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EGE UNIVERSITY

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APPLICABILITY OF A HYBRID ADVANCED OXIDATION SYSTEM TO AGRICULTURAL WASTEWATERS: WET AIR OXIDATION AND MICROBIAL FUEL CELL METHODS

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Gizem Civan tarafından Yüksek Lisans tezi olarak sunulan "Tarımsal Atık Sulara Bir Hibrit İleri Oksidasyon Sisteminin Uygulanabilirliği: Islak Hava Oksidasyonu ve Mikrobiyal Yakıt Hücresi Yöntemleri/ Applicability of a Hybrid Advanced Oxidation System to Agricultural Wastewaters: Wet Air Oxidation And Microbial Fuel Cell Methods" başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 26 Ağustos 2019 tarihinde yapılan tez savunma sınavında aday oybirliği/~~oyçokluğu~~ ile başarılı bulunmuştur.

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ÖZET

TARIMSAL ATIK SULARA BİR HİBRİT İLERİ OKSİDASYON SİSTEMİNİN UYGULANABİLİRLİĞİ: ISLAK HAVA OKSİDASYONU VE MİKROBİYAL YAKIT HÜCRESİ YÖNTEMLERİ

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Bu tez kapsamında, zeytin karasuyunun ana kirleticilerinin ceviz kabuklarından hazırlanan katalizör varlığında çeşitli ileri oksidasyonu yöntemleri ve mikrobiyal yakıt hücresi ile arıtımı çalışılmıştır. İleri oksidasyon yöntemleri ve mikrobiyal yakıt hücresi sistemleri bir hibrit sistem olarak uygulanmıştır.

Hedef zeytin karasuyu bileşikleri süksinik asit ve fumarik asit olarak seçilmiştir. Bu çalışma iki aşamada tamamlanmıştır. Çalışmanın ilk aşaması La Sapienza Üniversitesi Roma İtalya'da fumarik asit arıtımı mikrobiyal yakıt hücresi kullanılarak yapılmıştır. Çalışmanın ikinci aşaması Ege Üniversitesi İzmir Türkiye'de, ileri oksidasyon yöntemi ve mikrobiyal yakıt hücresi içeren hibrit sistem geliştirilmesi üzerine fumarik asidin eş-kristalı olan süksinik asit giderimi üzerinde tamamlanmıştır. Fumarik asit giderimi mikrobiyal yakıt hücresi ile incelenmiştir. Süksinik asit giderimi ise hibrit artıma sisteminin ilk aşaması olarak ileri oksidasyon yöntemlerinden katalitik ıslak hava oksidasyonu ve foto-Fenton benzeri oksidasyon yöntemleri ile incelenmiştir. Bu sistemin ikinci aşamasında mikrobiyal yakıt hücresi kullanılmıştır.

İlk aşama fumarik asit gideriminin ve elektrik enerjisi davranışının mikrobiyal yakıt hücresi ile incelenmesidir. Altı günlük deney süresince, fumarik asit giderimi %100 sağlanmıştır, Toplam Organik Karbon (TOK) giderimi ise %97 olarak, 0,2 V başarılı bir elektrik enerjisi üretimi ile pH 7,35-7,99 koşullarında elde edilmiştir.

Çalışmanın ikinci aşamasında, Co/ZrO_2, Bi/ZrO_2, Co-Bi/ZrO_2 ve ceviz kabuğundan hazırlanan aktif karbon üzerinde (AK) Demir-titanyum dioksit (Fe-TiO_2(1:99)) katalizörleri hazırlanmıştır. Katalizörün elde edilmesinden sonra, süksinik asit hedef kirleticisi için uygulanan tüm yöntemlerden hangi tip ileri oksidasyon yönteminin (Katalitik Islak Hava Oksidasyonu ve Foto-Fenton benzeri Oksidasyon) hibrit sisitemin ilk arıtma aşaması için uygun olduğu belirlenmiş ve en uygun çalışma koşulları incelenmiştir. Optimum çalışma koşulları her iki yöntem için test edilmiştir. Başlangıç konsantrasyonu tüm deneylerde 600mg/L kirletici ve 250 mg/L başlangıç toplam karbon olarak sabit tutulmuştur.

Süksinik asit için Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ katalizörleri ıslak hava oksidasyonun yönteminde kullanılmıştır. Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ katalizörleri ıslak hava oksidasyonu yönteminde süksinik asit gideriminde çok başarılı olmamalarına rağmen Co/ZrO_2 katalizörü Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ katalizörlerine göre dikkate değer bir giderim sağlanmıştır. %8.21 süksinik asit giderimi, 0.1 g/L Co/ZrO_2 katalizör varlığında 100°C sıcaklık ve 20 bar basınç çalışma koşullarında elde edilmiştir.

Islak hava oksidasyonu deneyleri sonuçlarından sonra Co/ZrO_2, $Fe\text{-}TiO_2/AK$ katalizörlerinin süksinik asit giderimindeki etkisi foto-Fenton benzeri katalitik oksidasyon incelenmiştir. $Fe\text{-}TiO_2/AK$ katalizörü Co/ZrO_2 katalizörüne göre daha başarılı sonuçlar vermiştir. En yüksek süksinik asit giderimi 4g/L $Fe\text{-}TiO_2/AK$ katalizörü varlığında 25°C sıcaklık 10 mM H_2O_2 ve UV ışık altında %61,37 olarak elde edilmiştir.

Hidrojen peroksit ve UV ışık süksinik asit üzerinde foto-Fenton benzeri oksidasyonda etkili olmuştur. UV ışık ve H_2O_2 kullanılmadan sadece katalizör varlığında $Fe\text{-}TiO_2/AK$ katalizörünün adsorpsiyon davranışı gösterdiği anlaşılmıştır. 4 g/L $Fe\text{-}TiO_2/AK$ katallizör ile nötral pH ile Süksinik asitin %40 oranında giderildiği tespit edilmiştir.

Toplam organik karbon (TOK) ve kimyasal oksijen ihtiyacı (KOİ) değerleri incelendiğinde, %32,2 TOK ve %35 KOİ giderimi elde edilmiştir.

Foto-Fenton benzeri oksidasyon sonrası elde edilen arıtımlı suya sodyum asetat ve NaOH eklenerek mikrobiyal yakıt hücresi deneyi uygulanmıştır. Hacimce %50 olarak eklenen sodyum asetat, 203,4 Ω dış direnç ve 25°C sıcaklıkta, 1ml süzüntü mikroorganizma eklenerek gerçekleştirilen 20 günlük deney sonunda %90 süksinik asit giderimi, %35,45 TOK giderimi ve %41,24 KOİ giderimi elde edilmiştir.

Anahtar Sözcükler: İleri oksidasyon yöntemleri, Mikrobiyal Yakıt Hücresi, Hibrit Arıtım Sistemleri, atıksu, süksinik asit, fumarik asit, yeşil katalizör

ABSTRACT

APPLICABILITY OF A HYBRID ADVANCED OXIDATION SYSTEM TO AGRICULTURAL WASTEWATERS: WET AIR OXIDATION AND MICROBIAL FUEL CELL METHODS

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Within the scope of this thesis, the main pollutants found in olive oil mill wastewaters were treated in the presence of walnut shell based catalysts by advanced oxidation methods and Microbial Fuel Cell (MFC) system. Advanced oxidation methods and Microbial Fuel Cell treatment were applied sequentially in a hybrid treatment system.

The target olive olive mill wastewater contaminants were selected as succinic acid (SA) and fumaric acid (FA). This study was accomplished in two stages. The first part of study was performed in La Sapienza University Rome/Italy by the investigation of fumaric acid degradation in Microbial Fuel Cell. The second part of study was carried out in Ege University İzmir/Turkey by the application of a hybrid wastewater system including AOPs and MFC for succinic acid degradation which is the co-crystal of the fumaric acid. In the first step of the hybrid treatment system catalytic wet air oxidation or photo-Fenton-like oxidation method was applied whereas the wastewater obtained from advanced oxidation treatment was treated with microbial fuel cell in the second step.

The first part of the study comprised of the investigation of fumaric acid degradation and the electrical potential behavior by Microbial Fuel Cell. H-type Microbial Fuel Cell was used. Complete (100%) fumaric acid degradation and 97% Total Organic Carbon (TOC) removal was achieved in 6 days with a good electrical potential value (0.2 V) at nearly neutral pH (7,35-7,99).

In the second part of the study, Co/ZrO_2, Bi/ZrO_2, $Co-Bi/ZrO_2$, and $Fe-TiO_2/AC$ (AC: Activated carbon derived from walnut shells) catalysts were prepared. After the catalyst preparation, it was determined that which type of advanced oxidation method (Catalytic Wet Air Oxidation and Photo-Fenton-like Oxidation) was the most suitable for the first stage of the hybrid treatment system among all of the methods applied for the succinic acid degradation. The optimum operating conditions were determined for both of the methods. The initial pollutant concentration and the initial total organic carbon were kept constant at 600 mg / L and 250 mg / L, respectively, in all of the experiments.

Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts were used in wet air oxidation. Even though Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalyst did not work inside the wet air oxidation process for succinic acid degradation, Co/ZrO_2 showed remarkable effect according to Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ during the wet air oxidation treatment process for succinic acid. 8.21% succinic acid degradation was achieved by using 0.1 g/L Co/ZrO_2 catalyst under 100^{o}C, 20 bar operation condition.

Co/ZrO_2, $Fe\text{-}TiO_2/AC$ catalysts were tested in photo-Fenton like oxidation of succinic acid. $Fe\text{-}TiO_2/AC$ was succesfull catalyst with respect to Co/ZrO_2. Experimental results showed that succinic acid degradation efficiency was obtained as 22.2% with 1g/L $Fe\text{-}TiO_2/AC$ catalyst under optimum operation condition which is 25^{o}C temperature, 5mM H_2O_2 and UV light.

In this situation, while $Fe\text{-}TiO_2/AC$ promoted of adsorption for succinic acid, hydrogen peroxide and UV light gave photo-Fenton like oxidation effect. Succinic acid was degraded around 40% during the adsorption of 4 g/L $Fe\text{-}TiO_2/AC$ in natural pH condition.

When TOC and COD values were investigated, 32.02% TOC and 35% COD degradation was achieved for succinic acid. According to this study for first step of hybrid system, adequate treated waste water was achieved for Microbial Fuel Cell that is hybrid system second step.

For Microbial Fuel Cell, effluent of photo-Fenton like oxidation was charged to the system after the adding sodium acetate (50% v/v) and NaOH by adjusting pH condition as neutral. 1ml supernatant was added to intermediate waste water which was obtained from adsorption, 203.4 Ω external resistant was used in this system and 25^{o}C temperature was adjusted as operation conditions. After twenty days, succinic acid degradation around 90%, TOC degradation around 35.45%, COD degradation around 41.24% and electrical potential around 0.2 V were achieved successfully.

Keywords: Advanced oxidation methods, Microbial Fuel Cell, Hybrid Treatment Systems, wastewater, succinic acid, fumaric acid. Green catalyst.

PREFACE

In this study, treatment of model pollutants in olive oil mill wastewaters by advanced oxidation methods and microbial fuel cell was investigated.

It is aimed to determine an innovative, environmental, economic and sustainable treatment system for wastewater treatment.

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1.0 INTRODUCTION

In Mediterranean countries, one of the most important problems is the treatment of olive oil mill wastewater (OMWW). The wastewater includes some hard biodegradable organic chemicals and long-chain fatty acids.

In addition, it includes phyto-toxic materials and various phenol and poly-phenol compounds, which are very difficult to treat. On the other hand, olive oil producing plants are small and spread out, and their operating seasons depend heavily on climate. For this reason, a centralized treatment of the wastewater is impossible. It means that a solution must be found for the small plants, which makes OMWW treatment simple, cheap and effective. Currently there is no such economical and easy solution. Physical and chemical methods, such as flocculation, coagulation, filtration, lagoon of evaporation and burning systems solve the problem partially (İnan et al., 2004).

Olive-oil mills generate dark coloured, foul-smelling and turbid aqueous wastes. These wastewaters consist of acidic effluents with high conductivity, especially those coming from traditional mills. Typically, olive-oil mills wastewaters (OMWW) are rich in inorganic ions (sodium, chloride and phosphorus), organic matter and suspended solids. According to the literature, OMWW are characterized by the great variety of pollutants contained, including aromatics (such as cathecol, p-coumaric acid, 4-methylcathecol, benzeneacetaldehyde, phenyl ethyl alcohol, benzofurane, and tyrosol) and also aliphatic compounds (such as hexane, octane, nonanol nonanoic acid, decanoic acid, dichloropropene, pentadecene, and hexadecane). The pH of OMWWs is in the range 4.9-5.3 due to the presence of organic acids such as acetic, malic, fumaric, lactic, malonic, citric, tartaric, ossalic and succinic. In additionally, succinic acid, fumaric acid and maleic acid were investigated as co-crystal (Childs et al.,2004, Canizares et al., 2007).

OMWW is characterized by a very high Chemical Oxygen Demand (COD up to 200 g l^{-1}), a high content in phenol-like substances (in the range 1–5 g l^{-1} measured as phenol) and acidity. Treatment of OMWW is very hard by using classical biological treatment because of its highly phytotoxicity and strong antimicrobial properties. Most physical and physicochemical methods, such as precipitation, flocculation/clarification, coagulation, filtration, evaporation in open ponds give only partial solution to the problem. Reverse osmosis or ultrafiltration are usually costly. Anaerobic biological digestion with production of biogas is increasingly being used, but is not yet completely satisfactory (Minh et al.,2006).

On the other hand, OMWW includes hydroxyl compounds and during the reaction, opening of aromatic ring and further oxidation of intermediates can happen in any of phenolic acidic intermediates formed. These organic intermediates can be formed in each other.

Treatment and disposal of olive oil mill waste water (OMWW) is problematic issue because of its ingredients as organic acids and phenolic compounds Many problems concerning the high toxicity and inhibition of biodegradation of these effluents were encountered during anaerobic treatments, because some bacteria, such as methanogens, were particularly sensitive to the organic contaminants present (Khoufi et al.,2006).

For this reason, only, biological treatment activity is not effectively treatment system because of low pH and biotoxicity problem. Researchers focused improving novel systems which include chemical pre-treatment to remove the toxic compounds of OMWW before biological treatment activity. The AOPs namely Fenton-like oxidation, catalytic wet air oxidation and photocatalytic oxidation can be applied. But these methods could not give %100 treatment always. In additionally, Microbial fuel cell is very advantages biological treatment system nowadays. Electrical power generation and water treatment in the same time are very advantages point. Therefore, more effective, ecofriendly, and economical methods were planned to be developed for the treatment of wastewater with this study by using microbial fuel cell for second treatment system. For this reason, Microbial Fuel Cell combining with AOPs as first treatment method can be novel research point.

The main objective of this study is to investigate the treatment of OMWW ingredients pollutants fumaric acid and succinc acid. It was aimed to develop an innovative degradation method as hybrid system which includes chemical and biological treatment combination. In this context, AOP methods investigated such as catalytic wet air oxidation and photo-Fenton-like oxidation in the presence of the catalysts prepared from walnut shells as the first treatment step for the hybrid system. After that, biological treatment was performed by using Microbial Fuel Cell. During this study, degradation efficiency and optimum values of operating parameters were determined. The main contribution of this study to literature is to improve low degradation efficiencies of these target compounds by biological methods and to apply AOPs in the presence of organic waste catalyst. Furthermore, it was aimed to search for the most suitable hybrid system method for treatment of Olive oil mill wastewater's target pollutants.

2.0 THEORETICAL BACKGROUND

2.1 Organic Pollutants in Wastewater

Organic pollution is the term used when large quantities of organic compounds exist. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater. Sewage treatment plants and industry which includes food processing, pulp and paper making, agriculture are some important areas that cause organic pollution. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates. Wastewater which includes these kinds of organic pollutants reduces the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates because of its large quantities of suspended solids. On the other hand, during the decomposition process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota (Rashed, 2013).

Nowadays, being the most importance of water the need of water quality improvement and preservation growing continuously. The quality of water resources has been deteriorated day by day due to the continuous addition of undesirable chemicals in them (Lvovich, 1979). Few hundred organic pollutants have been found to contaminate water resources and, contamination of water sources with organic pollutants is very dangerous due to their various side effects and carcinogenic nature. The main sources of water contamination are industrialization, civilization, agricultural activities and other environmental and global changes (Yang, 2011). Therefore, the removal of toxic organic pollutants from water is essential for the future planning.

2.2 Olive Oil Mill Waste Water

The treatment of olive oil mill wastewater (OMWW) is one of the most important environmental problems in the Mediterranean countries. Because this wastewater includes organic chemicals and long-chain fatty acids and these substances are not biodegraded easily in nature. In addition, it includes photo-toxic materials and various phenol and poly-phenol compounds, which are very difficult to treat. On the other hand, olive oil producing plants are small and spread out, and their operating seasons depend heavily on climate. For this reason, a centralized treatment of the wastewater is impossible. It means that a solution must be found for the small plants, which makes OMWW treatment simple, cheap and effective currently there is no such economical and easy solution (Inan, et.al, 2004).

The main olive oil manufacturer countries are located in the Mediterranean coast. Due to the manufacture of olive oil is typically carried out by small companies in small facilities, the management of the liquid wastes generated in mills is a subject of the major importance for these companies according to large companies (Canizares, et. al, 2007).

Liquid olive oil mill wastewater (OMWW) has dark-colour and contains high amounts of organic materials. They are composed of many complex substances that are not easily degradable. Colouring, appearance of an oily shine, and increasing of oxygen demand are indicator of the deterioration of natural waster due to olive oil mill wastes. They also affect the soil quality, are toxic to plant life, and create odor nuisance when disposed into the soil. Therefore, directly discharging of olive mill wastewater into media is not permissible and certain measures must be taken before disposal of the OMWW into the environment (Azbar, et al., 2004)

High content of organic molecules, especially polyphenolic mixtures (4-10g/L) with different molecules (Hamdi, 1991) and high concentration of potassium, magnesium and phosphate salts raise of OMWW polluting activity (Arienzo and Capasso, 2000). Additionally, it contains other organic molecules including nitrogen compounds, sugars, organic acids, and pectin that increase organic load of OMWW (Della Greca et al., 2000).

There is no economical and easy solution for OMWW treatment. Physical and chemical methods can solve this problem partially, such as flocculation, coagulation, filtration, lagoon of evaporation and burning systems. On the other hand, biological treatment of OMWW is difficult because of phenolic chemicals, which possess antibiotic characteristics (Inan, et.al, 2004).

Olive oil mill wastewater has general properties shown in Table 2.1 (Azbar et. al, 2004):

- Intensive dark brown to black color.
- Strong acidic smell unique to olives.
- High organic content (COD values around 220 g L^{-1} in three-phase units)
- A COD/BOD5 ratio between 2.5 and 5, indicating low biodegradability
- Acidic character with pH values between 3 and 5.9.
- High concentrations of phenolic compounds (up to 80 g L^{-1}).
- High content of solid matter (total solids up to 20 g L^{-1})

Table 2. 1 Characteristics of Olive Oil Mill Wastewater (Azbar,et.al, 2004)

Parameter	Value
pH	3.0–5.9
Chemical oxygen demand (COD), g L^{-1}	40–220
Biochemical oxygen demand (BOD), g L^{-1}	23–100
Total solids (TS), g L^{-1}	1–102.5
Organic total solids (OTS), g L^{-1}	16.7–81.6
Fats, g L^{-1}	1–23
Polyphenols, g L^{-1}	0.002–80
Volatile organic acids, g L^{-1}	0.78–10
Total nitrogen, g L^{-1}	0.3–1.2

2.2.1 Organic Acids as Organic Pollutants in Olive Oil Wastewater

Characteristics of OMWW cause severe environmental problems such as having low pH and biodegradability as well as extremely high solids and organic compounds content. The low pH of OMWW (in the range of 3.0–5.9) is due to the presence of organic acids such as acetic, malic, fumaric, lactic, malonic, citric, tartaric, ossalic and succinic acids. At the same time, the organic fraction contains sugars, tannins, polyphenols, polyalcohols, pectins, lipids, proteins and organic acids. All these compounds contribute to the high polluting load of OMWW (El-Abbassi, et al., 2012).

2.2.1.1. Succinic acid as a carboxylic acid

Olive Oil mill wastewater includes some important organic acids as pollutant. According to this, as important environmental parameter is pH has low level because of these acidic pollutants. Normally, the pH of OMWWs is in the range 3-5 due to the presence of organic acids such as acetic, malic, fumaric, lactic, malonic, citric, tartaric, ossalic and succinic (Cassano et al., 2011).

Succinic acid (SA) was first purified from amber by Georgius Agricola in 1546, also it called amber acid or butanedioic acid, is one of the dicarboxylic acids with the molecular formula of $C_4H_6O_4$ (see Table 2.2). It has been produced by microbial fermentation for the use in agricultural, food and pharmaceutical industries (Zeikus, et al., 1999).

Succinic acid is synthesized from liquefied petroleum gases (LPG) or petroleum oil commercially and it is also found in samples of atmospheric aerosol particles. Additionally, SA has been widely used as a precursor of many industrially important chemicals including adipic acid, 1,4-butanediol, tetrahydrofuran, N-methylpyrrolidinone, 2-pyrrolidinone, succinate salts and γ-butyrolactone. Figure 2.1 demonstrates the products obtained by succinic acid. Recently, SA has been employed as an anti-ablative material for boundary layer control system (BLCS) in high pressure graphite rocket nozzle. However, the thermal statistics of SA and kinetics for its uni molecular decomposition are still unknown (Hsin-Tsung, et al., 2008).

