewater was diluted in different dilution ratios. These were the preparation for the experiments. Figure 3.3 represents the experimental setup. Current and voltage control were provided by a digital power source. Mixing was achieved with a magnetic stirrer. As shown in Figure 3.4, after the anode electrode and cathode electrode were submerged in the reactor, one liter of prepared wastewater was poured into the reactor for each experiment. When operating the magnetic stirrer, pH and conductivity values were read. The system was started after the direct current power supply was arranged to the desired current value. Then, samples were taken from the reactor at regular intervals. Also, the voltage values of the samples were recorded. All the experiments were accomplished at constant temperature (25 °C) and mixing speed (400 rpm). At the end of each experiment, samples were filtered and prepared for analysis. The used BDD anode and cathode electrodes were washed regularly with water and phosphoric acid to remove solid residuals on the surface of the electrodes.

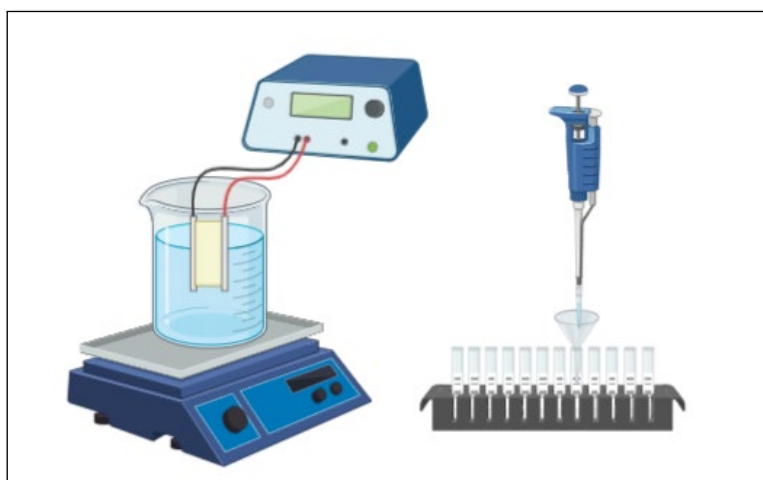


Figure 3.3: The experimental setup.

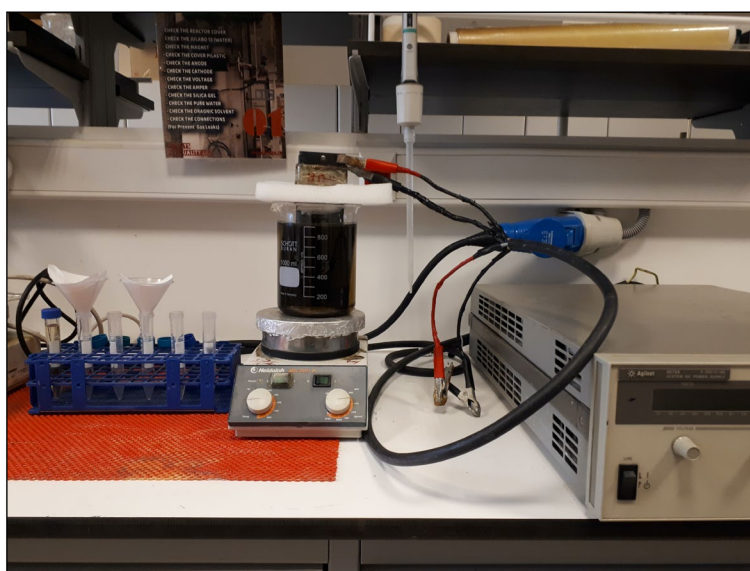


Figure 3.4: The experimental setup in the laboratory.

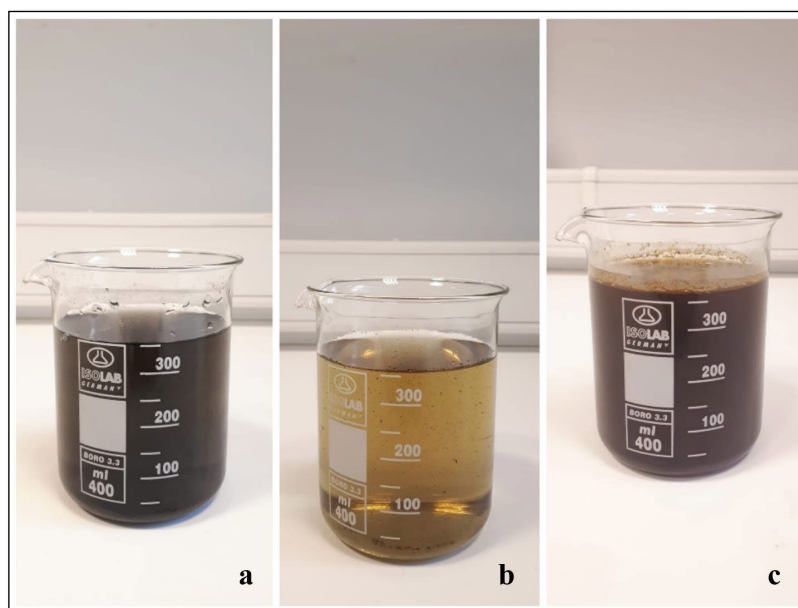


Figure 3.5: a) 7.6% of diluted wastewater, b) Filtered of a, and c) After 300 min EO of b.

Different sets of experiments were carried to understand the effect of different parameters on removal efficiencies.

To investigate the effect of pH, the experiments were accomplished at different pH values (3-6-9). NaOH and H₂SO₄ solutions were used for the desired pH arrangement.

To investigate the effect of current density, different current values (1A, 3A, 5A) were operated in the EO process.

To investigate the effect of electrolyte concentration, different amount of NaCl (1 g/L, 3 g/L, 5 g/L) was added to the system.

To investigate the effect of wastewater dilution ratio, different dilution ratios (2%, 7.6%, 25%) were operated in the EO process.

3.4. Analytical Methods

In this study, some important equations were used to calculate experimental results. For the calculation of COD and TOC removal efficiencies (Re %), the following equation was used.

$$\text{Re (\%)} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (3.1)$$

where C_0 is the initial PAP concentration in mg/L, C_f is the final PAP concentration in mg/L [Koby et al., 2009].

For the calculation of electrical energy consumption (ENC kWh/m³), the following formula was used.

$$\text{ENC (kWh/m}^3\text{)} = \frac{U \times i \times t}{v \times 1000} \quad (3.2)$$

where U is the cell voltage (V), i is the current (A), t is the operating time (h) and v is the volume of PAP wastewater (m³) [Gengec, 2017].

Chemical oxygen demand, total organic carbon analyses were determined according to Standard Methods [APHA, 2012]. The COD analysis was performed according to 5220 C. Closed Reflux Titrimetric Method. TOC analysis was performed according to 5310 B. High-Temperature Combustion Method.

4. RESULTS AND DISCUSSION

4.1. Effect of Current Density on Process Efficiency

One of the major parameters that influence the efficiency of the EO process and operating cost is the current density. In this study, to observe the effect of current density in removing PAP from the wastewater, different currents were operated. By keeping some parameters such as initial COD (55000 mg/L) and TOC (20000 mg/L) concentrations, pH (6.0), EO time (300 min.), same dilution ratio, and BDD anode amount constant, current densities were set as 15, 45, and 75 mA/cm². Figure 4.1: a and b represent the removal efficiencies of COD and TOC as a function of operating time. In Figure 4.1, for the 15, 45, and 75 mA/cm² current densities, COD removal efficiencies were 56.05%, 84.8%, and 95.45% in 300 minutes, respectively. For the 15, 45, and 75 mA/cm² current densities, TOC removal efficiencies were observed as 48.37%, 71.32%, and 75.91% in 300 minutes, respectively. PAP oxidation is more effective at raising current densities arriving at 90.69% COD and 66.81% TOC removal after 180 minutes at 75 mA/cm². Surprisingly, COD removal decreased during the first hour of operation at 45 mA/cm². The reason for this situation can be the oxidative polymerization of phenols and other complex compounds. Therefore, this polymerization can cause an increase in wastewater COD. And another reason can be the decomposition of matters in the wastewater by the EO process. Decomposition of solids can deliver organic solids to the wastewater and thus, the COD of wastewater can increase. However, this decomposition cannot be expected for this experiment because the wastewater was filtered before the experiment. From Figure 4.1: a and b, it is clear that COD and TOC removal increases with raising current density. The reason for this can be the complex reaction pathways such as partial and total oxidation, polymerization, and depolymerization, which are susceptible to the EO process, of complex PAP wastewater [Papastefanakis et al., 2010].