Table 2. 2 Structural Information of Succinic Acid

Substance	**Structural Formula**	**Formula**
Succinic Acid		$C_4H_6O_4$

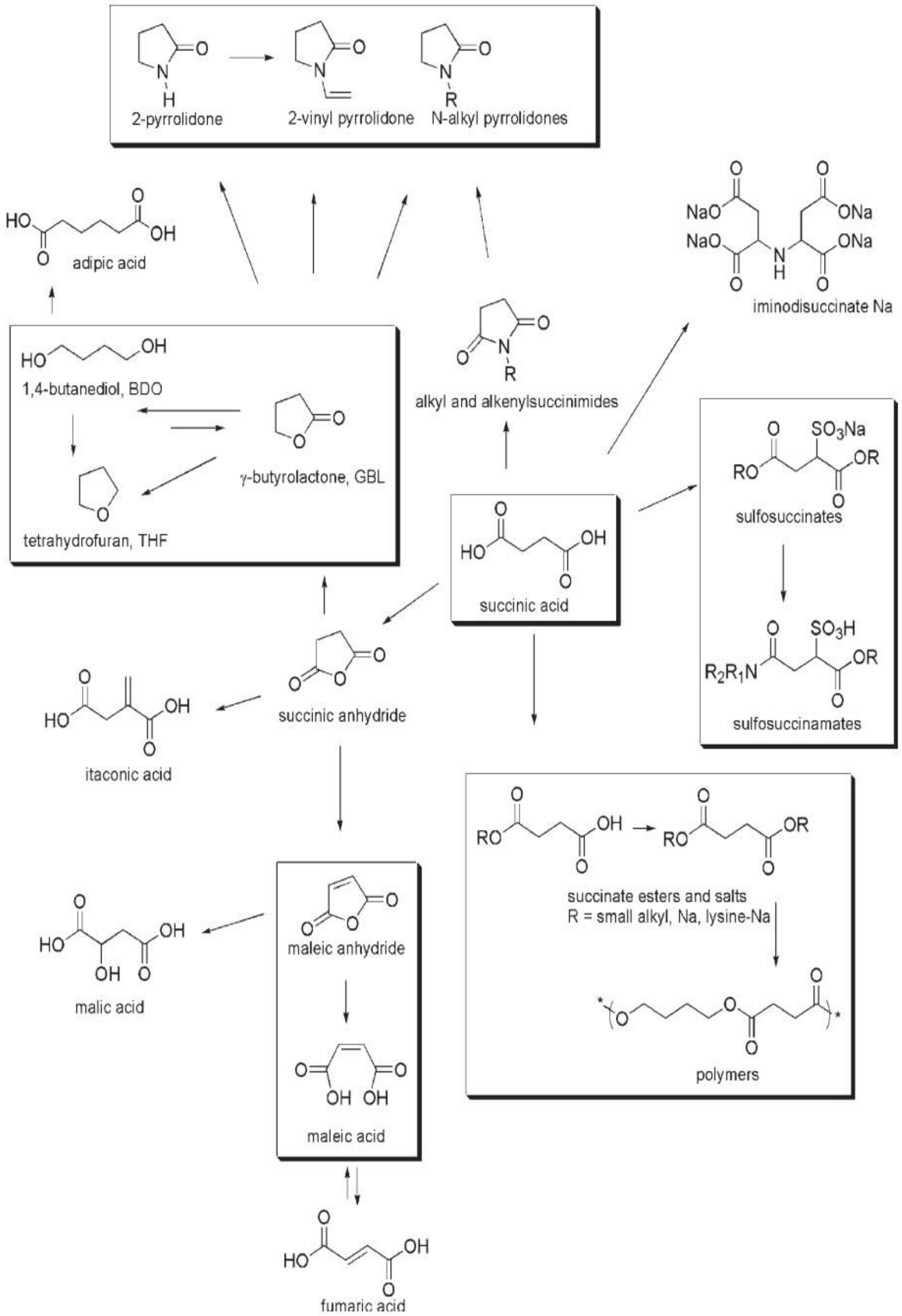


Figure 2. 1 Overview of products obtained by succinic acid (Cukalovic and Stevens, 2008).

2.3 Waste Water Treatment Methods

The pollution of water resources and soil with chemical contaminants is one of the most crucial environmental problems. For this reason, water treatment methods have gained importance. Water treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic matter and, sometimes, nutrients from wastewater (Sonune and Ghate, 2004).

2.3.1 Chemical Treatment Methods

Wastewater treatment and reuse is an important issue and scientists are looking for inexpensive and suitable technologies. Water treatment technologies are used for three purposes i.e. water source reduction, wastewater treatment and recycling (Gupta et al, 2012). For this purpose, different chemical treatment methods are tried to improve by scientists.

2.3.1.1 Advanced Oxidation Methods

Oxidation processes commonly employed in water treatment can be investigated in two categories: conventional oxidation and advanced oxidation methods. Conventional oxidation involves the addition of an oxidant to the water that then reacts directly with the target contaminant. Conventional oxidants are selective, specific oxidants that must be used to remove specific contaminants. The conventional chemical oxidants used in water treatment include chlorine, chlorine dioxide, ozone, potassium permanganate, and hydrogen peroxide. Several of these oxidants are also disinfectants (Crittenden et al., 2012).

Additionally, to conventional oxidation, other oxidation techniques was defined as advanced oxidation processes (AOP) which usually operate at or near ambient temperature and pressure (Andreozzi et al., 1999). These processes include highly reactive radicals (especially hydroxyl radicals) in sufficient quantity to effect water purification. Hydroxyl radicals are extraordinarily reactive species that attack most organic molecules. The kinetics of the reaction are generally first order with respect to the concentration of hydroxyl radicals and to the concentration of the species to be oxidized (Ricciardi, 2006).

Common AOPs involve Fenton and Fenton-like oxidation, photo-Fenton-like oxidation, wet air oxidation, ozonation, photochemical and electrochemical oxidation, photocatalytic oxidation, photolysis with H_2O_2 and O_3, high voltage electrical discharge process, radiolysis, wet oxidation, treatment by electronic beams or γ-beams and various combinations of these methods (Abo-Farha, 2010).

AOPs can be categorized in five main groups such as AOPs based on ozone (O3), AOPs based on H_2O_2, AOPs based on photocatalysis, hot AOPs, and others which are mostly combination main AOPs. The main groups and subgroups are shown in Figure 2.2 schematically (Andreozzi et al., 1999).

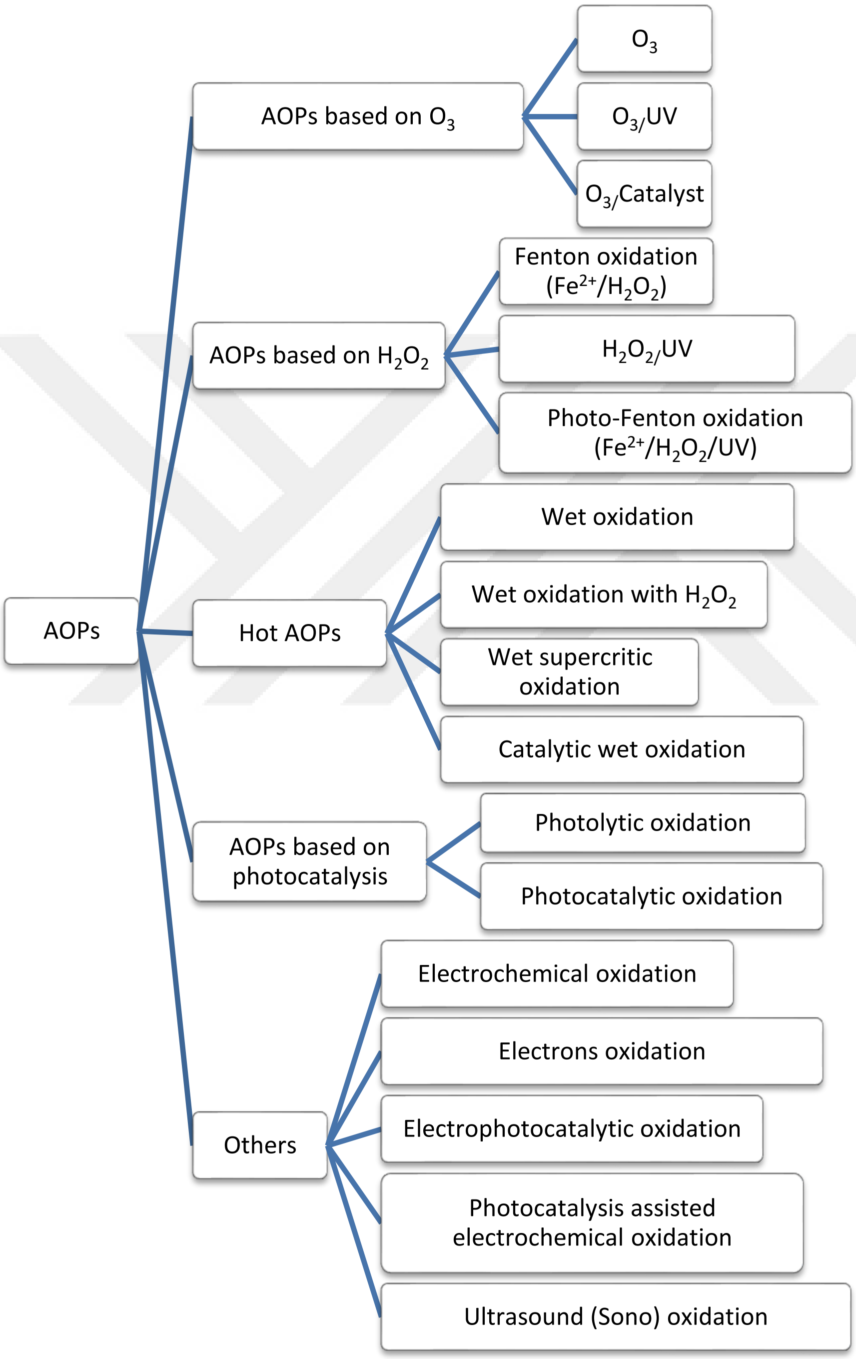


Figure 2. 2 Advanced oxidation processes based on oxidant type and/or catalyst

Fenton-like oxidation:

Fenton oxidation is one of the most common advanced oxidation processes and basically defined as the chemical oxidation of organic compounds by hydrogen peroxide (H_2O_2) using Fe^{2+} ions as a catalyst. It has been particularly attractive because of the advantages it provides such as low costs, the lack of toxicity of the reagents, the absence of mass transfer limitation due to its homogeneous catalytic nature, and the simplicity of the technology (Daud and Hameed, 2010).

The below reaction shows how capable the Fenton reaction is to eliminate organic pollutants. Reduction of hydroxide ion and the hydroxyl radical is being made and oxidation from Fe(II) to Fe(III) has been observed.

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

But this reaction is also of biological relevance because for most living organisms, the alteration of the intracellular concentration of Fe^{2+} and H_2O_2 can increase the intracellular formation of •OH, leading to DNA and cell damage. Hence reduction of the ferric ion (Fe^{3+}) produced to ferrous ion (Fe^{2+}) by a second molecule of hydrogen peroxide, can be used as a regeneration of ferrous ions and it is called Fenton-like reactions (Spuhler et al., 2010).

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

Catalytic wet air oxidation:

Wet air oxidation (WAO) is an attractive technique for industrial wastewater treatment. WAO involves the combustion of pressurized organic matter at relatively high temperatures. The main drawback of this technique is its high energetic requirements. In order to be able to employ milder operating conditions and reduce the operating costs, catalytic wet air oxidation processes (CWAO) have been developed. The presence of catalyst may improve the overall reaction rate and enhances the removal of reaction intermediates compounds, which are refractory to the WAO process, improving the formation of hydroxyl radicals, well-known promoters of the oxidation (Ovejero et al., 2013).

The basic idea of the wet air oxidation (WAO) process is to enhance contact between molecular oxygen and the organic matter to be oxidized. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by a high pressure which also increases the concentration of dissolved oxygen and thus the oxidation rate (Debellefontaine et al, 1996).

Compared to conventional wet-air oxidation, catalytic wet-air oxidation (CWAO) has lower energy requirements. Due to the presence of a catalyst much higher oxidation rates are achieved and consequently, one can use less severe reaction conditions to reduce chemical oxygen demand to the same degree as in the case of noncatalytic process (Levec and Pintar, 2007)

Kim and Ihm discuss why Wet air oxidation (WAO) and catalytic wet air oxidation processes (CWAO) are desirable and conclude that both methods are environment friendly while managing industrial wastewaters. (Kim and Ihm, 2011).

Photocatalytic oxidation:

Photocatalytic processes use a semiconductor metal oxide as catalyst and of oxygen as oxidizing agent. Many semiconductor catalysts have been so far tested, although only TiO_2 in the anatase form seems to have the most interesting attributes such as high stability, good performance and low cost. Electron-hole pairs helps to consume the radiation in the beginning of photocatalytic operation:

$$TiO_2 \xrightarrow{h\nu} e^- + h^+$$

The considerable reducing power of formed electrons allows them to reduce some metals and dissolved oxygen with the formation of the superoxide radical ion $O_2^{\bullet-}$whereas remaining holes are capable of oxidizing adsorbed H_2O or $HO^-$to reactive •OH radicals:

$$TiO_2(h^+) + H_2O_{ad} \rightarrow TiO_2 + HO_{ad}^- + H^+$$

$$TiO_2(h^+) + HO_{ad}^- \rightarrow TiO_2 + HO_{ad}$$

Above reactions have a major role in oxidative degradation due to the huge absorption of H_2O and HO which eventually cause the biological pollutant to deteriorate. Direct electron transfer is another way for oxidization process.

$$TiO_2\,(h^+) + RX_{ad} \rightarrow TiO_2 + RX_{ad}.^+$$

Unfortunately, a significant part of electron-hole pairs recombine thus reducing the quantum yield. Intensive researches are carried out worldwide to obtain modified (doped) TiO_2 with broader absorption spectrum and characterized by higher quantum yield. Although, in theory, it has been spent great amount of time on this process, it is almost impossible to see any implication of photocatalytic operations in the scale of industry (Andreozzi et al.,1999).

UV Radiation and hydrogen peroxide:

The H_2O_2/UV process is an example of an advanced oxidation process (AOP), defined as those which involve the production of reactive radicals, in this phenomenon, OH radical is able to oxidize biological impurities in water and H_2O_2/UV process may include some photolysis of biological impurities. Primarily, AOPs' capability is narrow as they are contingent on some radical scavengers or UV absorbers (Glaze et al.,1995).

UV/Peroxide treatment uses ultraviolet radiation to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. UV/Peroxide treatment uses ultraviolet radiation to cleave the O Ɵ-bond in hydrogen peroxide and generate the hydroxyl radical and hydroxyl radicals commonly attack organic molecules by abstracting a hydrogen atom from the molecule (Chang and Young,1999):

$H_2O_2 \xrightarrow{h\nu} \bullet OH + \bullet OH$

$\bullet OH + H_2O_2 \rightarrow H_2O + OH\bullet$

$HO_2\bullet + H_2O_2 \rightarrow H_2O + O_2 + \bullet OH$

$2HO_2\bullet \rightarrow H_2O_2 + O_2$

Hydroxyl radicals commonly attack organic molecules by abstracting a hydrogen atom from the molecule (Clarke and Knowles, 1982). For example, one pathway proposed for the degradation of methyl tert-butyl ether by hydroxyl radical is shown below (Barreto et al., 1995):

$\bullet OH+(CH_3)_3COCH_3 \rightarrow H_2O+(CH_3)_3COCH_2\bullet$

$(CH_3)_3COCH_2\bullet+O_2 \rightarrow (CH_3)_3COCH_2OO\bullet$

$(CH_3)_3COCH_2OO\bullet+(CH_3)_3COCH_3 \rightarrow$

$(CH_3)_3COCH_2OOH+(CH_3)_3COCH_2\bullet$

$(CH_3)_3COCH_2OOH \rightarrow (CH_3)_3COCHO+H_2O$

2.3.2 Biological Methods

Industrial effluent usually contains non-biodegradable pollutants. In addition, the existence of toxic chemicals makes the biological treatment more difficult. Hence, different approaches are being discovered for non-biodegradable wastes. (Chen et al., 2007).

2.3.2.1 Microbial Fuel Cell

Microbial fuel cell (MFC) is the best proposal for wastewater treatment, which can use bacteria as the catalysts to produce electricity and oxidize organic matters (Logan et al., 2006; Wang et al., 2009). The greatest potential of MFC lies in the use of wastewater as a substrate (fuel), which breaks the traditional concept of sewage treatment and allows combining wastewater treatment with power generation. However, the electron transfer process within MFC devices involves complicated mechanism among different cells or cell systems, which directly lead to poor cell performance. Furthermore, MFC also possess disadvantages such as complex operation, bacteria cultivation, long start up time, and stringent working conditions (Yanbiao et al.,2011).

Microbial fuel cells (MFCs) have drawn increasing attention in using wastewater as the anodic “fuel” to generate electricity and accomplish pollutant treatment simultaneously. Recently, electricity generation from landfill leachate in both dual- and single chamber MFCs have been reported as an economical method for power energy recovery in leachate treatment (Li et al., 2010).

Microbial fuel cells (MFCs) can be described as bio-electrochemical system that use bacteria to oxidize organic wastes and generate electricity. Microorganisms on the anode oxidize organic substrates and simultaneously generate electrons and protons. The electrons are transferred to the cathode through external circuit, and protons are released into solution. At the cathode, oxygen reacts with electrons and protons to form water. In the past decade, MFCs have been investigated due to the advantage of recovering green energy (electricity) from wastewaters and waste biomass sources (Zhu and Logan, 2013).

Microbes in the anodic chamber of an MFC oxidize added substrates and generate electrons and protons in the process. Carbon dioxide is produced as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the renewable biomass originally comes from the atmosphere in the photosynthesis process. Unlike in a direct combustion process, the electrons are absorbed by the anode and are transported to the cathode through an external circuit. After crossing a PEM (Proton Exchange Membrane) or a salt bridge, the protons enter the cathodic chamber where they combine with oxygen to form water. Microbes in the anodic chamber extract electrons and protons in the dissimilative process of oxidizing organic substrates (Rabaey and Verstraete, 2005). Electric current generation is made possible by keeping microbes separated from oxygen or any other end terminal acceptor other than the anode and this requires an anaerobic anodic chamber. Typical electrode reactions are shown below using acetate as an example substrate. The overall reaction is the breakdown of the substrate to carbon dioxide and water with a concomitant production of electricity as a by-product. Based on the electrode reaction pair above, an MFC bioreactor can generate electricity from the electron flow from the anode to cathode in the external circuit (Du et al., 2007).

Anodic reaction:

$CH_3COO^- + 2H_2O \xrightarrow{microbes} 2CO_2 + 7H^+ + 8e^-$

Cathodic reaction:

$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

2.3.3 Hybrid Treatment System

The removal of toxic and bio-refractory organic substances from groundwater and wastewater has been of great significance to prevent water environment from contamination of hazardous chemicals for years. Utilizing conventional methods to treat these substances, such as adsorption, coagulation, filtration and sedimentation have been proved to be technically feasible. However, these approaches maybe problematic and unsustainable, due to potential production of various secondary wastes which need further treatments (Fu et al.,2010).

Wastewater reclamation and reuse is essential to avoid water shortages and degradation of the environment. Sustainable and low-energy demanding technologies are especially important for achieving these goals. A microbial fuel cell (MFC) is a technology that uses exoelectrogenic biofilms on the anode to degrade organic matter and produce renewable energy in the form of electricity. However, MFCs may not be sufficient as a stand-alone wastewater treatment technology to achieve high effluent quality. Several methods have been proposed to improve treatment, such as integrating the MFC with a nitrification step, submerging the MFC reactor in the aeration tank of an activated sludge process, combining the MFC with a sequencing batch reactor or a membrane-aerated biofilm process, or integrating the MFC into a rotating biological contactor (Malaeb et al., 2013).

2.4 Heterogeneous Catalyst

The common catalysts used in AOPs are metals, metal oxides, photons (from UV light) and ultrasound. Catalysts can be homogeneous, for which the catalysts and the reactants are in the same phase; or heterogeneous, for which the catalysts are in different phases than the reactants. There are wide range of combinations of oxidants and catalyst that can generates •OH radicals the AOPs are widely categorized (Umar et al, 2010).

Homogeneous catalysts used in AOPs have several drawbacks such as leaching of the catalyst to the treated waste and generation of secondary waste. As an example homogeneously catalyzed reactions in homogeneous Fenton-like process need up to 50–80 ppm of Fe ions in solution, which is well above the

European Union directives that allow only 2 ppm of Fe ions in treated water to be dumped directly into the environment. But the removal/treatment of the of the generated secondary waste at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower (Ramirez et al., 2007). In photocatalytic oxidation applications in which TiO_2 used as photocatalyst, TiO_2 suspensions or agglomerations cannot be removed from the reaction medium (Foo and Hameed, 2010). To overcome the disadvantages of the homogeneous catalysis processes, the immobilization of the catalyst on inert support surfaces known as heterogeneous catalysis becomes forward. It prevents the drawbacks of high amount of metals in treated water and secondary waste generation. In this manner, a catalyst support is used which bonds to the metal ion and that provides an efficient separation of the catalyst at the end of operation (Pariente et al., 2008, Duarte et al., 2011).

2.4.1 Activated Carbon as Catalyst Support

Activated carbon materials have been extensively used as adsorbents, catalysts and catalyst supports for removal of pollutant species from gases or liquids, and for purification or recovery of chemicals. Pore structure is an important factor for physical adsorption, while surface chemistry plays a key role in specific adsorption and surface reactions (Liu et al., 2010).

Recently, activated carbon (AC) has proven to be an excellent catalytic support in the oxidation of aromatic compounds which have high chemical resistance to breakage and attrition and easy to recover that increases reusability of the catalyst. Among its excellent properties, it can be emphasized that their high surface area, well developed and different porous structure which leads homogeneous distribution of catalyst and variable surface composition which determine important differences in their reactivity allows to study the effects of these features on the catalytic behavior. Specifically, in environmental applications related to wastewater treatments, the structure of activated carbon plays an important role because the adsorption capacity is determined by both the porous structure and the chemical nature of the surface. Thus, it is very important to understand the role of the activated carbon surface in the preparation of optimized catalysts in terms of activity and stability. It is well known that some transition metal elements like iron promote hydrogen peroxide decomposition to hydroxyl radicals capable to efficiently oxidize organic matter (Puma et al., 2008, Rey et al., 2009).

2.4.2 Activated Carbon Production

Activated carbon can be produced from any solid precursor either natural or synthetic. Agricultural wastes are cheap, renewable, safe, available at large quantities, easily accessible sources and have high carbon and low ash content (Ahmed and Dhedan, 2012). This leads to reuse of organic wastes such as walnut shells which have almost no other use in any field for production of more valuable products like activated carbon (Aworn et al., 2008).

Generally, the activated carbons are manufactured in two stages that is, carbonization and activation processes. The carbonization process, which includes drying and then heating, is performed to eliminate byproducts such as tars and other hydrocarbons (including volatile organic compounds) from the raw material. The carbonized material is then activated in the second stage by exposing them to an activating agent. These two carbonization and activation processes can be combined and the activated carbon can be prepared by thermally treating the chemical reagent impregnated carbonaceous material which results a less time and energy consuming process (Yang and Lua, 2003 Ekpete and Horsfall, 2011).

The carbonization process is performed by heating the material in an inert atmosphere to remove volatile organic impurities and to obtain pure carbon structure. Activation is applied to the pure carbon mass by various chemical reactions resulting the porous structure of the activated carbon (Nowicki et al., 2010). The activation process can be applied by two different methods: Physical activation and chemical activation. For physical activation, heat treatment is applied in CO_2, water vapour, air or various gas atmospheres. These atmospheres react with some of the carbon atoms on the surface by producing gas and pores are formed. On the other hand, chemical activation is performed by heating the carbon mass in an inert atmosphere after impregnation of chemical reagents to the carbon mass. The impregnated reagents have the same role of the gas atmospheres in physical activation and they react with the carbon structure to create porous structure and retard the formation of tars during the carbonization process and increase the carbon yield. The most important and commonly used chemical activating agents are zinc chloride, potassium hydroxide and alkaline metals (Kim et al., 2001).

The chemical and physical activation of carbon determine the adsorption behavior of activated carbon. The chemical activation usually takes place at a temperature lower than that used in physical activation, therefore it can improve the pore development in the carbon structure because the effect of chemicals. The carbon yields of chemical activation are higher than physical one (Ahmadpour and Do, 1997).

Oxidized activated carbon is another common application of activated carbon as catalyst support especially for treatment of organic pollutants. Activated carbon as an efficient adsorbent both for metal catalysts and the contaminants present in wastewater, inhibit the efficiency of the catalyst because of the strong adsorption of the contaminants instead of catalyst. Oxidation of the activated carbon causes formation of the surface functional groups which increase the adsorption of catalysts, selectively. For this purpose, carbonized material is treated with HNO3 solution to oxidize surface groups (El-Sheikh et al., 2007).

2.4.3 ZrO_2 as Catalyst Support

ZrO_2 have been used as a catalyst support for the removal of the pollutant, and for the purification or recovery of chemicals especially CO. Chemical adaptation with metals, pore structure, physical adsorption are very important properties for it.

ZrO_2 has been preferred by researchers as catalyst as well as catalyst support in recent years. Higher thermal stability, extreme hardness, high specific mass of zirconia are the advantages for its use as catalyst and as support. It has both acidic and basic properties. Zirconia has been used as support for hydrotreating catalysts and the effect of support on catalytic functionalities for hydrotreating reactions and structure–activity relationship has not yet fully understood (Maity et al.,2000).

Researchers took ZrO_2 as the main research object for iso-synthesis reaction. Zirconia itself has versatile chemical and physical properties such as acidic-basic properties, redox properties and different crystalline phases. In the past, many researchers have studied the catalytic properties of pure or modified ZrO_2 used in the iso-synthesis reaction. For example, the effect of different ZrO_2 phases (cubic, tetragonal and monoclinic phase) on isobutene synthesis was investigated. It was proposed that the monoclinic phase was the most beneficial for the formation of isobutene from CO, which could be attributed to more vacant sites and stronger basicity caused by the shorter Zr-O bond in the monoclinic structure. The effects of acidic-basic properties on the isosynthesis ability of ZrO_2 was also investigated. According to this study, a large ratio of basic to acidic sites on ZrO_2-based catalyst was required to produce isobutane and isobutene from CO hydrogenation (Wu et al., 2019).

3.0 LITERATURE SURVEY

The studies found in literature survey were categorized according to target compounds, methods, and catalysts.

3.1 Studies About Olive Oil Mill Wastewater Treatment by Biological Methods

In 1996, Ramos-Cormenzana et al. examined removal of phytotoxic compounds (i.e., monoaromatic or simple phenolics) from OMWW by using Aerobic bacteria in orbital incubator at 28°C and at 150 rpm. After 5 days the phenol content of the various samples was determined. According to this report, the phenol content was measured using HPLC techniques, and results were obtained showing that the bacterium had most effect in reducing the phenol content of OMWW at concentrations of between 40 and 100%. The effectiveness of aerobic bacteria in reducing the phytotoxicity of OMWW varies greatly. Aerobic bacteria appear to be very effective against some phenolic compounds and relatively ineffective against others. For example, B. pumilus was able to completely degrade protocatechuic acid and caffeic acid, but had much less effect on tyrosol (Ramos-Cormenzana et al., 1996)

In 1997, Benitez et al. studied biodegradation of olive oil mill wastewater by using aerobic microorganisms in a batch reactor. They examined the chemical oxygen demand, biomass and the total contents of phenolic and aromatic compounds through each experiment. According to these experiments, phenolic compounds was followed in every experiment. In addition, for experiments with the same initial COD, the initial biomass X_0 hardly affects the COD removal, giving overall reductions higher than 80%. On the other hand, in experiments where the initial COD was varied, a direct effect of this variable on the total COD removal was deduced (Benitez et al., 1997)

In 2004, Ammary examined the impact of the removal efficiency and the observed biomass yield on nutrient requirements for anaerobic treatments of OMWW by using laboratory scale anaerobic sequencing batch reactors. The researcher found more than 80% of COD removal could be achieved by varying the COD: N: P ratio. In addition, the observed biomass yield was about 0.06 kg volatile suspended solids (VSS) per kg of COD degraded. Thus, it was concluded that OMWW have sufficient nitrogen and phosphorous concentrations, and the addition of such nutrients was not necessary (Ammary, 2004).

In 2013, Sciarria et al. studied on improving electricity generation and COD degradation by using OMWW and using single-chamber microbial fuel cells (MFC). Doing so single-chambers air cathode MFCs with platinum anode were fed with domestic wastewater (DW) alone and mixed with OMWW at the ratio of 14:1 (w/w). MFCs fed with DW + OMWW gave 0.38 V. The process allowed a total reduction of COD and BOD_5 of 60% and 69%, respectively, recovering the 29% of the coulombic efficiency. The maximum voltage obtained from MFC fed with DW + OMWW was 2.9 times higher than that of cell fed with DW (Sciarria et al.,2013).

3.2 Studies About Olive Oil Mill Wastewater Treatment by Adsorption and AOPs

In 2002, Galiatsatou et al. in the study named as “Treatment of olive mill waste water with activated carbons from agricultural by-products” investigated treatment of OMWW by activated carbons adsorption. They prepared a series activated carbons by a two-step steam activation of olive stone and solvent extracted olive pulp (SEOP). These activated carbons have been used in an attempt to investigate the total phenol removal and chemical oxygen demand (COD) decrease in olive mill waste water (OMWW) by spectrophotometric method. They found OMWW total phenols degradation between 73%-13% with respect to activated carbons (Galiatsatou et al.,2002).

In 2004, Azzam et al. studied “Dynamic Post-Treatment Response of Olive Mill Effluent Wastewater Using Activated Carbon” to investigate degradation of COD value for OMWW by adsorption. They observed that COD, phenols pH values during the 48 hours experimental time. The maximum adsorption capacity for the tested concentrations of activated carbon is reached in less than 4 h. The maximum removal of phenols is about 94%, while it reaches about 83% for organic matter (Azzam et al.,2004).

In 2006, Minh et al. published their study “Degradation of olive oil mill effluents by catalytic wet air oxidation:1. Reactivity of *p*-coumaric acid over Pt and

Ru supported catalysts" which focused on catalytic wet air oxidation of model pollutant *p*-coumeric acid. The most important intermediates determined by HPLC measurements suggest a rapid attack by oxygen of the side-chain of *p*-coumaric acid, and the mineralization proceeds through different aromatic compounds reacting further to aliphatic intermediates (mainly acids). Important mineralization yields were achieved in the presence of the catalysts at 140 ^{o}C and 50 bar. The importance of the nature of the support (TiO_2, ZrO_2) on the adsorption of p-coumaric acid was demonstrated (Minh et al.,2006).

In 2007, Cañizares et al. have another study also focused on treatment of OMWW named as" Advanced oxidation processes for the treatment of olive-oil mills wastewater". They studied on the treatment of an actual industrial waste with three advanced oxidation processes (AOP) has been studied: conductive diamondelectrooxidation (CDEO), ozonation and Fenton oxidation. They concluded that the three AOPs studied (CDEO, ozonation and Fenton oxidation) are able to treat OMWW. However, only CDEO allows achieving the complete mineralization of the waste with high efficiencies. Both ozonation at alkaline pH and Fenton oxidation lead to the generation of high concentration of intermediates (mainly carboxylic acids) that cannot be further oxidized by hydroxyl radicals. As a consequence, TOC around 30% remains at the end of the process (Cañizares et al.,2007)

3.3 Studies About Olive Oil Mill Wastewater Treatment by Combined Hybrid Processes

In 2004, Drouiche et al., investigated treatment of OMWW by combining UF and UV/H_2O_2 techniques. In this study, UF reduced the pollutants contained in the OMWW with an apparent rejection coefficient R_{COD} in the range of 94%. UV/H_2O_2 process was observed in continuous mode and in batch mode. Results showed that continuous mode is slightly slow than batch mode as second step treatment (Drouiche et al.,2004).

In 2006, Khoufi et al. published their study" Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion" which focused on OMWW treatment by combined processes allowing water recovery and reuse for agricultural purposes. The combined method involved an electrochemical pre-treatment step of the wastewater using the electro-Fenton reaction followed by an anaerobic bio-treatment. The electro-Fenton process removed 65.8% of the total polyphenolic compounds and subsequently decreased the OMWW toxicity from 100% to 66.9%, which resulted in improving the performance of the anaerobic digestion. They concluded that, in the combined process, a high overall reduction in COD, suspended solids, polyphenols and lipid content was achieved by the two successive stages (Khoufi et al.,2006).

In 2009, Lafi et al. studied on combined treatment systems named as “Treatment of olive mill wastewater by combined advanced oxidation and biodegradation”. In this study, olive mill wastewater (OMWW) treatment is investigated experimentally in various stage processes of advanced oxidation with ozone (O_3), photodegradation by UV radiation, and an aerobic biodegradation. During this study, they monitored the effects of these treatment processes on the removal of chemical oxygen demand (COD) of OMWW. They concluded that, for both single-stage treatment of O_3 and two-stage treatment of O_3/UV, the chemical oxygen demand remains quite high. In contrast, a combination of biological and UV/O_3 process for the OMWW treatment seems to be a serious alternative in the reduction of the COD. In particular, biodegradation of UV/O_3 pre-treated OMWW found to have the highest removal levels; the percent of COD removal reaches about 91% (Lafi et al.,2009).

3.4 Studies About TiO_2 Supported on Activated Carbon Catalysts

In 2005, Carpio et al. studied Photocatalytic degradation of phenol using TiO_2 nanocrystals supported on activated carbon. Titanium oxide was deposited on activated carbon (AC) in two forms, as powder and as a pellet. This oxide was obtained using sol–gel process based on titanium isopropoxide and isopropyl alcohol. Nanocrystalline TiO_2 anatase phase on activated carbon was obtained using an adequate thermal treatment of 325 ◦C for 5 h considering the thermal instability of the AC. Activity measurements performed under UV lamp and solar irradiation have shown good results for the photo degradation of phenol in aqueous solution. For solar applications, a polyethylene terephthalate bottle containing the photocatalyst was filled up with the contaminated water and placed a few hours under the solar radiation for a couple of sunny days. The results indicate that 20 ppm of phenol can be removed by using this method. They concluded that, the TiO_2/AC pellet and TiO_2/AC powder have good photocatalytic performance (Carpio et al.,2005).

In 2010, Gu et al. perfomed a study on “Photocatalytic degradation of 2, 4 dichlorophenol using granular activated carbon supported TiO_2”. Catalyst was prepared by using sol-gel method. They found that dichlorophenol removal increases with the increase of Ti–Activated Carbon, its removal decreases with the increase of initial dichlorophenol concentration (Gu et al., 2010).

The summary of the studies in the literature is given in Table3.1.

Table3. 1 Summary of literature survey

TARGET COMPOUND	METHOD/CATALYST	RESULT	REFERENCE
• Purified olive oil wastewater(alpechin)	Biotransformation Method	The bacterium had most effect in reducing the phenol content of alpechin at concentrations of between 40 and 100% . It was also observed that at concentrations of 80%, new phenolic compound were generated.	Ramos-Cormenzana et al., 1996
• The original olive mill wastewaters	Aerobical degradation in batch reactor	Overall COD reduction (80%)	Benitez et al., 1997
• The original olive mill wastewaters	Anaerobic degradation in batch reactor	COD removal (80%)	Ammary, 2004

Table 3.1 (Continued)

TARGET COMPOUND	METHOD/CATALYST	RESULT	REFERENCE
• The original olive mill wastewaters (OMWW)s + domestic wastewater (DW)	Single-Chamber Microbial Fuel cell	• MFCs fed with DW + OMWW gave 0.38 V. • The process allowed a total reduction of TCOD and BOD_5 of 60% and 69%, respectively.	Sciarria et al.,2013
• The original olive mill wastewater(OMWW)	Adsorption/ Different activations methods and carbonization and activation time Activated Carbons	• Maximum adsorption for each system follows the order; • ACOP <ACO<CAOB<ACOP2< ACO2 < ACOUr	Galiatsatou et al.,2002
• The original olive mill wastewater(OMWW)	Adsorption/ Activated Carbon	The maximum removal of phenols is about 94%, while it reaches about 83% for organic matter.	(Azzam et al.,2004).

Table 3.1 (Continued)

TARGET COMPOUND	METHOD/CATALYST	RESULT	REFERENCE
• *p*-coumaric acid	Catalytic wet air oxidation/ Pt and Ru supported catalysts (TiO_2/ZrO_2)	Maximum TOC reduction was found 28% by 3%Ru/ZrO_2 Mel Catalyst. This results can explain also hydroxyl radicals generation as by-products.	Minh et al.,2006
• The original olive mill wastewater(OMWW)	Advanced oxidation methods	TOC around 30% remains at the end of the process. The different behaviour observed can be explained taking into account that besides hydroxyl radicals generation.	Cañizares et al.,2007
• The original olive mill wastewater(OMWW)	Combining UF and UV/H_2O_2 techniques	• After UF COD decrease (about 94%) • After UV/H_20_2 process in batch mode 80% of the TOC was reduced after 40 min. • After UV/H_20_2 process in continuous mode TOC removal obtained with an exposure time of 35min was about 56%.	Drouiche et al.,2004

Table 3.1 (Continued)

TARGET COMPOUND	METHOD/CATALYST	RESULT	REFERENCE
- The original olive mill wastewater(OMWW)	Electro-Fenton reaction followed by an anaerobic biotreatment	- The electro-Fenton process removed 65.8% of the total polyphenolic compounds - Toxicity decreased from 100% to 66.9% with anaerobic digestion	Khoufi et al.,2006
- The original olive mill wastewater(OMWW)	Combined advanced oxidation and biodegradation	COD removal (91%)	Lafi et al.,2009
- Phenol	Photocatalytic degradation with TiO_2 nanocrystals supported on activated carbon	20 ppm of phenol can be removed by using this method.	Carpio et al.,2005
- 2,4-dichlorophenol	Photocatalytic degradation with granular activated carbon supported TiO_2	Dichlorophenol removal increases with the increase of Ti–Activated Carbon.	Gu et al., 2010

4.0 FOREWORD TO STUDY

In the worldwide, many industries recently deal with huge water supply and water purification problems. These Industrial wastewaters contain organic and inorganic pollutants even being highly dangerous both for humans and environment, cannot be treated efficiently yet and remain as threat. Olive oil mill wastewater is one of them and its treatment has been a great challenge for scientists Drouiche et al,2004).

The environmental impact of olive mill wastewater (OMWW) pollution is a public concern. OMWW contains high levels of phenols, organic compounds, chemical oxygen demand (COD), biological oxygen demand (BOD), microorganisms, nutrients, and toxic compounds (Minh et al.,2006).

Recent advances in research areas focusing on the treatment of olive oil waste water have been reviewed. This review revealed that there are very few studies about treatment of OMWW by chemical and biological treatment and also researchers focused on OMWW by-products

The conclusions extracted from literature review assisted and guided in developing the outline of the study. Main reasons for selection of pollutants, methods and catalysts according to these conclusions are explained in detail below.

4.1 The Choice of Pollutants

Olive oil manufacturing is an important industry and economic activity of many countries particularly throughout the Mediterranean Sea. However, olive oil extraction is one of the most pollution intensive food-processing industry. It involves a high consumption of water and large volumes of strongly polluted astewaters known as olive mill wastewater (OMWW) are generated.

OMWW is characterized by a very high Chemical Oxygen Demand (COD up to 200 g l^{-1}), a high content in phenol-like substances (in the range 1–5 g l^{-1} measured as phenol) and acidity. Treatment of OMWW is very hard by using classical biological treatment because of its highly phytotoxicity and strong antimicrobial properties. Most physical and physicochemical methods, such as precipitation, flocculation/clarification, coagulation, filtration, evaporation in open ponds give only partial solution to the problem. Reverse osmosis or ultrafiltration are usually costly. Anaerobic biological digestion with production of biogas is increasingly being used, but is not yet completely satisfactory (Minh et al.,2006).

On the other hand, OMWW include hydroxyl compounds and during the reaction, opening of aromatic ring and further oxidation of intermediates can happen in any of phenolic acidic intermediates formed. These organic intermediates can form in each other.

The pH of OMWWs is in the range 4.9-5.3 due to the presence of organic acids such as acetic, malic, fumaric, lactic, malonic, citric, tartaric, ossalic and succinic. In additionly, succinic acid, fumaric acid and maleic acid were investigated as cocrysal (Childs et al.,2004).

Since the studies were missing in literature about application of combined hybrid system of model cocrystal low pH pollutants succinc acid and fumaric acid of olive oil wastewater in detail and there are many open ends in this field, it has been selected as the thesis topic.

4.2 Choice of Method and Catalyst

4.2.1 The Choice of Chemical and Biological Treatment System

Treatment and disposal of olive oil mill waste water(OMWW) is really problematic issue because of its ingredients as organic acids and phenolic compounds. Many problems concerning the high toxicity and inhibition of biodegradation of these effluents were encountered during anaerobic treatments, because some bacteria, such as methanogens, were particularly sensitive to the organic contaminants present. The phenolic compounds severely limit the possibility of using anaerobic digestion. Therefore, the elimination of phenolic compounds from OMWW was considered as an important objective in order to reduce its toxicity and to permit the occurrence of microbial fermentation (Khoufi et al.,2006).

For this reason, only, biological treatment activity is not effectively treatment system because of low pH and biotoxicity problem. Researchers focused on improving novel systems which include chemical pre-treatment to remove the toxic compounds of OMWW before biological treatment activity.

AOPs namely, catalytic wet air oxidation and Photo Fenton-like catalytic oxidation were chosen to be applied. The reason of selecting these methods is they have wide application in recent studies due to some advantages they provide such as easy application for Fenton-like oxidation, using non-toxic chemicals for catalytic wet air oxidation and being effective on highly recalcitrant organic compounds for photocatalytic oxidation.

In recent years, Microbial fuel cell has been new researchers' focus point as biological treatment method. Electrical power generation and water treatment in the same time is very advantages point. Therefore, more effective, ecofriendly, and economical methods were planned to be developed for the treatment of wastewater with this study by using microbial fuel cell for second treatment system. Furthermore, the application of microbial fuel cell was used as previous application trial on fumaric acid degradation. After that advanced oxidation techniques and new biological methods were thought to be stimulated for the treatment of succinic acid as hybrid system

4.3 The Choice of Catalyst

Recent studies focused on using heterogeneous catalysis since it eliminates many drawbacks of homogeneous catalysis such as metal leaching and generation of secondary waste (Ramirez et al., 2007). Activated carbon (AC) has been widely used as catalyst support in many studies due to the several advantages it provides (Liu et al., 2010). Walnut shells as an organic precursor were being used for this study as agricultural wastes that have almost no industrial use and easy to find especially in Turkey. This study aimed both reuse of an organic waste and to develop and eco-friendly catalyst for environmental applications.