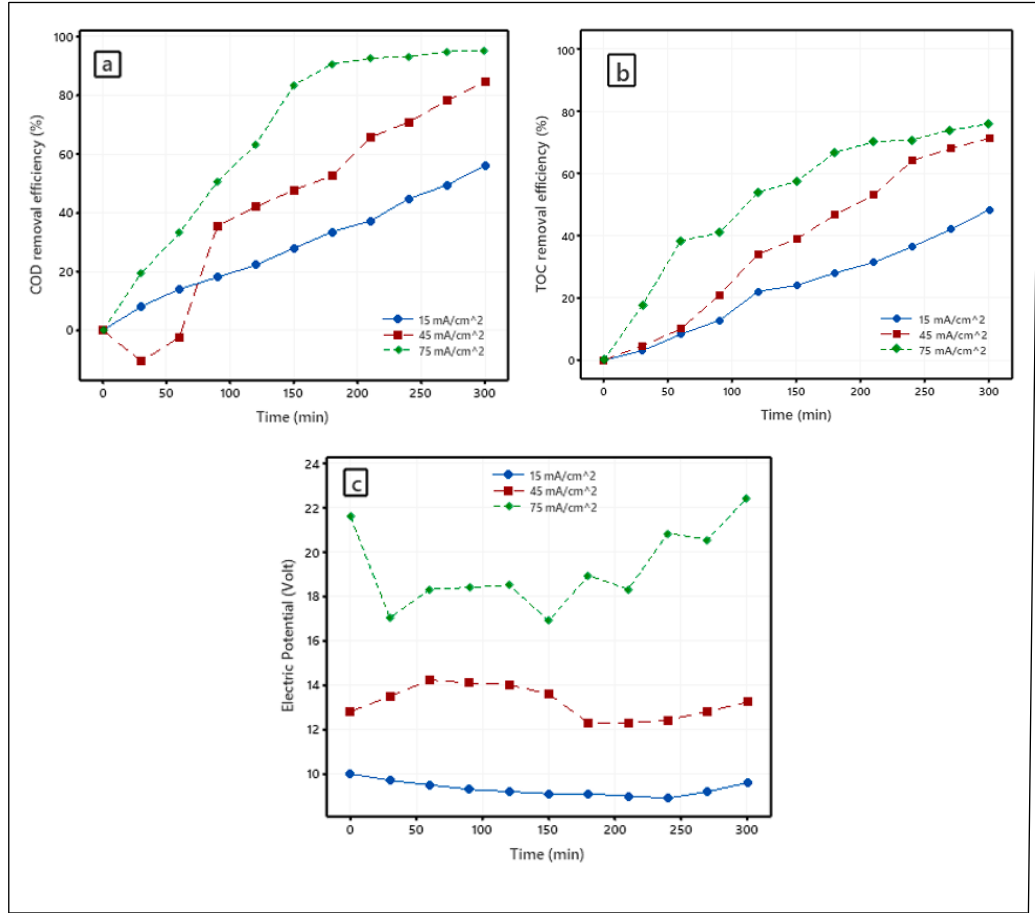


Figure 4.1: Effect of current density on a) COD removal efficiency, b) TOC removal efficiency, and c) Electric potential.

In this set of experiments, for the 15, 45, and 75 mA/cm² current densities, average voltages were recorded as 9.3 V, 13.2 V, and 19.2 V, respectively, as shown in Figure 4.1: c. Therefore, electrical consumptions were calculated as 46.5 kWh/m³, 198 kWh/m³, and 480 kWh/m³, respectively. Obviously, as the applied current density increases, electrical consumption increases. Low electricity consumption is preferred economically [Gengec, 2017].

4.2. Effect of Initial pH on Process Efficiency

One of the major factors that influence the efficiency of the EO process is the pH of the wastewater. In this study, to observe the effect of the initial pH in removing PAP from the wastewater, different pH values were operated. By keeping operating

parameters such as initial COD (55000 mg/L) and TOC (20000 mg/L) concentrations, EO time (300 min.), current density (75 mA/cm²), same dilution ratio, and BDD anode amount constant, pH values were set as 3.0, 6.0, and 9.0. The removal efficiencies of COD and TOC were observed concerning operating time, as shown in Figure 4.2: a and b. For the 3.0, 6.0, and 9.0 pH values, COD removal efficiencies were 96.41%, 95.45%, and 96.36% in 300 minutes, respectively. The COD removal efficiency raised almost continuously within the operating time, as shown in Figure 4.2: a, and there was no significant effect of different pH values on COD removal. Because all the obtained removal efficiencies for 3 pH values were more or less the same. Within 300 minutes, almost complete degradation of PAP was achieved for 3 cases. However, for the TOC reduction, pH had a remarkable effect in Figure 4.2: b. For the 3.0, 6.0, and 9.0 pH values, TOC removal efficiencies were 93.64%, 75.91%, and 95% in 300 minutes, respectively. Interestingly, TOC removal efficiencies were very satisfactory at pH 3.0 and 9.0 values, compared to normal pH (6.0) of wastewater. This situation can be because of different reaction mechanisms at different initial pH of the wastewater. When the wastewater medium was acidic or alkaline, this could support BDD to generate more hydroxyl radicals. Therefore, many electrochemical reactions could happen on the surface of BDD to degrade PAP completely [Zhang et al., 2020].

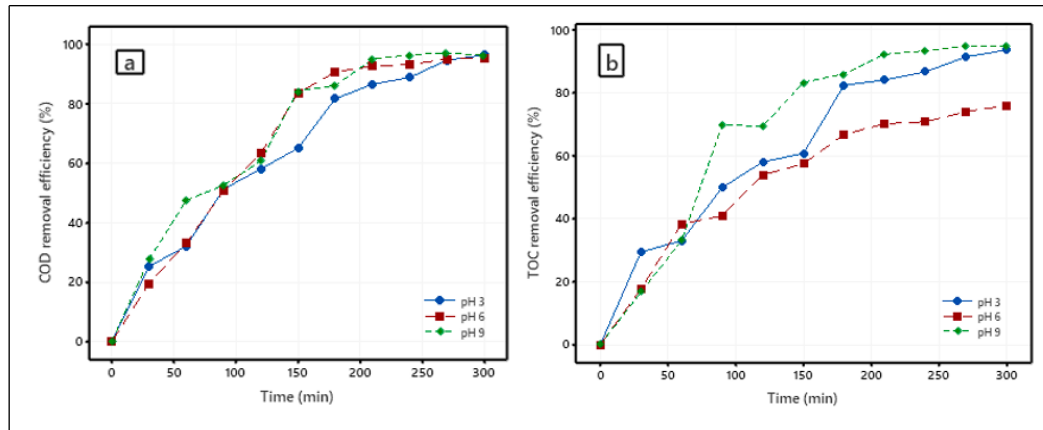


Figure 4.2: Effect of pH on a) COD removal efficiency, and b) TOC removal efficiency.