5.0 EXPERIMENTAL STUDY

The experimental study has been carried out for selected model target compounds to represent organic pollutant as succinic acid and fumaric acid by a hybrid system consisting of chemical and biological oxidation. The study was performed in two main groups:

- Pre-study for Fumaric Acid Degradation by Microbial Fuel Cell
- Succinic Acid Degradation by Hybrid System
  - Catalyst Preparation
  - Advanced Oxidation Experiments
    - Catalytic Wet Air Oxidation
    - Photo Fenton-like Catalytic Oxidation
  - Hybrid System Experiments with Microbial Fuel Cell

In catalyst preparation for chemical oxidation, Co doped ZrO_2 (Co/ZrO_2), Bi doped ZrO_2 (Bi/ZrO_2), Co and Bi doped together ZrO_2 (Co-Bi/ZrO_2) and Fe-TiO_2 doped activated carbon (Fe-TiO_2/AC) catalysts were prepared.

In catalyst screening experiments for chemical oxidation, all catalysts Co/ZrO_2, Bi/ZrO_2, Co-Bi/ZrO_2, Fe-TiO_2/AC prepared were tested in terms of degradation for model pollutant as succinic acid by different advanced oxidation methods.

In parametric study experiments for chemical oxidation, the selected catalysts from catalyst screening experiments were used to determine the suitable operating conditions of hybrid system's first step for target compound.

The hybrid system experiments were started with the optimum conditions determined by chemical oxidation as first step. Thus, the performance of Microbial Fuel Cell and of hybrid system were investigated.

The schematic representation of the Hybrid System Steps and experimental Steps are given in Figure 5.1 and Figure 5.2.

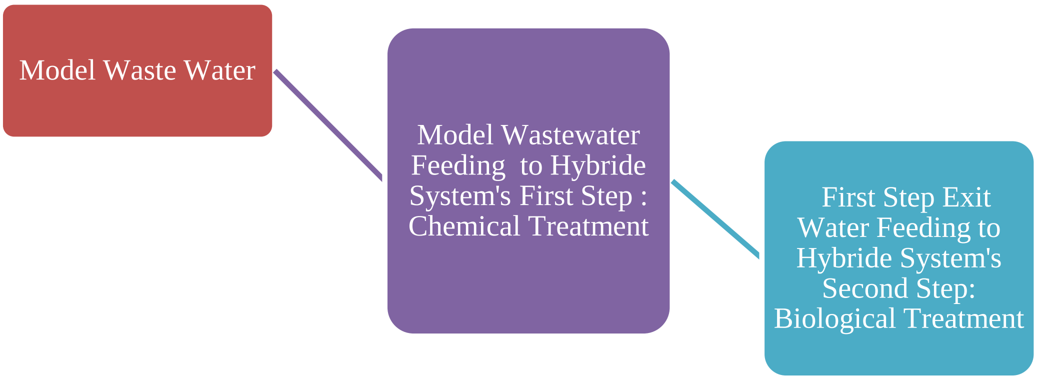


Figure5.1 The schematic representation of the Hybrid System

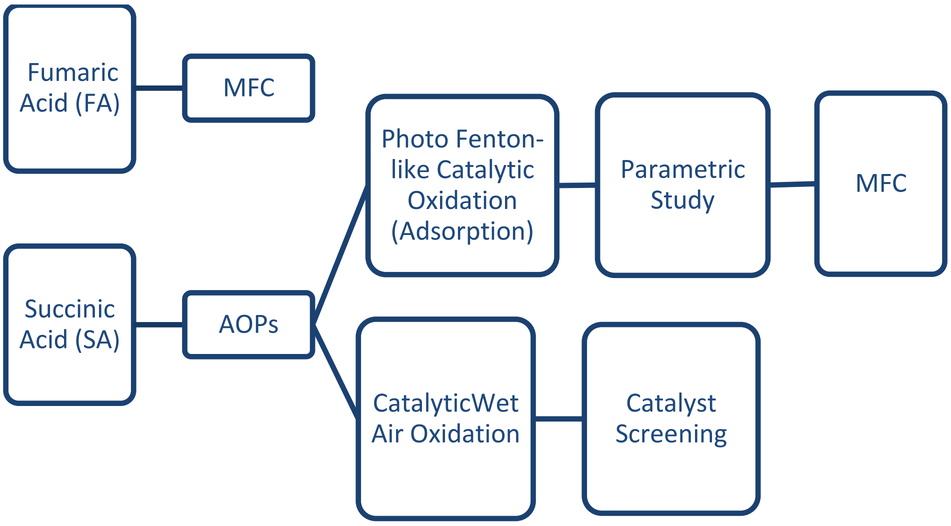


Figure5. 2 The schematic representation of the Hybrid System experimental steps

5.1 Pre-Study for Fumaric Acid Degradation by Microbial Fuel Cell

Pre- study of Microbial Fuel Cell had been start in Rome, Italy with cooperation of La Sapienza Di Roma University. For this purpose, target compound Fumaric Acid (trans-butene diacid) was chosen as organic pollutants and Microbial Fuel Cell method was tested.

H-type MFC system was used to perform all tests. Anodic and catodic chambers were in pyrex glass with a volume of 300 ml. Both chambers were provided by carbon paper electrode (Goodfellow Cambridge Limited, LS366112 SJP Carbon Foil) connected by a titanium wire closed with a resistor (see Table 5.1). Ultex-CMI 7000 was used as Protonic Exchange Membrane.

A reference electrode (Crison Ag/AgCl) was used in anodic chamber to monitor the potential. The cells were closed by a clamp; microaerobic condition was created in anodic chamber while catodic chamber was continuously aerated by an air diffuser to improve reduction reactions.

5.1.2 Experiments

Different amount of the organic compound was used to prepare synthetic wastewaters solutions characterized by Total Organic Carbon content in the range of 670-680 mg/L. Buffer phosphate solution (50 mM) (Kim et al., 2007) was used to prepare anodic and catodic solution: sodium acetate and fumaric acid were added in anodic solution. All synthetic solutions prepared are shown in Table 5.1.

Anaerobic digestion supernatant was used as bacterial source: it was filtered (filter 0,45 µm) and added to synthetic solution.

Table5. 1 Synthetic solutions and operating conditions used.

Run	Sodium Acetate (% v/v)	Fumaric Acid (% v/v)	Starting Total Organic Carbon [mg/L]	External resistance [Ω]
1	100	-	680,5	203,4
2	50	50	682,5	203,4
3	-	100	669	203,4

TOC, fumaric acid degradation, pH and OCV were monitored in Run 1, Run 2 and Run 3 in order to evaluate MFCs performances in synthetic wastewaters treatment.

Chemical properties were daily monitored: Organic carbon (Total Organic Carbon analyzer TOC-L Shimadzu) and pH (Crison GLP21). Fumaric acid degradation was evaluated through UV spectroscopy in a wavelength range of 190-310 nm and absorbance measured at 204 nm (T80+ UV/VIS Spectrometer PG Instruments Ltd). Open Cicuit Voltage (OCV) was recorded using multi-meter (FLUKE 87); all electrochemical properties were evaluated by a saturated Ag/AgCl electrode

5.2 Study for Succinic Acid Degradation by Hybrid System

5.2.1 Catalyst Preparation

Co/ZrO_2, Bi/ZrO_2, Co-Bi/ZrO_2 and Fe-TiO_2/Activated Carbon catalysts were prepared and their catalytic performances were tried in advanced oxidation processes including catalytic wet air oxidation and photo-Fenton-like oxidation.

Firstly, Co/ZrO_2, Bi/ZrO_2, Co-Bi/ZrO_2 catalysts were prepared and on ZrO_2 that was used as a catalyst support synthesized by sol-gel method.

Secondly, activated carbon were prepared from walnut shells by chemical activation method and used as a catalyst support. Fe-TiO_2/AC photocatalysts were prepared by Sol-gel method. The preparation of the catalysts was carried out in two steps. In the first step, the production of activated carbon was accomplished and in the second step, the Fe/TiO_2were doped to the prepared activated carbon.

5.2.1.1 Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts preparation

The Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts were prepared according to different amount of Bi and Co by wt.

Table5. 2 The prepared catalysts

10% (by wt.)	5%+5% (by wt.)
Co/ZrO_2	**$Co+Bi/ ZrO_2$**
Bi/ZrO_2	

Different amount of supported of cobalt and bismuth based on zirconium catalysts were prepared by using Sol-gel method. The catalyst preparation steps are the same for all catalysts, only first step of solvent can change according to cobalt and bismuth solubility:

- Dissolving the desired amount of $Co(NO_3)_2.6H_2O$ in water or dissolving the desired amount of $BiN_3O_9.5H_2O$ in methanol
- Addition of desired amount of ZrO_2
- Sonication of the mixture
- Evaporation of the water in mixture under vigorous stirring at 80 °C
- The solid calcination at 700°C for 3 h in ash oven

All the preparation procedures are modified according to literature and explained in detail, in Figure 5.3 (Rohr et al., 2000, Tichit et al., 1996, Ward and Ko,1995).

5.2.1.2 $Fe\text{-}TiO_2$/Activated Carbon catalyst preparation

For the purpose of preparing $Fe\text{-}TiO_2$/AC catalyst, activated carbon was prepared from walnut shells by chemical activation methods and used as a catalyst support firstly. $Fe\text{-}TiO_2$/AC photocatalyst was prepared by Sol-gel method.

Preparation of the catalyst was carried out in two steps. In the first step, the production of activated carbon was accomplished and in the second step, Fe/TiO_2 was doped to the prepared activated carbon.

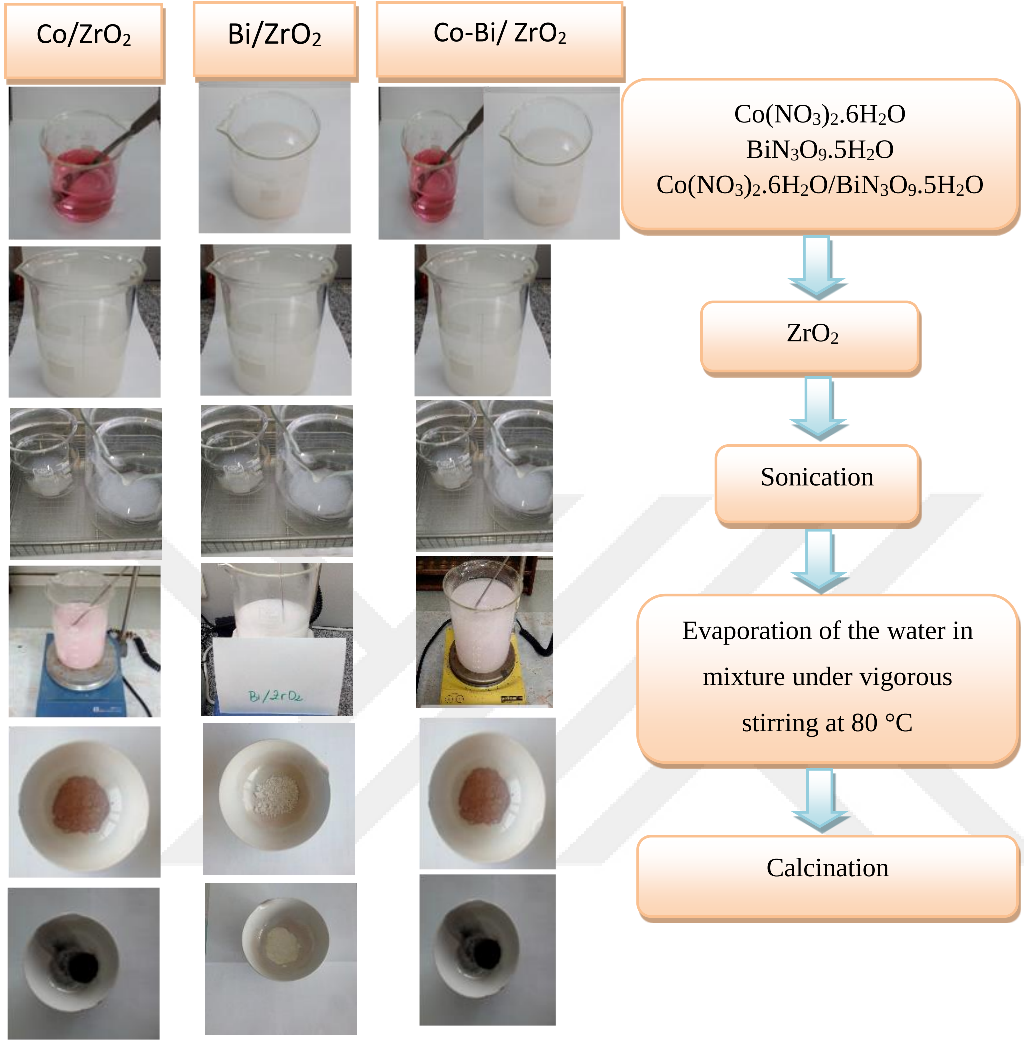


Figure5. 3 Catalyst preparation steps for Co/ZrO$_2$, Bi/ZrO$_2$, Co-Bi/ZrO$_2$ catalysts

Activated carbon preparation:

The production of activated carbon involves two main steps: the pre-treatment and carbonization-activation. Pre-treated walnut shells were activated by chemical activation method using chemical reagents ZnCl$_2$ (neutral) activation.

All the preparation procedures are explained in detail, below and also shown in Figure 5.4 (Choi et al., 2012, Kalderis et al., 2008, Nowicki et al., 2010, Rambabu et al., 2013, Rey et al., 2011).

Pre-treatment:

The walnut shells were obtained from a local Turkish bazaar. In pre-treatment step, walnut shells were first crushed into smaller particles and ground to increase surface area. Then they were washed with distilled water to remove impurities and dried at 110^{o}C for 6 h to remove moisture.

Carbonization-activation:

For physical activation method, the pre-treated walnut shells were carbonized at 400°C for 2 hours under N_2 flow. Then the carbonized shells were activated at 800°C for 2 hours under CO_2 flow.

For neutral activation methods, the pre-treated walnut shells were impregnated with $ZnCl_2$ for a weight ratio of 1:1 (walnut shells (WS): $ZnCl_2$). Then impregnated walnut shells were carbonized and activated at 800^{o}C for 3 hours under N_2 flow separately.

The activated carbons obtained by different activation methods except for neutral activation were washed with 1 M HCl to remove inorganic impurities and then washed with distilled water for neutralization. The activated carbon obtained by neutral activation was only washed with distilled water for neutralization because of the previous acid treatment which had already completed the removal of inorganic impurities.

Metal doping:

The Fe-TiO_2/AC catalyst was prepared by doping Fe-TiO_2 by using impregnation or Sol-gel methods, respectively. The procedures applied for all activated carbons obtained by all activation methods are given in detail below.

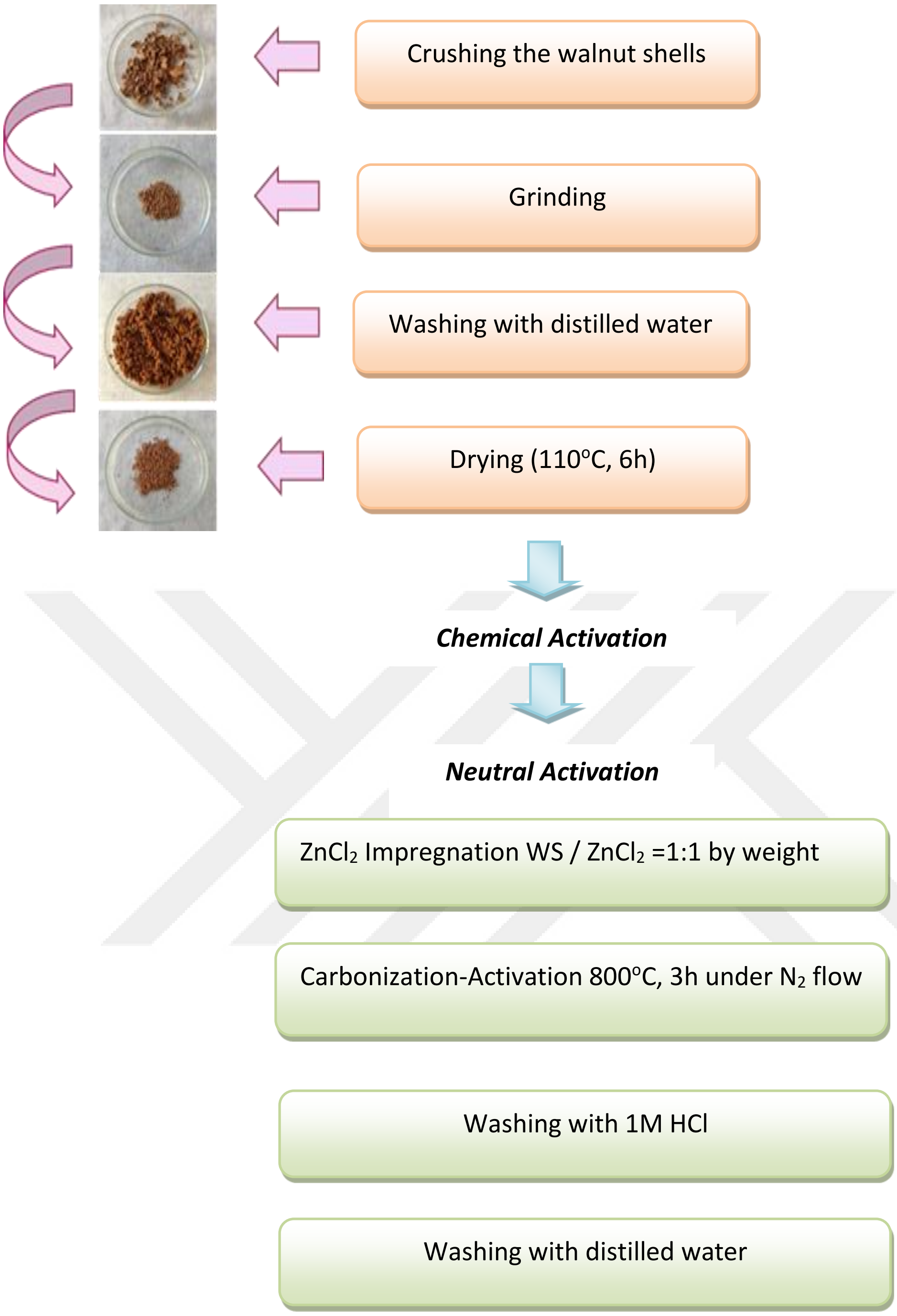


Figure5. 4 Schematic representation of activated carbon preparation

Fe-TiO_2/AC photocatalyst preparation:

The catalyst used in photocatalytic experiments so called as photocatalyst and consisted of trace amount of iron containing titanium dioxide supported on activated carbons prepared by different activation methods. Fe ions were used for improving the photocatalytic activity of TiO_2 which has been proven in previous studies (Banic et al., 2011, Teh et al., 2011).

The photocatalyst (Fe-TiO_2/AC) was prepared by sol-gel method which is widely used in many studies. It is a convenient low temperature method for preparation of homogeneous materials, especially inorganic materials which provides great homogeneous structure in atomic level (Asiltürk and Şener, 2012, Huang et al., 2011, Tang et al., 2011).

Preparation of the catalyst was performed in two steps. First, Fe-TiO_2 sol (1% Fe, w/w) was prepared which included the use of Fe $(NO_3)_3.9H_2O$ and $Ti(OBu)_4$ as metal precursors. Then, prepared Fe-TiO_2 sol was mixed with activated carbon at a weight ratio of 1:10 (Fe-TiO_2: photocatalyst). The mixture was kept under stirring until homogeneous mixture was observed. Photocatalytic oxidation parameters are shown in Figure 5.5.

The photocatalyst was prepared by following procedure:

Fe-TiO_2 Sol preparation

- $Ti(OBu)_4$ and $Fe(NO_3)_3.9H_2O$ were dissolved in methanol and mixed.
- pH of the mixture was adjusted with NaOH solution for neutral pH (pH=7) and Fe-TiO_2 sol was obtained.

Fe-TiO_2/AC preparation

- The desired amount of activated carbon is then added to the Fe-TiO_2 sol.
- Fe-TiO_2 Sol and activated carbon mixture was kept under stirring until homogeneous mixture was observed.
- Fe-TiO_2 Sol coated activated carbon was kept at room temperature for gelation.
- The catalyst in gel form is vacuum dried to remove methanol and butyl content.
- The obtained particles are treated at 500°C for 2 h under N_2 flow for calcination.

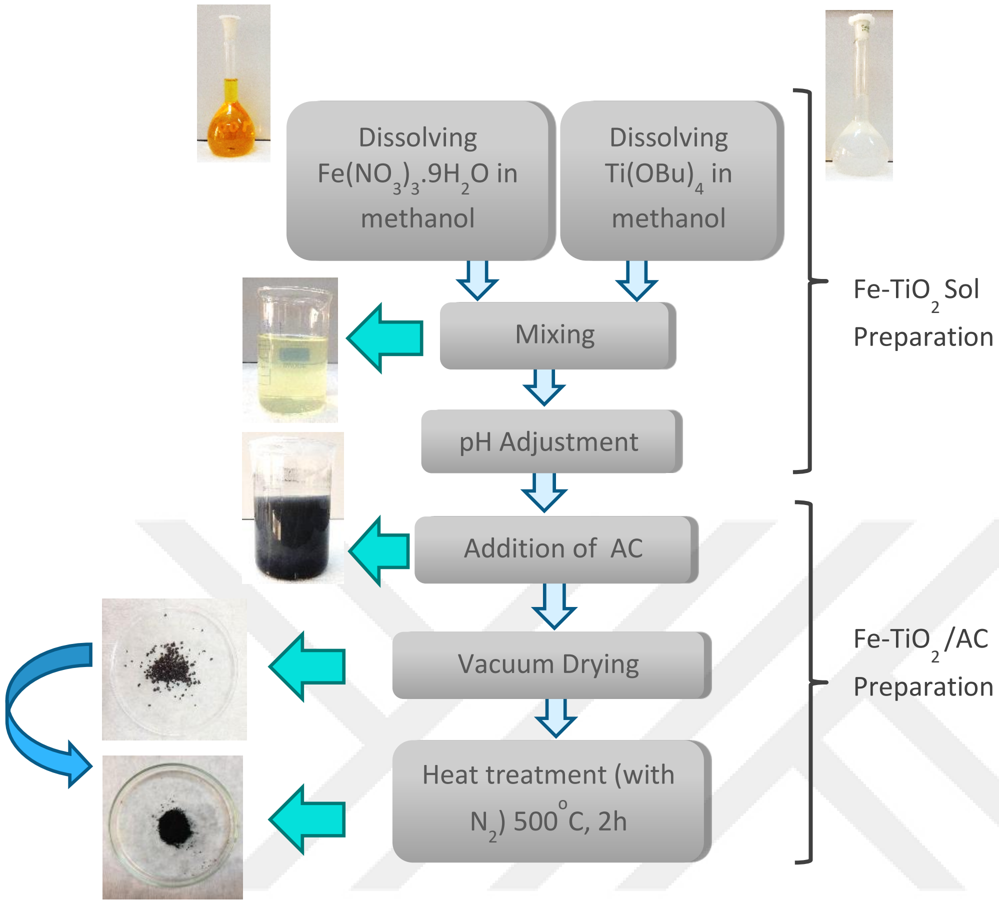


Figure5. 5 Schematic representation of Fe-TiO_2/AC preparation

5.2.2 Experimental Setups

In this study, three experimental setups were used.