4.3. Effect of Electrolyte Concentration on Process Efficiency

Another parameter that influences the efficiency of the EO process is the electrolyte concentration. The high conductivity can increase the activity of the current density. The wastewater conductivity was changed to the desired levels in the set of experiments [Kobyta et al., 2009]. In this study, to observe the effect of the electrolyte concentration in removing PAP from the wastewater, different amounts of NaCl electrolytes were added. By keeping operating parameters such as initial COD (55000 mg/L) and TOC (20000 mg/L) concentrations, EO time (300 min.), current density (45 mA/cm²), same dilution ratio, and BDD anode amount constant, different amount of NaCl salts were added as 1 g/L, 3 g/L, and 5 g/L. For the 1, 3, and 5 g/L of NaCl amounts, COD removal efficiencies were achieved as 96.73%, 92.88%, and 84.6% in 300 minutes, respectively. For the 1, 3, and 5 g/L of NaCl amounts, TOC removal efficiencies were observed as 71.79%, 77.98%, and 71.66% in 300 minutes, respectively. Without adding NaCl salt to wastewater, COD and TOC removal efficiencies were 84.8% and 71.32% at 45 mA/cm², respectively. As seen in Figure 4.3: b, TOC removal efficiencies adding NaCl salts were almost the same with no NaCl adding efficiency, and there was no enhancement for TOC removal. However, the addition of 1 g/L and 3 g/L of NaCl to the wastewater increased the COD removal efficiency. As the amount of NaCl added to wastewater increases, COD removal efficiency decreases. This is due to the net effect of chloride on BDD is unknown [Aquino et al., 2011]. Zhu et al. [2019] found an enhancement of the COD removal efficiency with NaCl salt, however, Cabeza et al. [2007] did not. The lack of increase in COD removal efficiency can be related to the pH of wastewater, hydrodynamic conditions, current density, and concentration of chloride ions. Another reason can be electro-produced active chlorine species like chlorites, perchlorates, and chlorates which are not efficient to degrade organics. Also, they can cause a low surface concentration of •OH radicals [Aquino et al., 2011].

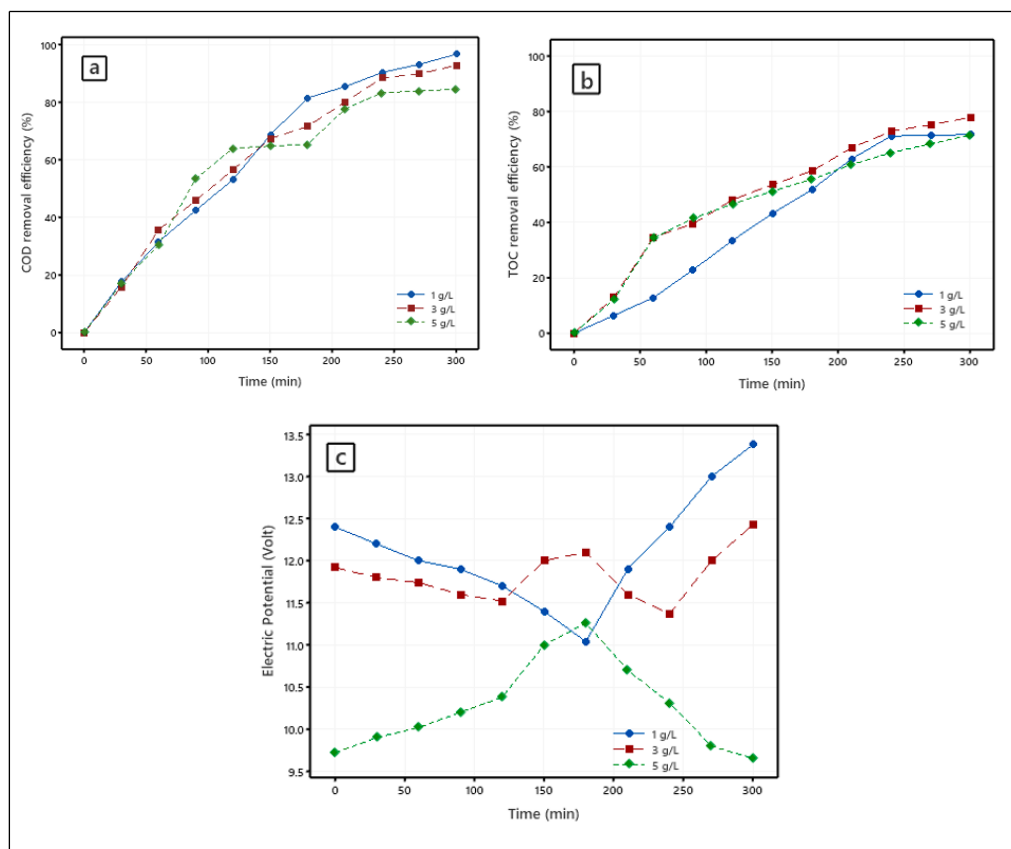


Figure 4.3: Effect of NaCl concentration on a) COD removal efficiency, b) TOC removal efficiency, and c) Electric potential.

In this set of experiments, for the 1 g/L, 3 g/L, and 5 g/L of NaCl added, average voltages were measured as 12.15 V, 11.85 V, and 10.2 V, respectively, as seen in Figure 4.3: c. Thus, electrical consumptions were calculated as 182.25 kWh/m³, 177.75 kWh/m³, and 153 kWh/m³, respectively. Without adding NaCl to the wastewater, the electrical consumption was recorded as 198 kWh/m³. In the electrochemical treatment processes, electrolyte addition reduces the wastewater resistance, and thus electrical consumption decreases [Gengec, 2017].

4.4. Effect of Dilution on Process Efficiency

Since the PAP wastewater has a complex character and difficult to treat, the effect of dilution on the removal of PAP was investigated. In this study, different dilution factors of wastewater were operated. By keeping operating parameters such

as initial COD (55000 mg/L) and TOC (20000 mg/L) concentrations, EO time (300 min.), current density (75 mA/cm²), and BDD anode amount constant, the wastewater was diluted into different proportions like 25, 7.6, and 2% (volume/volume, %). For the 25, 7.6, and 2% of dilution rates, COD removal efficiencies were observed as 95.45%, 94.5%, and 24.9% in 300 minutes, respectively. For the 25, 7.6, and 2% of dilution rates, TOC removal efficiencies were achieved as 75.91%, 93.55%, and 23.4% in 300 minutes, respectively. Figure 4.4: a and b, high COD, and TOC removal efficiency were achieved for the 7.6% diluted wastewater compared to 2% diluted wastewater. COD removal efficiencies were almost the same or 25% and 7.6% dilution ratios. However, for TOC removal efficiency, 7.6% diluted wastewater degraded almost all PAP in the wastewater compared to 25% diluted wastewater. According to Kul et al. [2015], the dilution factor has an importance on wastewater treatment. When the dilution factor decreases, removal efficiencies increase. As can be seen in Figure 4.4: a and b, removal efficiencies began to be observed in the second hour of the experiment for 2% diluted wastewater. 2% of diluted wastewater means a high initial concentration of PAP in the wastewater. Thus, the reason for no COD and TOC removals during the early stages of the experiment can be a limited amount of hydroxyl radicals in the wastewater [Zhang et al., 2020]. Or the other reason can be the generation and accumulation of intermediates [Akyol et al., 2019]. Moreover, during this experiment, heat generation was observed as an adverse effect. Mollah et al. [2004] found that excessive oxygen evolution causes heat generation.

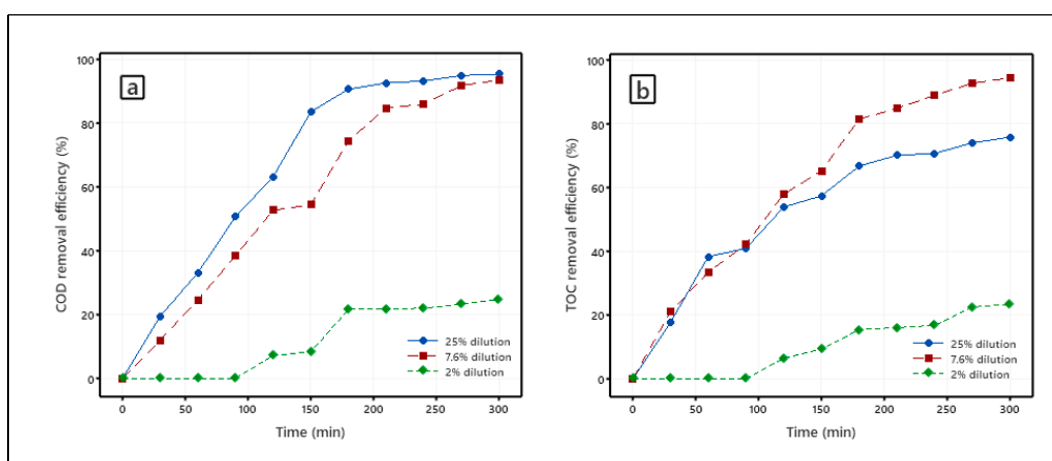


Figure 4.4: Effect of dilution on a) COD removal efficiency, and b) TOC removal efficiency.