5.2.2.1 Catalytic wet air oxidation setup

- The experiments were carried out by using a high pressure stirred lab autoclave reactor system shown in Figure 5.6.
- The reactor has 450 mL of capacity and the maximum allowable operating pressure and temperature are 100 bar and 500°C, respectively.
- The temperature is controlled by a PID controller. The mixing is maintained by a 100-1450 rpm turbine type mixer with 4 blades.

Figure5. 6 The high pressure stirred lab autoclave reactor system

5.2.2.2 Photo-Fenton like oxidation setup

- The photocatalytic oxidation experiments were carried out in glass beakers using temperature controlled magnetic stirrers.
- 100 Watt of a visible light source lamp or two 6 Watt of UV light source were placed above the reaction mixture.

Figure5. 7 The picture of experimental setup for photocatalytic oxidation

5.2.2.3 Microbial Fuel Cell setup

- H-type Microbial Fuel Cell system with glass anodic and cathodic chambers, which was similar to the experimental system that was used in La Sapienza University, was used.
- Both chambers were provided by carbon paper electrode connected by a copper wire closed with a resistor.
- Ultrex- CMI 7000 was used as Protonic Exchange Membrane.
- A reference electrode (Ag/AgCl) was used in anodic chamber to monitor the potential.
- The cells were closed by a clamp; microaerobic condition was created in anodic chamber while cathodic chamber was continuously aerated by an air diffuser to improve reduction reactions. The Microbial Fuel Cell system is illustrated in Figure 5.8.

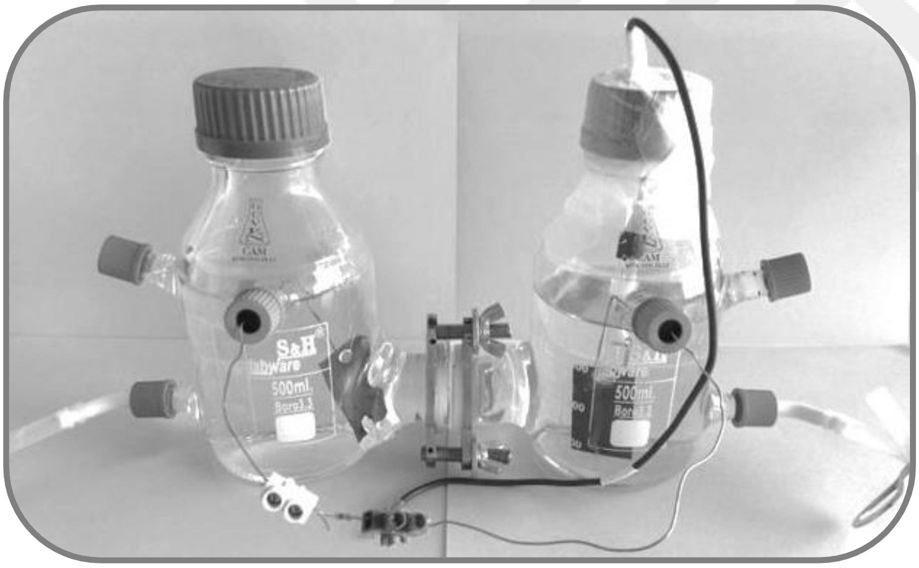


Figure5. 8 Microbial Fuel Cell set-up

For the potential measurements a Crison 52 40 electrode was used, Ag / AgCl type. This is a silver filament coated with a layer of silver chloride, immersed in an electrolyte solution (CRISOLYT, made up of KCl at 3M concentration) and saturated with AgCl. The interior of the window is separated from the outside through a diaphragm, which must be kept immersed during the measurements. In the unused phase it is to be placed in an electrolyte filled housing.

The electrode generates a constant potential, with respect to which is calculated the amount of graphite electrode in the cell through a potential measurer. This value depends: at 20 ° C, it is 0,208 V, at 25 ° C it is 0,205 V.

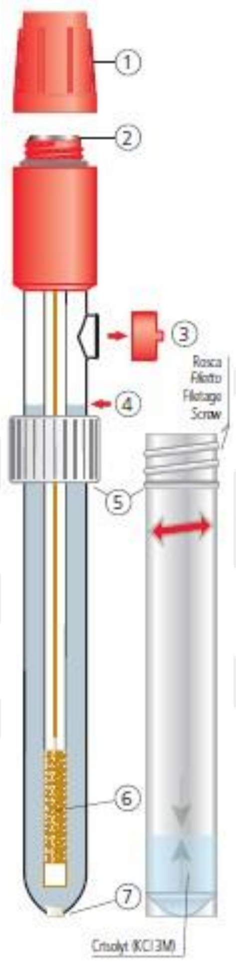


Figure5. 9 Reference electrode

The electrodes used are derived from graphite sheets on pre-compressed paper. The electrodes, prior to cell installation, undergo pre-treatment: immersion for 30 minutes in pure ethanol, and then for 60 minutes in 1M HCl solution. They were secured to the copper wire used for the external circuit via a screw, and are closed on a 220.3 Ω resistor.

The ULTREX CMI-Cation exchange membrane was used (Membranes International, USA). Starting from the membrane sheet, disks of the same diameter as the cell link were cut out. Prior to commissioning, these were pre-treated by immersion in a 5% NaCl solution for 12 h, maintaining the temperature at about 40 ° C in order to expand the pores of the membrane and make it operative.

5.2.3 Experimental Procedures

5.2.3.1 Catalytic wet air oxidation experimental procedure

For a typical run the following procedure is as follows:

- Synthetic aqueous target compound solution with 250 mg/L carbon content were prepared with distilled water as 350 ml in a flask.
- Catalyst was added to the wastewater and a sample as an initial sample was taken.
- The prepared wastewater was charged to the reactor.
- The reaction temperature and pressure were set to the desired values.
- Experiment was ended at 120 min and the heater was turned off.
- The reactor was allowed to cool and the final sample was taken. pH and the volume of the reaction medium were measured.
- Samples were diluted with 1:10 ratio of distilled water.
- The samples were analyzed by using HPLC and TOC analyzers.

5.2.3.2 Photo-Fenton like oxidation experimental procedures

For a typical run the following procedure is as follows:

- Synthetic aqueous target compound solution with an initial concentration of 250 mg/L was prepared with distilled water as 350 mL in flask.
- Catalyst was added to the wastewater and a sample initially was taken.
- The prepared wastewater was charged to the reactor.
- The UV lamp was turned on.
- During the experiments, samples from reaction medium were taken at 0,15, 30, 60, 90 and 120 minutes.
- Experiment was ended at 120 min and the UV lamp is turned off.
- Samples were diluted 1:10 ratio of distilled water
- The samples were analysed by using HPLC and TOC Analyzers.

5.2.3.3 Microbial Fuel Cell experimental procedure (Ege University)

For a typical run the following procedure is as follows:

- The solution treated by advanced oxidation system was used in Microbial Fuel Cell as 350 ml for each cell.
- 1 ml animal manure was added to anodic cell as organic source.
- N_2 was added to anodic cell for microorganism's activity
- During the experiments, samples from reaction medium were taken every day for two weeks.
- Samples were diluted 1:10 ratio of distilled water
- The samples were analysed by using HPLC and TOC Analyzers.

5.2.4 Analysis

In this study, degradation of succinic acid concentration was analyzed by using HPLC (Shimadzu LC 20A). The prepared mobile phase has:

- CH_3OH
- 0.1 % H_3PO_4 in H_2O
- A/B = 2/98, v/v
- Flow Rate: 1.0 mL/min Col., Temp. : 30 ℃ Detection: UV 214 nm (GL-7452 PDA Detector) ,Injection Vol.: 20 µL Sample : Standard

Total Organic Carbon (TOC) removal was investigated by using TOC analyzer (Shimadzu TOC-L) and The Chemical Oxygen Demand (COD) removal was analyzed by using WTW Thermoreactor and Merck Nova 400 Spectrophotometer.

The target compound removal efficiency was calculated by the formula given below:

$$x(\%) = \frac{m_0 - m_f}{m_0} \times 100$$

where m_0 and m_f were initial and final weight of target compound, respectively..

5.2.5 Catalyst Screening Experiments

The catalyst screening experiments were performed for succinic acid compound to determine the most efficient catalyst which were used in further parametric studies. For this purpose, catalytic advanced oxidation process was investigated in presence of based different amount of Bi, Co on ZrO_2 types of catalysts and photo-Fenton like catalytic oxidation was investigated in presence of Fe-TiO_2/AC catalyst. In order to see which advanced oxidation system is more suitable for hybrid system with microbial fuel cell and which kind of catalyst more effective within degradation of organic acids as organic pollutants were carried out.

Three types of catalysts including Co/ZrO_2, Bi/ZrO_2 and Bi-Co/ZrO_2 were prepared and their catalytic performances were compared in the catalyst screening experiments for wet air oxidation system. In the Photo Fenton-like method, Fe-TiO_2/AC catalyst was prepared in addition of Co/ZrO_2, and their catalytic performances were compared in the catalyst screening experiments.

5.2.5.1 Catalyst screening for wet air oxidation

In this part of the study, catalytic wet air oxidation performance was investigated. In the catalyst screening for wet air oxidation experiments 0.1 and 1 g/L of catalyst loadings and 100 and 150℃ of reaction temperatures, 10 bar and 20 bar reaction pressure were examined. Experiments were carried out using Co/ZrO_2, Bi/ZrO_2 and Bi-Co/ZrO_2 catalysts for catalytic wet air oxidation of Succinic acid. Eight conditions studied for each catalyst are shown in Table 5.3.

Table5. 3 Catalyst screening experiments for catalytic wet air oxidation.

		Catalyst Loading (g/L)	Pressure (bar)	Temperature (°C)
Catalytic Wet Air Oxidation	Condition 1	0.1	10	100
	Condition 2			150
	Condition 3		20	100
	Condition 4			150
	Condition 5	1	10	100
	Condition 6			150
	Condition 7		20	100
	Condition 8			150

5.2.5.2 Catalyst screening for photo-Fenton like oxidation

Experiments were carried out using Co/ZrO_2 and $Fe\text{-}TiO_2/AC$ catalysts for Photo-Fenton-like catalytic oxidation experiments. For each catalyst the experiments were carried out by using two different temperatures 25°C and 60°C, two different light types, same H_2O_2 concentrations ($[H_2O_2]$) 5 mM and same amount of catalyst 1g/L for the removal of 615 ppm SA. Eight conditions carried out for each catalyst are shown in Table 5.4.

Table5. 4 Catalyst screening experiments for Photo- Fenton-like catalytic oxidation.

		Catalyst (4g/L)	Light Type	Temperature (°C)
Photo-Fenton Like Catalytic Oxidation	Condition 1	Co/ZrO_2	UV Light	25
	Condition 2			60
	Condition 3		Visible Light	25
	Condition 4			60
	Condition 5	$Fe\text{-}TiO_2/AC$	UV Light	25
	Condition 6			60
	Condition 7		Visible Light	25
	Condition 8			60

5.2.6 Parametric Study Experiments

5.2.6.1 Photo-Fenton-like oxidation

The main operating parameters of Photo-Fenton-like oxidation can be considered as Fe-TiO_2/AC catalyst loading, H_2O_2 concentration, temperature and UV light according to reference catalyst loading, H_2O_2 concentration, temperature and UV light. The ranges of these parameters studied for Succinic acid are given in detail in Table 5.5-Table 5.6.

Table5. 5 Effect of parameters on succinic acid degradation

Investigation Goal	**Temperature (°C)**	**UV Light**	**H_2O_2 Concentration (mM)**	**Catalyst Loading g/L**
Effect of Fe-TiO_2/AC Catalyst Loading on succinic acid degradation	25	+	5mM	1
	25	+	5mM	2
	25	+	5mM	3
	25	+	5mM	4

Effect of the presence of Fe-TiO_2/Activated carbon catalyst for first thirty minutes dark period on succinic acid degradation	25	+	5mM	-
Effect of the hydrogen peroxide presence on succinic acid degradation	25	+	-	4
Effect of the synergic effect of UV light irradiation and hydrogen peroxide on succinic acid degradation	25	-	-	4
Effect of the synergic effect of UV light irradiation and Fe-TiO_2/Activated carbon catalyst on succinic acid degradation	25	-	+	-
Reference Experiment Condition	*25*	+	*5mM*	*4*

Table5. 6 Effect of the initial hydrogen peroxide concentration on succinic acid degradation

Investigation Goal	**Temperature (°C)**	**UV Light**	**H_2O_2 Concentration (mM)**	**Catalyst Loading g/L**
Effect of the initial hydrogen peroxide concentration on succinic acid degradation	25	+	-	4
	25	+	2,5 mM	4
	25	+	10 mM	4
Reference for comparing	*25*	+	*5mM*	*4*

5.5.1.2. Microbial Fuel Cell treatment

In Microbial Fuel Cell step for Hybrid System, operation parameters were kept for microbial activity performance stability. These parameters studied for Succinic acid are given in detail in Table 5.7.

Table5. 7 Microbial Fuel Cell treatment of the succinic acid solution previously treated with Fe-TiO_2/Activated carbon catalyst at the determined optimum conditions

Run	**Sodium Acetate (%wt)**	**Anaerobic Digestion Supernatant (ml)**	**pH**	**External Resistant [Ω]**
1	50	1	7.0-8.0	203.4

6.0 RESULTS AND DISCUSSION

6.1. Pre-Study for Fumaric Acid Degradation by Microbial Fuel Cell (Study in Rome/Italy)

6.1.1 Total Organic Carbon Degradation

This work aims to confirm that MFCs can be used for wastewater treatment. The degradation of organic matter was monitored for six days in tests with different fumaric acid and sodium acetate ratios. All runs were performed twice and the validity of results was confirmed. The presence of both compounds (Run 2) increase the organic removal rate and the degree of organic carbon reduction was the highest in six days yet (Figure 6.1).

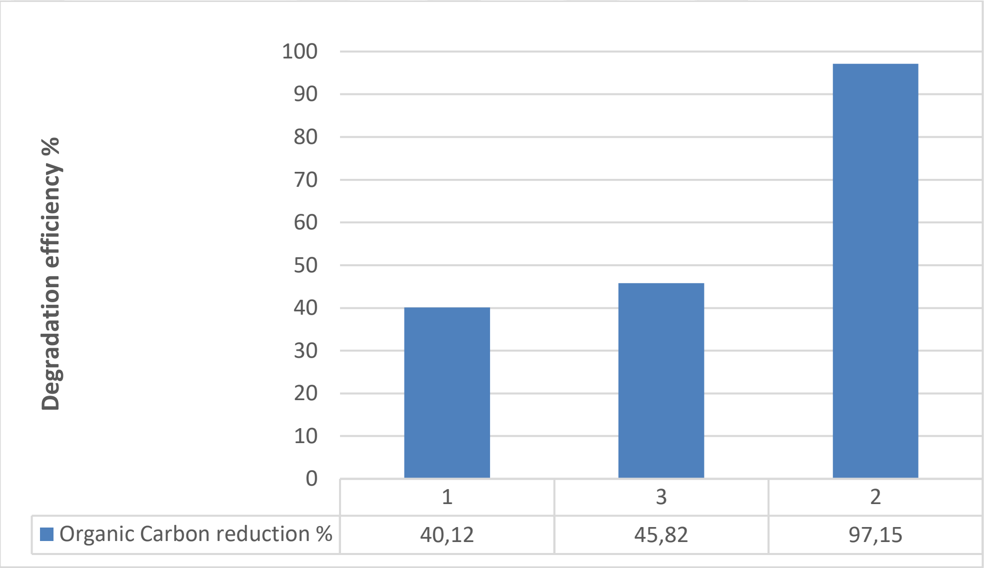


Figure 6. 1 Microbial Fuel Cell experimental results of fumaric acid (FA) concentration degradation reaction conditions: $25^{o}C$ operation temperature, 650 ppm Organic Carbon Content of Succinic Acid for Microbial Fuel Cell starting point

6.1.2 Fumaric Acid Degradation

Spectrophotometric analysis was performed to check the trend of fumaric acid concentration in Run 2 and Run 3. UV spectra reported in figure 6.2 and 6.3, show the decrease of the absorption peak during the test and its definitive disappearance after six days of treatment indicating the complete degradation of fumaric acid. The concentration of fumaric acid was estimated by means of absorbance measure at 204 nm and rate of removal was calculated according to equation 1:

$$\text{FA removal\%} = [(FA_0 - FA_f)/FA_0] *100 \qquad (1)$$

A comparison between removal rates observed in Run 2 and Run 3 was reported in Figure 6.4.

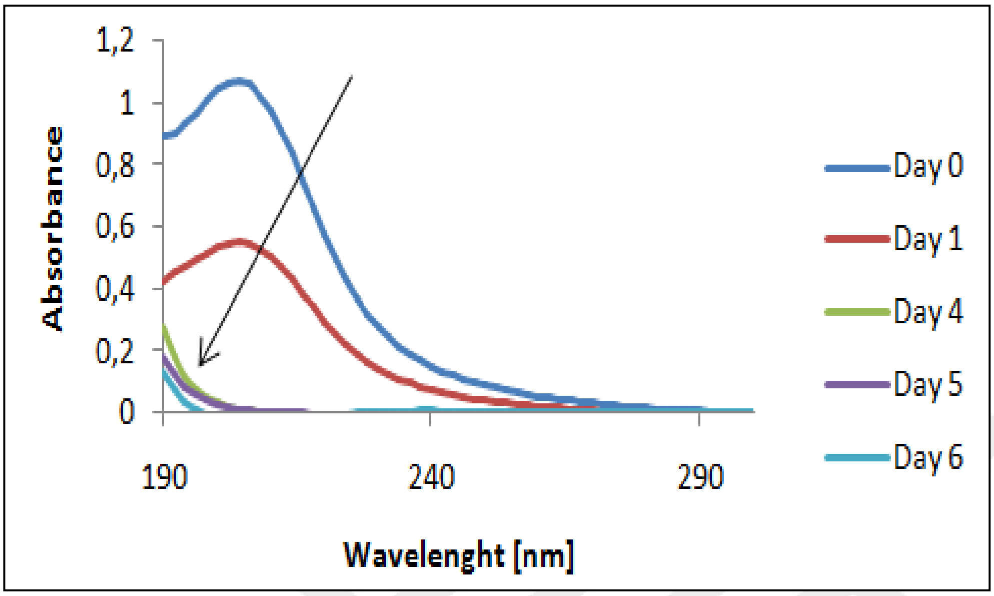


Figure 6. 2 Spectrum of fumaric acid. Daily degradation in Run 2.

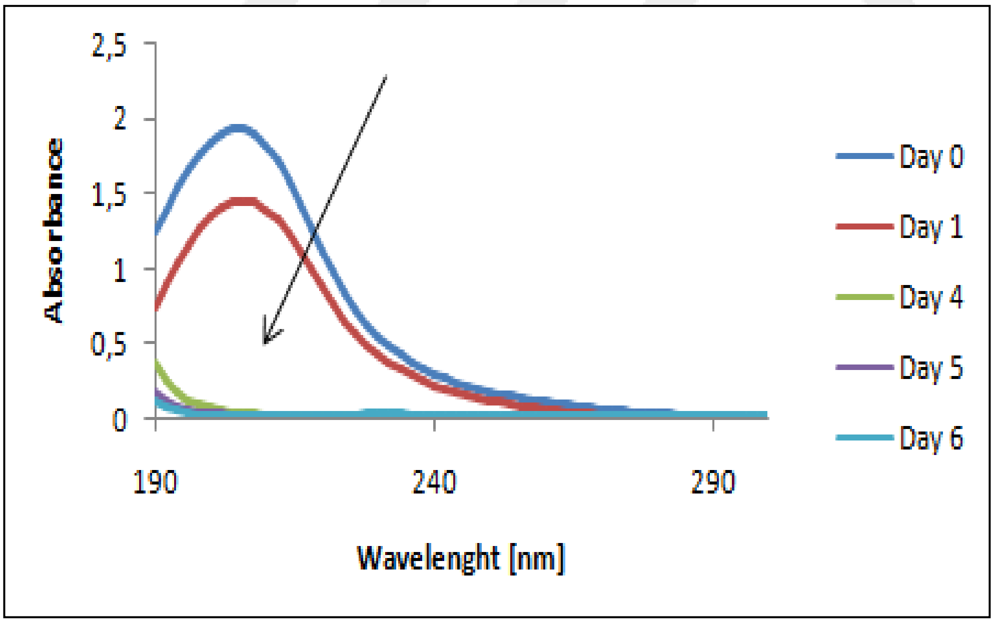


Figure 6. 3 Spectrum of fumaric acid. Daily degradation in Run 3

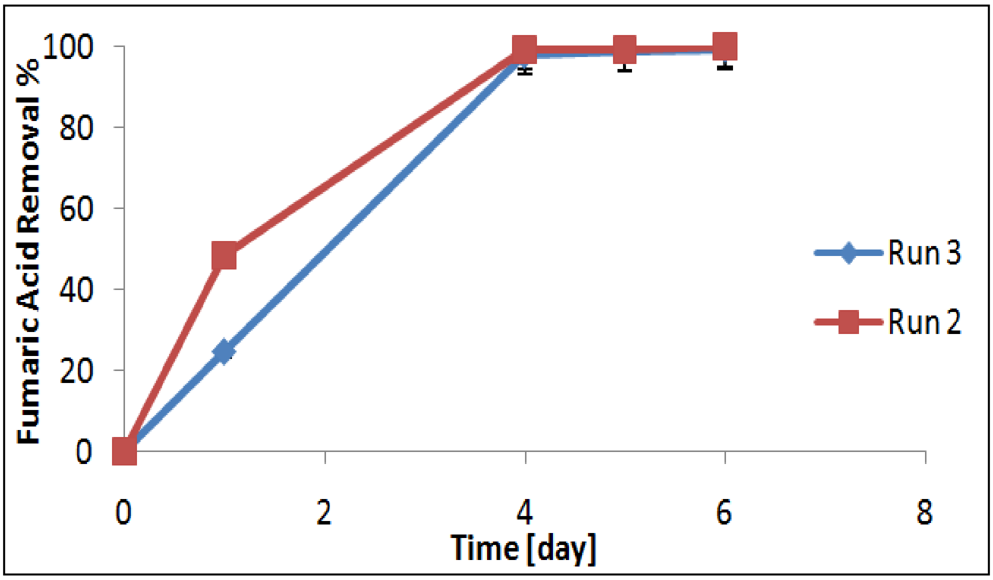


Figure 6. 4 Fumaric acid removal % in Run 2 and Run 3.

6 days were necessary to observe a completely degradation of fumaric acid. This result confirmed that MFCs were good systems to achieve high removal degree of organic matter and fumaric acid was also a good substrate for microorganisms. The presence of fumaric acid and sodium acetate energized microbial activity as suggested by the higher rate of fumaric acid degradation at the beginning of the test in Run 2 (see Figure 6.4).

It was interesting to observe that although complete removal of fumaric acid was achieved after six days in both Run 2 and Run 3 the organic carbon reduction was higher in Run 2. This suggest that in Run 3, where solution only containing fumaric acid was treated, fumaric acid was converted in other substrates following different pathways (Song and Lee, 2006). For this reason, TOC value was high after 6 days.

6.1.3 pH

Trend of pH in Run 1, Run 2 and Run 3 is reported in Figure 6.5. As can be seen neutral condition was ensured during the treatment in all cases. In the previous works in the literature tests performed with glucose ($C_6H_{12}O_6$) as substrate showed a decrease in pH value resulting in inhibition of microorganism activity (Bavasso et al., 2016). We conclude that the buffering capacity of buffer phosphate used in these tests can prevent pH variation only with organic substrate characterized by a low number of hydrogen atoms converted in protons during the treatment such as fumaric acid ($C_4H_4O_4$) and sodium acetate ($C_2H_3NaO_2$).

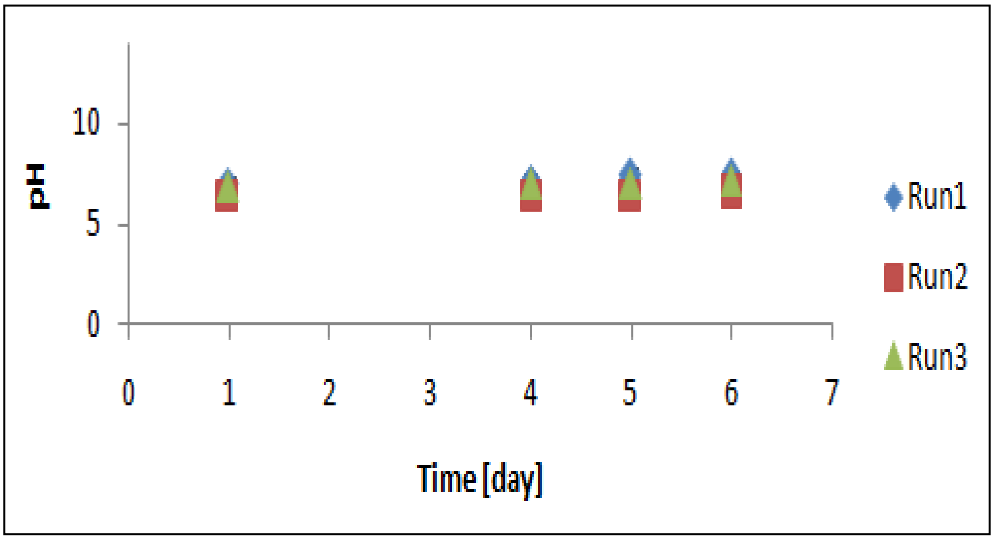


Figure 6. 5 pH trend in Run 1, Run 2 and Run 3.

6.1.4. Electrochemical performances open circuit voltage (OCV)

The open circuit voltage was daily monitored in Run 1, Run 2 and Run 3. Figure 6.6 shows that the composition of synthetic wastewaters does not affect the potential thus indicating that fumaric acid and sodium acetate exhibit the same electron donor capacity and the value of potential only depends on initial TOC value.

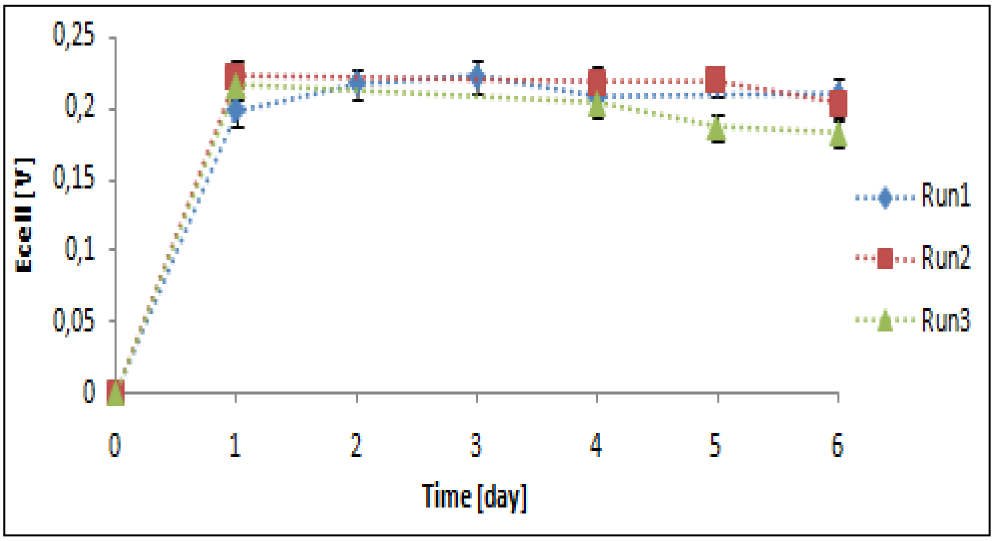


Figure 6. 6 Cells potential evaluated against a saturated Ag/AgCl electrode

6.2. Succinic Acid Degradation by Hybrid Process

6.2.1. Catalytic Wet Air Oxidation

6.2.1.1. Catalyst screening

The experiments were performed as explained in catalyst screening for wet air oxidation. According to the results of experiments degradation of succinic acid was not observed with Bi/ZrO_2 and Bi-Co/ZrO_2 in wet air oxidation system at all conditions.

The results of catalyst screening for the effect of those different catalyst loadings, temperatures, and pressures for Co/ZrO_2 catalyst are shown in Figure6.1 to Figure 6.4.

Increasing the wet air oxidation operation pressure from 10bar to 20bar with keeping catalyst loading and temperature constant (0.1g/L catalyst loading and 100^{o}C) caused to increase of degradation of succinic acid. The highest degradation achieved around 8.21% with high pressure value for Co/ZrO_2 catalyst (Figure 6.7).

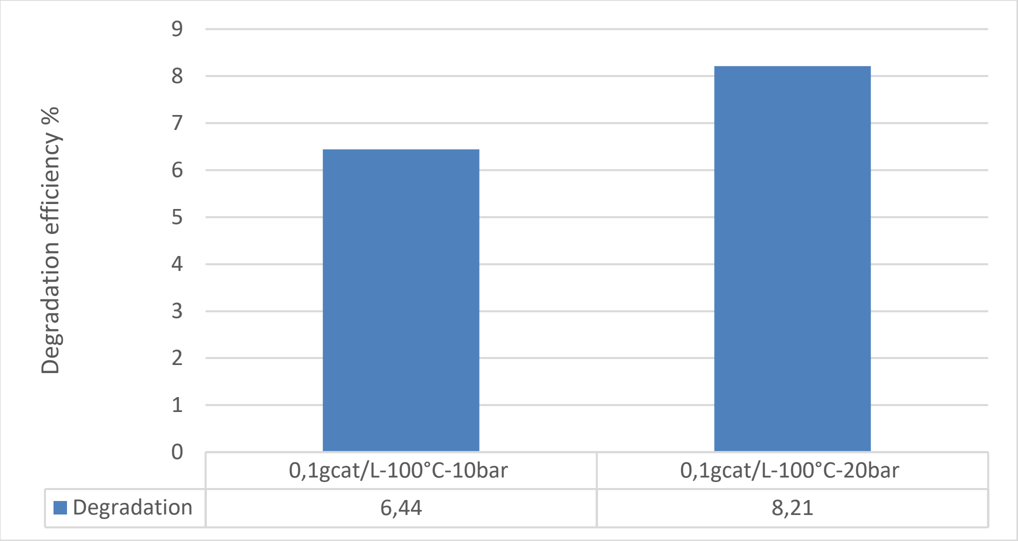


Figure 6. 7 Degradation efficiencies of Co/ZrO_2 catalyst for same amount of catalyst loading and same temperature ([SA]=250 ppm Organic Carbon Based , [Catalyst]=0.1 g/L, T=100^{o}C)

Increasing the wet air oxidation operation temperature from 100 ^{o}C to 150 ^{o}C while keeping constant the catalyst loading (0.1g/L) caused in decrease of degradation of succinic acid. For the experiments carried out 100^o C and 150^{o}C, increasing of degradation of succinic acid was observed when the operation pressure was increased while keeping operation temperature and catalyst loading constant The highest degradation achieved at 150°C was around 6,61 % with high pressure value for Co/ZrO_2 catalyst (Figure 6.8)

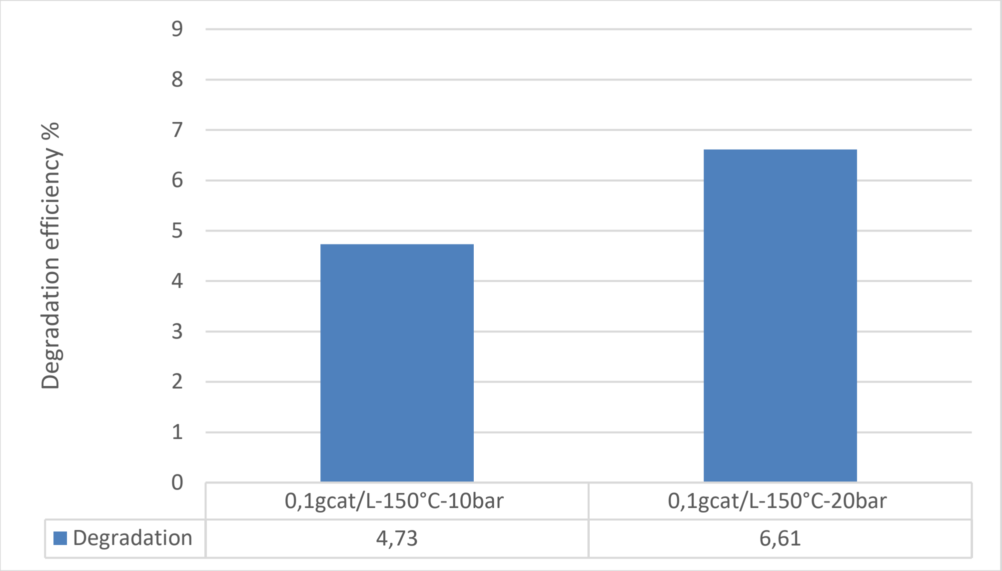


Figure 6. 8 Degradation efficiencies of Co/ZrO_2 catalyst for same amount of catalyst loading and same temperature ([SA]=250 ppm Organic Carbon Based , [Catalyst]=0.1 g/L, T=150°C)

The effect of catalyst loading was also tested by increasing of catalyst loading from 0.1 g/L catalyst to 1g/L catalyst. In this testing, pressure was increased under constant operation temperature and catalyst loading (1g/L catalyst Co/ZrO_2 and 100°C). The result showed that increasing of operation pressure affected positively succinic acid degradation efficiency (Figure 6.9).

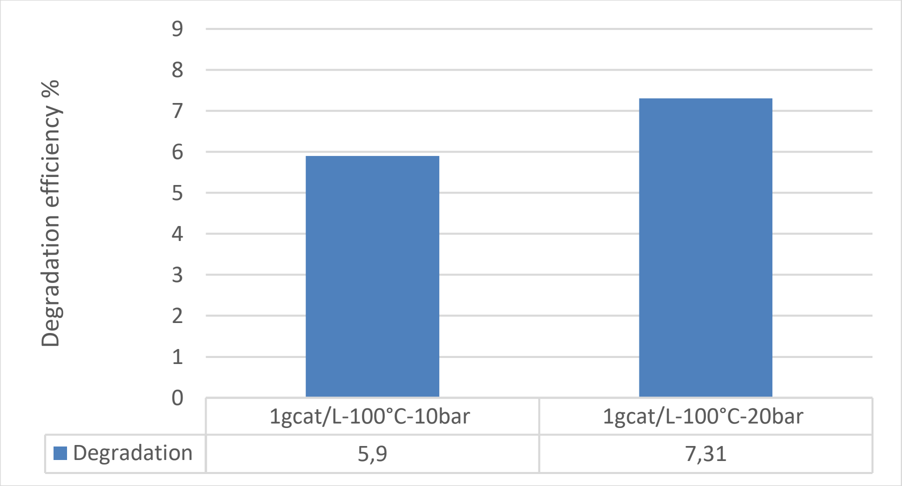


Figure 6. 9 Degradation efficiencies of Co/ZrO_2 catalyst for same amount of catalyst loading and same temperature ([SA]=250 ppm Organic Carbon Based, [Catalyst]=1 g/L, T=100°C)

Wet air oxidation temperature from 100°C to 150°C was increased and kept constant for operation condition. At the same time pressure was increased under constant operation temperature and catalyst loading (1g/L catalyst Co/ZrO_2 and 150°C). The results showed that increasing of operation pressure affected positively succinic acid degradation efficiency (Figure 6.10).

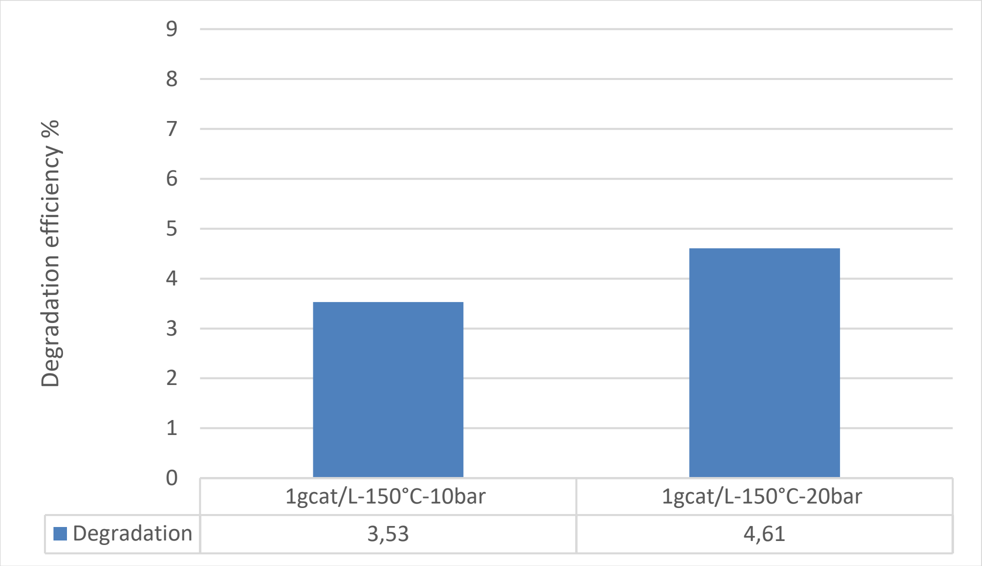


Figure 6. 10 Degradation efficiencies of Co/ZrO_2 catalyst for same amount of catalyst loading and same temperature ([SA]=250 ppm Organic Carbon Based , [Catalyst]=1 g/L, T=150°C)

In the experiments of wet air oxidation catalyst screening showed that the highest degradation was obtained by 0.1 g/L Co/ZrO_2 catalyst and under 100°C, 20 bar operation condition as 8.21% succinic acid degradation efficiency. Both increasing of temperature and catalyst loading did not positively affect degradation of organic carbon removal.

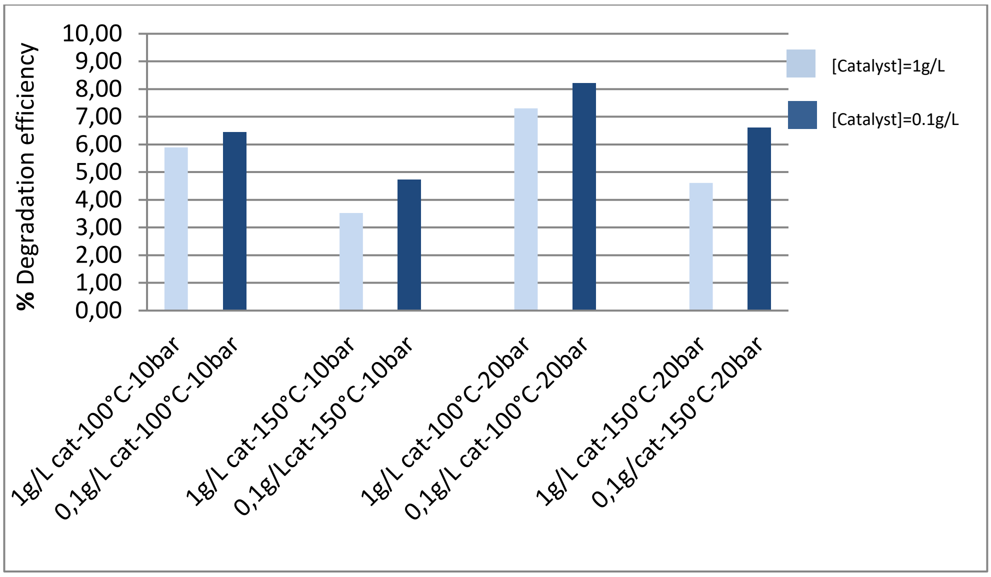


Figure 6. 11 Degradation efficiencies of Co/ZrO_2 catalyst for same amount of catalyst loading and same temperature

All of the experimental results in catalytic wet air oxidation are summarized in Figure 6.11. Since the optimum results were obtained by 0.1 g/L Co/ZrO_2 catalyst and at 100^{o}C and at 20 bar. Even though 8.21% degradation efficiency was achieved, degradation of succinic acid organic carbon was not remarkable for hybrid system which includes microbial fuel cell because of microorganism's activity. These results showed that wet air oxidation system was not effectively by using Co/ZrO_2 catalyst for hybrid system first removal step before the Microbial Fuel Cell. Because of these reasons, alternative advanced oxidation method and alternative compatible catalyst were investigated for first degradation step of hybrid system which includes Microbial Fuel Cell, subsequently.

6.2.2 Photo –Fenton like Catalytic Oxidation

6.2.2.1 Catalyst screening

Experiments were carried out using Co/ZrO_2 and Fe-TiO_2/AC catalysts for Photo-Fenton like catalytic oxidation. For each catalyst, two different temperature (25^{o}C and 60^{o}C) and two different light sources (UV light and Visible light) were studied by using 1 g/L catalyst loading for each experiment at pH = 3.34. In additionally, in the results for the effect of those different temperature and light sources for each catalyst are shown in Figure 6.12 to 6.13.

These results obtained by two catalysts as Co/ZrO_2 and $Fe\text{-}TiO_2/AC$ for two different operation temperatures under UV light source showed that degradation occurred. Effects of both parameters (temperature and catalyst type) on degradation of succinic acid were significantly. Highest degradation was seen under 60°C operation temperature for both of two catalysts. When the experiments had classified each other for optimum result, $Fe\text{-}TiO_2/AC$ was more effectively than Co/ZrO_2. Additionally, reaction condition optimization was investigated, no remarkable degradation efficiency difference was seen between 25°C and 60°C operation temperature for UV light source. These results showed that succinic acid degradation efficiency was obtained as 22.2% with 1g/L $Fe\text{-}TiO_2/AC$ catalyst under optimum operation condition which is 25°C temperature, 5mM H_2O_2 and UV light source (Figure 6.12).