4.5. Comparison with Different Studies

Treatment of phenol and derivatives has been a popular topic in the literature. Many different removal methods were studied. Also, advanced oxidation processes have been widely used for the treatment of phenolic compounds. Table 4.1 shows some different treatment methods and their efficiencies from the literature data.

Table 4.1: Comparison of phenol degradation methods and efficiencies.

Wastewater	Treatment method	Efficiency	Reference
Aqueous phenol solution	EO, PbO ₂ anode	86% TOC 91% COD	[Duan et al., 2013]
Aqueous phenol solution	EO, Ti/PbO ₂ anode	90% TOC 78% COD	[Saratale et al., 2015]
Aqueous para-aminophenol solution	EO, Ce-PbO ₂ anode	96.9% COD	[Weng and Yu, 2019]
	EO, La-PbO ₂ anode	89.3% COD	
	EO, PbO ₂ anode	77.5% COD	
Aqueous phenol solution	O ₃ -UV-TiO ₂	100% COD	[Suzuki et al., 2015]
Aqueous phenol solution	EO, Ti/BDD anode	95% COD	[Sun et al., 2012]
Real paracetamol wastewater	Fenton	92.7% COD 99.9% PAP	[Dalgic et al., 2017]
Real paracetamol wastewater	Photo-Fenton	91.2% COD 90.6% TOC	[Dalgic, 2013]
Real PAP wastewater	EO, BDD anode	95% COD 75.9% TOC	Present study

5. CONCLUSION AND RECOMMENDATIONS

Advanced oxidation processes are the most promising methods to treat non-biodegradable, toxic, complex contaminants in the wastewater. There have been many studies in the literature on different advanced oxidation processes. Generally, high removal efficiencies have been achieved in many studies. In this study, the treatment of p-aminophenol production wastewater by electrochemical oxidation has been investigated. Boron-doped diamond anodes were preferred due to their effectiveness. Effects of current density, initial pH, NaCl concentration, and dilution were examined. According to experiment results, 95% COD and 75.9% TOC removal efficiencies were achieved. Also, electrical consumption was calculated as 480 kWh/m³. Therefore, it can be concluded from this study that the electrochemical oxidation of PAP wastewater has been successful for the removal efficiencies.

Many studies examining the treatment of paracetamol and its derivatives have been studied with synthetic wastewater. This study researched real PAP wastewater treatment. As a recommendation for further researches, examining of treatment real wastewater can be beneficial. Another recommendation can be the improvement of the treatment time. In this study, the treatment time of PAP wastewater was obtained around 5 hours. By changing some factors like used anodes, current efficiency, or using different electrolytes can be shortened the operation time. The other recommendation can be the color removal of PAP wastewater. Although high COD and TOC removal efficiencies were achieved in this study, color removal was not achieved very well. Besides the EO with BDD, another advanced oxidation process can be added to the system to achieve decolorization. Hybrid systems can be effective to remove color.

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BIOGRAPHY

Mihrican Yurtarslan was born in 1992 in Ankara. In 2015, she completed a Bachelor's Degree in Environmental Engineering at Middle East Technical University. In 2017, she started her Master's Degree at Gebze Technical University, Institute of Science, Department of Environmental Engineering.

APPENDICES

Appendix A: Publications from this Thesis Study

Yurtarslan M., Kobyas M., (2019), “Treatment of p-aminophenol Production Wastewater by Electrochemical Oxidation Process Using Boron-Doped Diamond Anode”, 2nd International Eurasian Conference on Biological and Chemical Sciences (EurasianBioChem 2019), 818, Ankara, Turkey, 28-29 June.