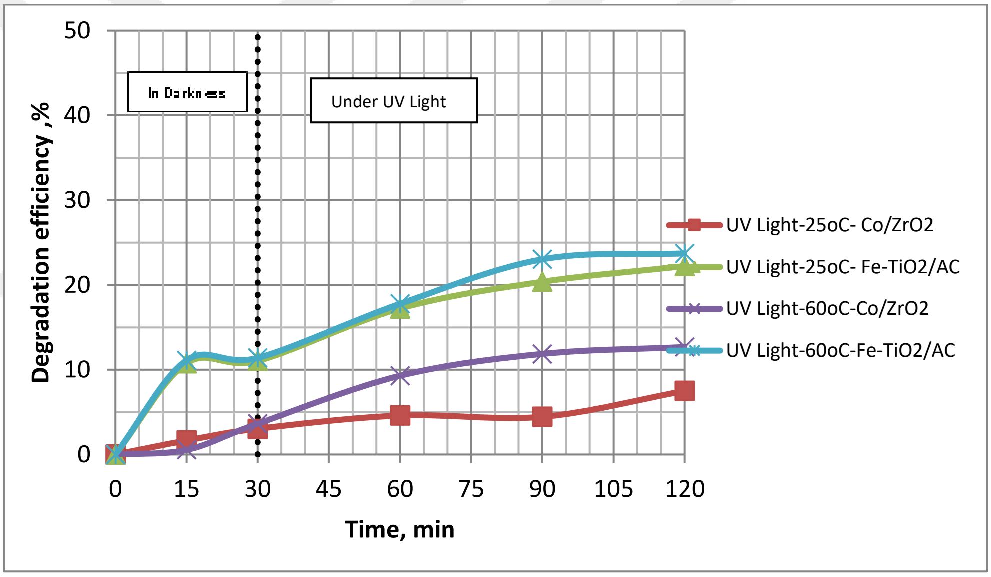


Figure 6. 12 Photo Fenton-like catalytic oxidation experiments performed under two 6 Watt UV light. Reaction conditions: 1g/L catalyst, 5mM H_2O_2, 250 ppm Organic Carbon Content Succinic Acid (615ppm Succinic Acid)

The experiments were performed under 100 Watt Visible light source for two different catalysts Co/ZrO_2 and $Fe\text{-}TiO_2/AC$ and two different operation temperatures as 25°C and 60°C with 1g/L catalyst loading with normal PH condition (3.34). When the degradation efficiency was investigated, results showed that $Fe\text{-}TiO_2/AC$ catalyst was more effective in darkness than Co/ZrO_2 When H_2O_2 was added to reaction in the 30th min, degradation efficiency of succinic acid with Co/ZrO_2 increased and approximated to degradation efficiency of $Fe\text{-}TiO_2/AC$. On the other hand, succinic acid degradation efficiency almost remained constant beyond 15 min with Fe-TiO_2/AC (Figure 6.13).

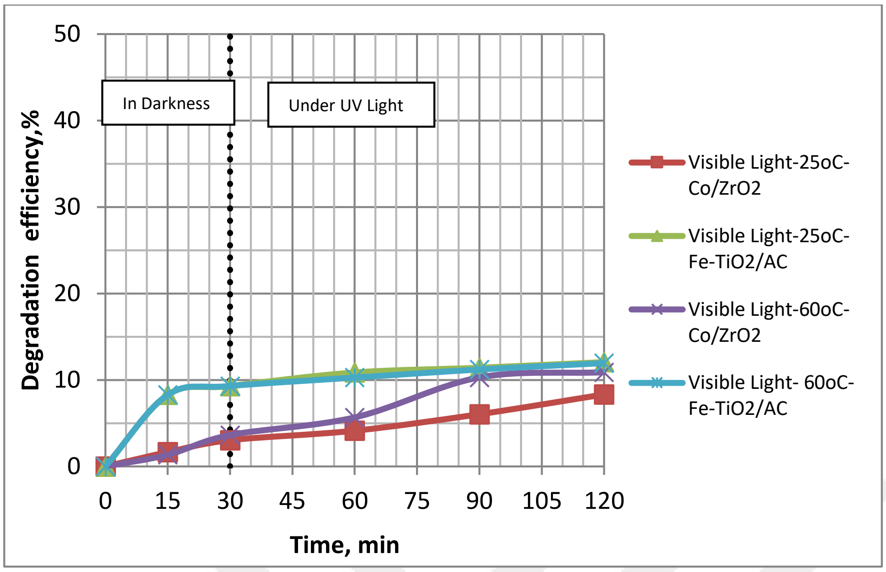


Figure 6. 13 Photo Fenton-like catalytic oxidation experiments performed under 100 Watt Visible light. Reaction conditions: 1g/L catalyst, 5mM H2O2, 250 ppm Organic Carbon Content Succinic Acid (615ppm Succinic Acid)

According to the catalyst screening study, succinic acid degradation with Fe-TiO_2/AC catalyst is the highest under reaction conditions (25^{o}C temperature, 5mM H_2O_2, 1g/L catalyst loading). It was decided that the parametric study is carried out by the Fe-TiO2/AC catalyst.

6.2.2.2 Parametric Study

Catalyst screening experiments showed that the highest degradation efficiency was (22.2%) achieved by Fe-TiO_2/AC catalyst. In this context, the effects of operational parameters such as catalyst loading ([Catalyst]), H_2O_2 concentration, UV light after darkness period on degradation efficiency were investigated.

Effect of Fe-TiO_2/AC Catalyst loading on succinic acid degradation

The experiments investigating the effect of catalyst loading showed increase in degradation for Fe-TiO_2/AC as the catalyst loading was increased. Catalyst loading experiment occurred under operation conditions which were defined in catalyst screening experiment as 25^{o}C operation temperature, UV light source, 5mM H_2O_2 adding in the 30th minute. Four different catalyst loadings of catalysts were used. Around the 22.2% degradation efficiency was achieved when 1 gram of per liter catalyst was present in reaction medium. When the catalyst loading was increased from 1g/L to 4g/L, the increase in degradation efficiency was more than triple in darkness and more than double under UV light source. The succinic acid degradation efficiency increased to around 52%. When the degradation trend was investigated on experimental results, degradation rise was regular in darkness and under UV light source (Figure 6.14).

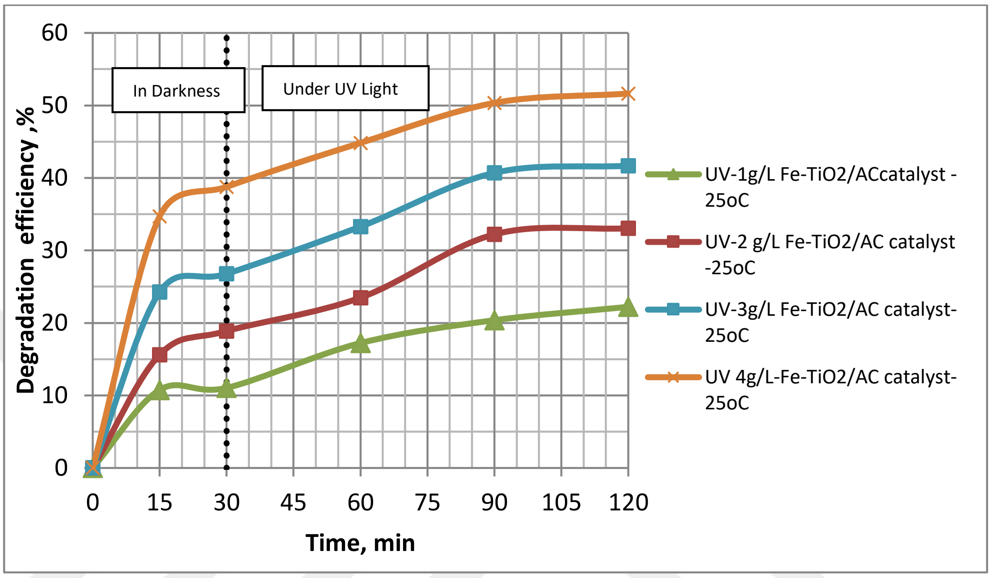


Figure 6. 14 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25°C operation temperature 5mM H_2O_2, 250 ppm Organic Carbon Content Succinic Acid (615ppm Succinic Acid)

Effect of the presence of Fe-TiO_2/Activated carbon catalyst for first thirty-minute dark period on succinic acid degradation

The results obtained by the experiments investigating the effect of presence of Fe-TiO_2/AC catalyst for thirty minutes dark period showed that it has a great influence on degradation efficiency during the dark period. To see the effect of the catalyst an experiment was performed without catalyst, under normal reaction condition as 25°C reaction temperature and UV light source and adding H_2O_2 after 30th minute dark period. When Fe-TiO_2/AC catalyst was absent in reaction medium, reaction degradation was not observed during the thirty minutes dark period. Even though reaction does not start till the 30th minute without catalyst, adding of H_2O_2 started the reaction and UV light and hydrogen peroxide presence decreased succinic acid concentration. Around 15.62 % degradation efficiency was achieved with these experimental conditions (Figure 6.15).

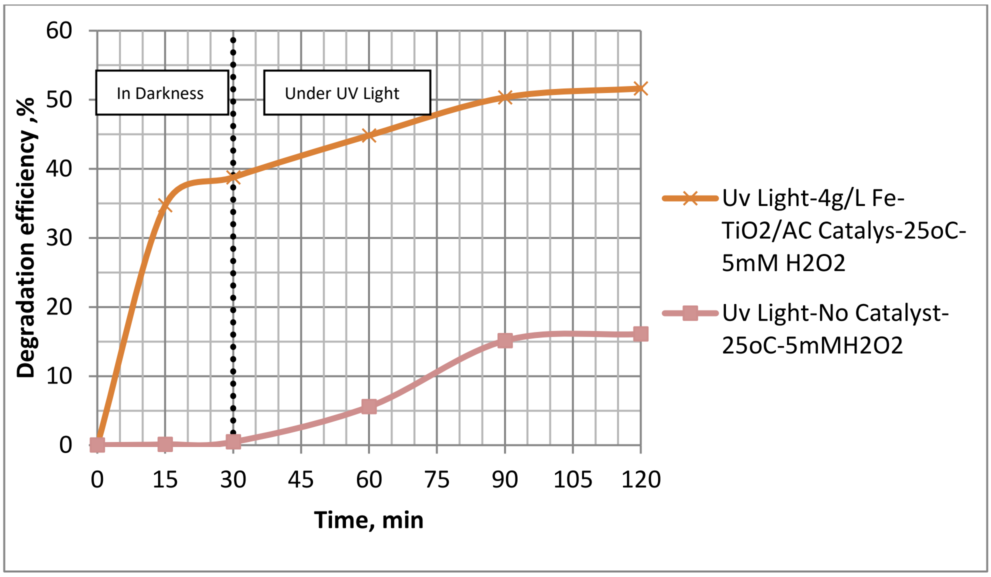


Figure 6. 15 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25°C operation temperature 5mM H_2O_2, 250 ppm Organic Carbon Content Succinic Acid (615ppm Succinic Acid)

Fe-TiO_2/AC had an important role on succinic acid degradation reaction (Figure 6.16). Even if experiment which had not catalyst showed succinic acid degradation, 15,62 % degradation was not enough for hybrid system which has microbial fuel cell.

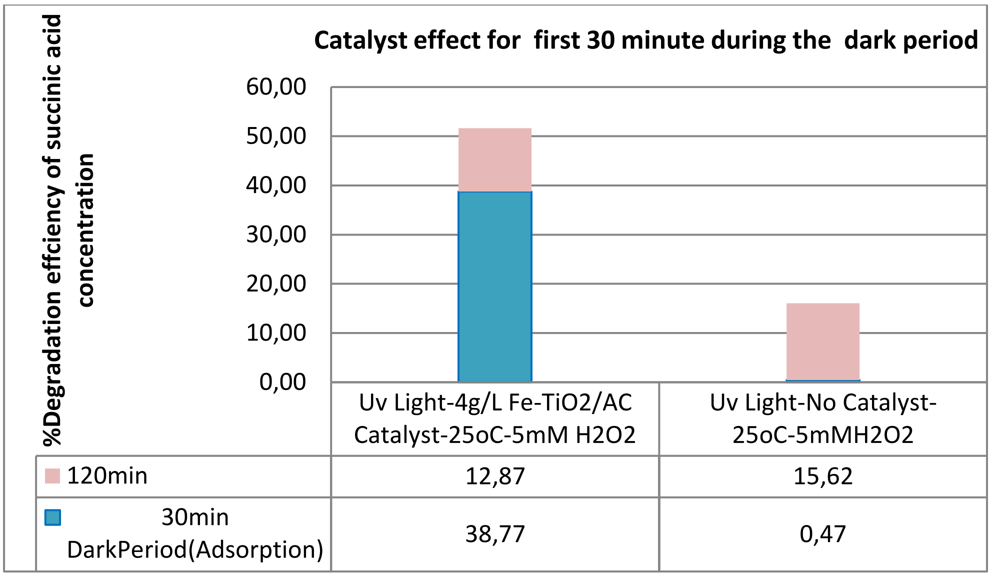


Figure 6. 16 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25°C operation temperature 5mM H_2O_2, 250 ppm Organic Carbon Content Succinic Acid (615ppm Succinic Acid)

Effect of the hydrogen peroxide presence on succinic acid degradation

The experiment investigating the effect of hydrogen peroxide presence on the succinic acid degradation efficiency showed hydrogen peroxide presence with UV light after the dark period affected degradation of succinic acid. In this experiment, under the operation conditions as 25°C operation temperature, UV light source and 4g/L Fe-TiO_2/ AC catalyst presence, around 40.1% degradation efficiency was achieved without hydrogen peroxide presence. According to results, remarkable increase of degradation efficiency was not observed after first thirty minutes dark period (Figure 6.17).

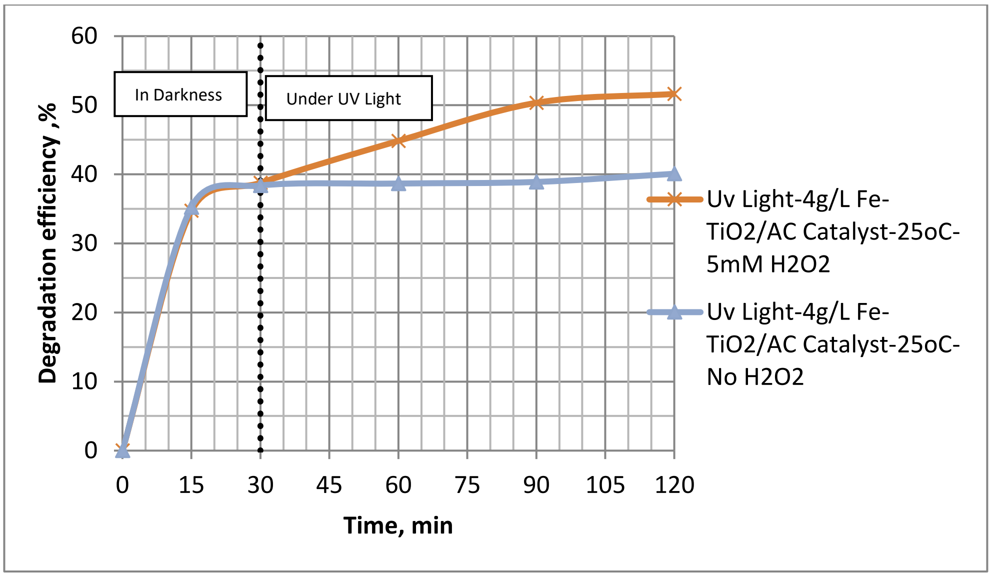


Figure 6. 17 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25^{o}C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

When the degradation trend was investigated according to experiment result, degradation efficiency was regular in the dark period because of possible adsorption on catalyst.. Despite the UV light was turned on after dark period, degradation efficiency increased only around 1.7%. When the reference experiment results which has hydrogen peroxide were compared with this experiment results, UV light and catalyst presence do have a remarkable effect degradation efficiency of succinic acid without hydrogen peroxide (Figure 6.18)

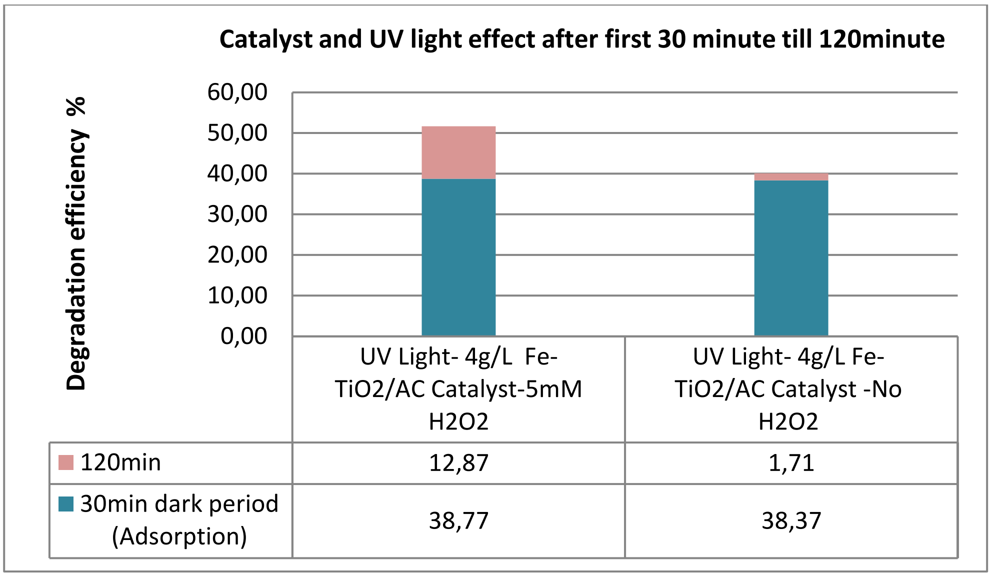


Figure 6.18 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

The synergic effect of UV light irradiation and hydrogen peroxide on succinic acid degradation

The experiments investigating the synergic effect of UV light irradiation and hydrogen peroxide in the darkness during the experiment with the presence of Fe-TiO_2/AC occurred with 4g/L catalyst, without UV light source and hydrogen peroxide, under normal reaction temperature as 25°C. The experimental results showed that it has no great influence on degradation efficiency in this experimental condition. During first 30 minutes dark period, Fe-TiO_2/AC catalyst adsorption was observed as degradation efficiency around 40%.

Even though the degradation has the same as previous experimentally in the darkness with catalyst, there was no remarkable performance after 30 minutes without hydrogen peroxide and UV light source (Figure 6.19).

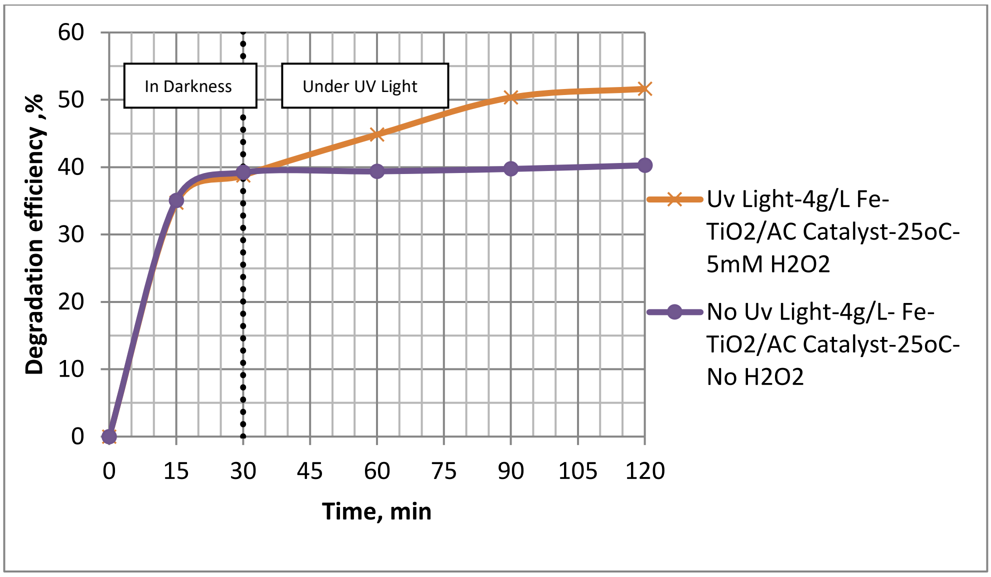


Figure 6. 19 Photo Fenton-like catalytic oxidation experiments performed in the darkness . Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

Accordingly, to experimental result, hydrogen peroxide and UV light showed synergic effect for succinic acid degradation efficiency. Only presence of catalyst without hydrogen peroxide and UV light source showed only adsorption effect in the dark period. When the degradation efficiency trend was compared with reference experiment which has hydrogen peroxide, UV light source and catalyst together, degradation efficiency changing was only 11% for thirty minutes after (Figure 6.20).

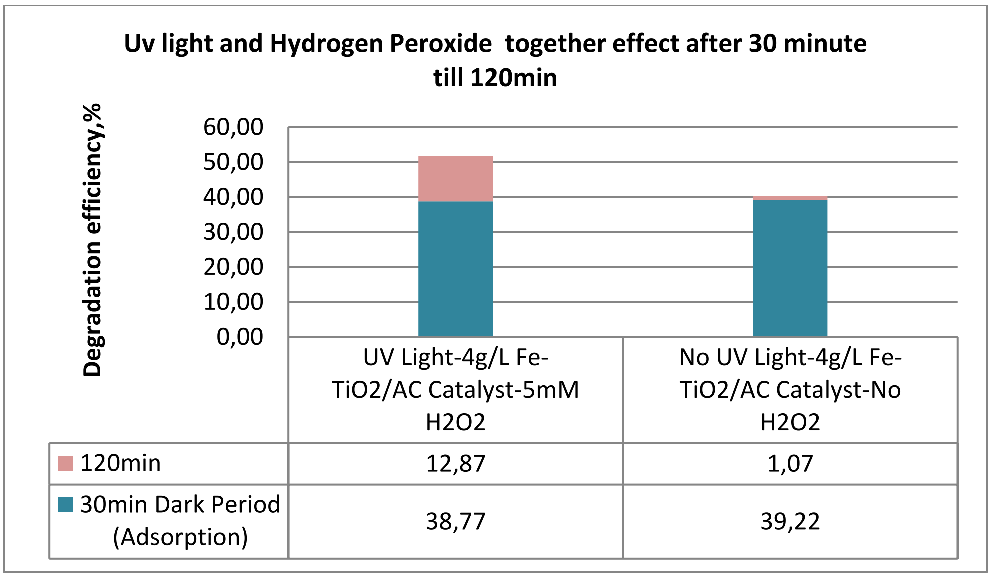


Figure 6. 20 Photo Fenton-like catalytic oxidation experiments performed in the darkness . Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

The synergic effect of UV light irradiation and Fe-TiO2/Activated carbon catalyst on succinic acid degradation

The experiments to investigate the synergic effect of UV light irradiation and Fe-TiO_2/AC catalyst in the presence of only hydrogen peroxide. Experiments are performed with 5mM H_2O_2, without UV light source and catalyst, at normal reaction temperature as 25°C. The experimental results showed that degradation of succinic acid was not observed remarkably during the experiment (Figure 6. 21).

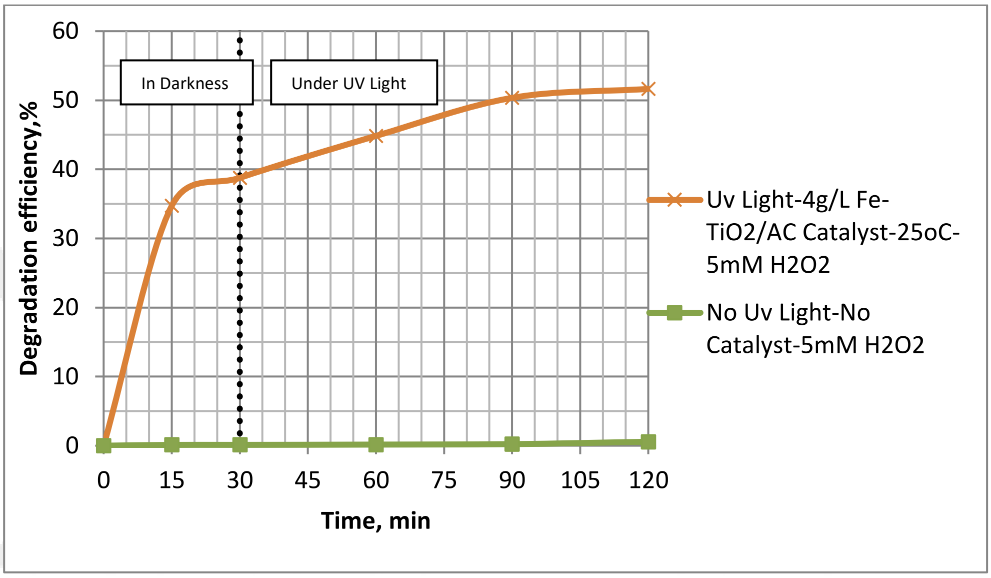


Figure 6. 21 Photo Fenton-like catalytic oxidation experiments performed in the darkness. Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

When the results of the having only hydrogen peroxide were compared it was seen that hydrogen peroxide alone did not affect the degradation of succinic acid. As the adsorption was not observed without catalyst for first thirty minute dark period, there was no degradation without UV light and catalyst during the experiment(Figure 6.22)

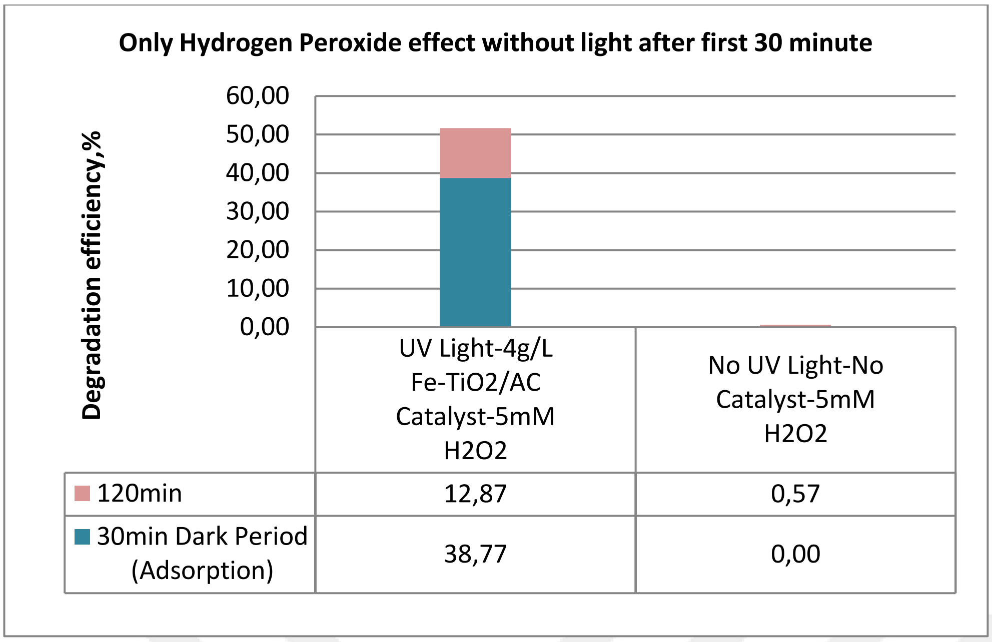


Figure 6.22 Photo Fenton-like catalytic oxidation experiments performed in the darkness. Reaction conditions: 25^{o}C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

In generally, the experimental investigation results showed that on Fe-TiO_2/AC catalyst the adsorption for first thirty minute in the darkness occurred. Even though hydrogen peroxide was added and UV light source was turned on after dark period, Fe-TiO_2/AC catalyst was effective with UV light and hydrogen peroxide. When the hydrogen peroxide and UV light irradiation effect were investigated, only UV light and only hydrogen peroxide was not effective on degradation of succinic acid. UV light and hydrogen peroxide gave synergic affect together for succinic acid degradation.

Effect of the initial hydrogen peroxide concentration on succinic acid degradation

According to previous experimental results, hydrogen peroxide presence with UV light source affected the degradation of succinic acid after the first thirty minutes dark period. In this case, hydrogen peroxide loading was investigated on succinic acid degradation efficiency with UV light source by using different concentration of hydrogen peroxide. Experiments were performed at 25^{o}C operation temperature, UV light source and 4g/L Fe-TiO2/ AC catalyst presence. Around the 39% degradation efficiency was achieved with adsorption in the darkness by the Fe-TiO_2/AC catalyst. After the dark period, different amount of hydrogen peroxide was added as 0mM, 2.5mM, 5mM and 10mM.

When the degradation trend was investigated on experimental results, degradation rise was around %39 for succinic acid in darkness as adsorption. Significant degradation efficiency was observed as hydrogen peroxide loading was increased (Figure6.23).

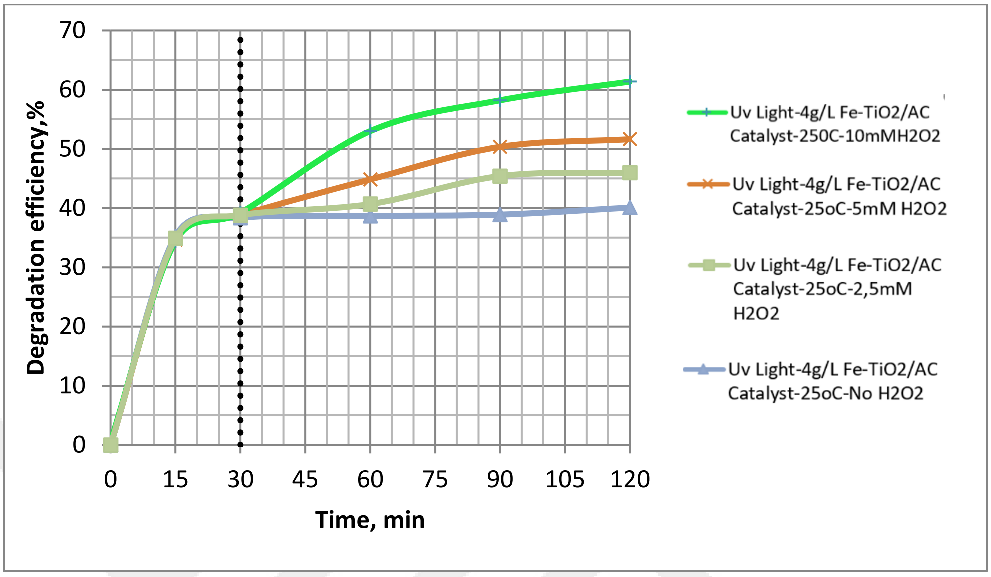
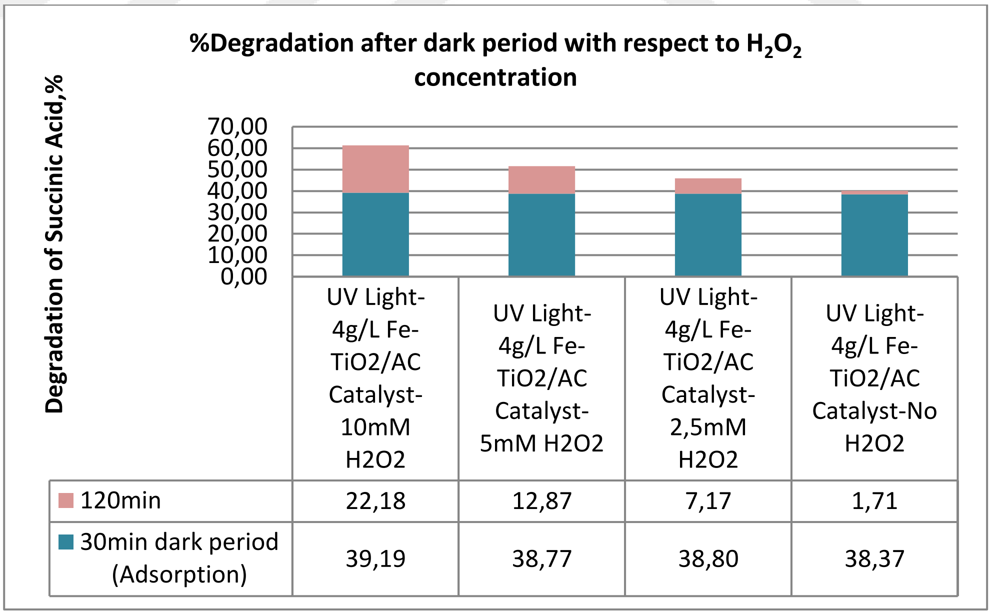


Figure 6. 23 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)



	UV Light-4g/L Fe-TiO2/AC Catalyst-10mM H2O2	UV Light-4g/L Fe-TiO2/AC Catalyst-5mM H2O2	UV Light-4g/L Fe-TiO2/AC Catalyst-2,5mM H2O2	UV Light-4g/L Fe-TiO2/AC Catalyst-No H2O2
🟥 120min	22,18	12,87	7,17	1,71
🟦 30min dark period (Adsorption)	39,19	38,77	38,80	38,37

Figure 6. 24 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

In consideration of these investigations, succinic acid degradation efficiency increased with increasing hydrogen peroxide loading (Figure 6.24). When the suitable operation conditions for the hybrid system including the microbial fuel cell is considered, high concentration of hydrogen peroxide can affect negatively microorganism’s activity. When the degradation efficiencies were compared in Figure 6.24, only very high amounts of hydrogen peroxide was effective which was not suitable for the subsequential microbial fuel cell treatment. Thefore, the addition of hydrogen peroxide into the photocatalytic oxidation reaction medium was not reccommended prior to the microbial fuel cell treatment.

Effect of the initial pH on succinic acid degradation (comparing of neutral and normal pH condition)

The results obtained by the experiments investigating the pH effect of succinic acid degradation under the reaction conditions. An experiment was caarried out with 4g/L catalyst, hydrogen peroxide, UV light source and under normal reaction temperature as 25^{o}C and pH as 7.11 for neutral medium. Main goal of this experiment is that investigating of optimum pH medium for hybrid system. According to hybrid system process, neutral medium is more suitable medium for microorganism’s activity in the Microbial Fuel Cell. For this reason, the pH values were tested as normal (pH=3.4) and neutral (pH=7.11).

According to experimental results, degradation efficiency of succinic acid decreased by the neutral pH (Figure 6.25).

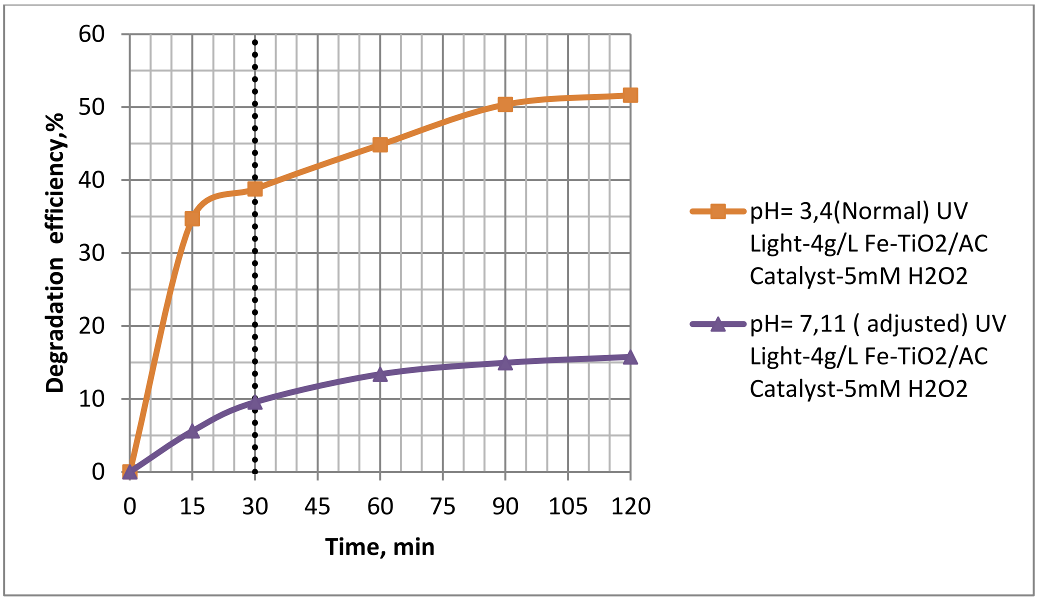


Figure 6. 25 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25ºC operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

In generally, around 50.1 % degradation efficiency was achieved for acidic medium 15.7% degradation of succinic acid for neutral medium. Therefore, acidic reaction medium was decided (Figure 6.26).

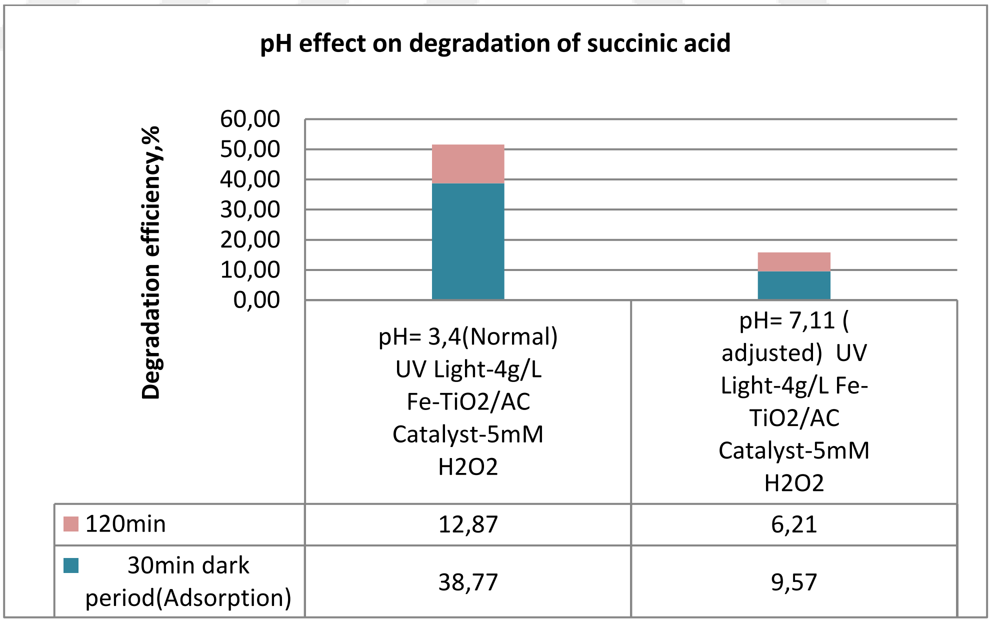


Figure 6. 26 Photo Fenton-like catalytic oxidation experiments performed under UV light. Reaction conditions: 25ºC operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

6.2.3 First Step Experiment Results for Hybrid System According to Parametric Study Results of Photo-Fenton like Oxidation Study

To prepare the solution for the hybrid treatment, an experiment was carried out with Fe-TiO_2/AC at the conditions of 4g/L of catalyst loading. The degradation efficiency vs time is presented in Figure 6.27.

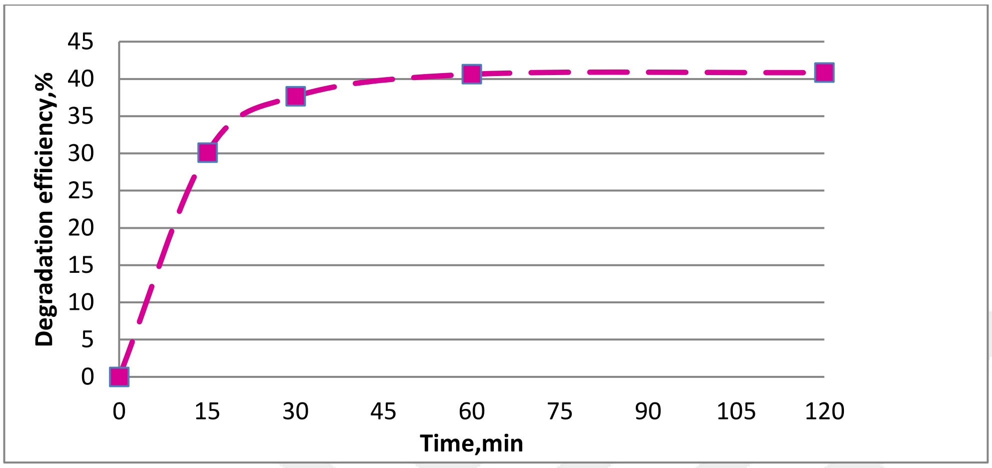


Figure 6. 27 Degradation efficiency of succinic acid vs time. Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

The pH trend of succinic acid during the reaction was also monitored. Experiment was carried out at normal succinic acid solution pH condition and pH trend did not show fluctuation during the adsorption ($pH_{succinic\ acid}$= 3.34) (Figure 6.28).

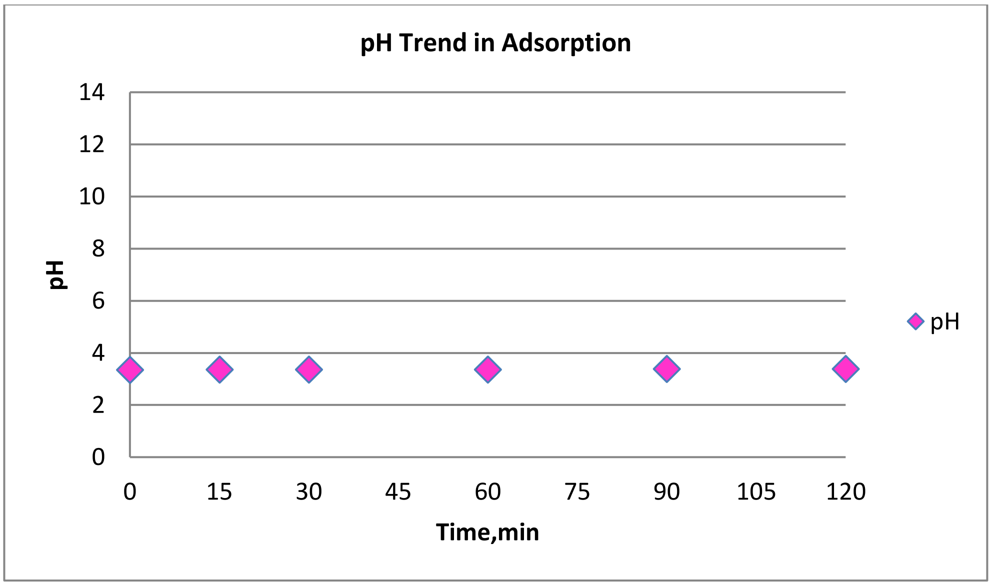


Figure 6. 28 Fe-TiO_2/AC catalyst adsorption experiments performed according to pH trend. Reaction conditions: 25°C operation temperature, 250 ppm Organic Carbon Content Succinic Acid (615 ppm Succinic Acid)

6.2.4 Second Step Experiment Results for Hybrid System: Application of Microbial Fuel Cell to The Effluent Treated By Fenton-Like Oxidation

The effluent of the Fenton-like oxidation experiments was charged to H-type Microbial Fuel Cell. Before the charging of succinic acid solution to Microbial Fuel Cell, sodium acetate was added to solution as organic nutrient. Degradation of succinic acid and other parameters were monitored for twenty days. When the results were investigated, degradation of succinic acid increased during the microbial activity remarkably in Microbial Fuel Cell. In hybrid system, final degradation efficiency of succinic acid was achieved around 90% after twenty days (Figure 6.29).

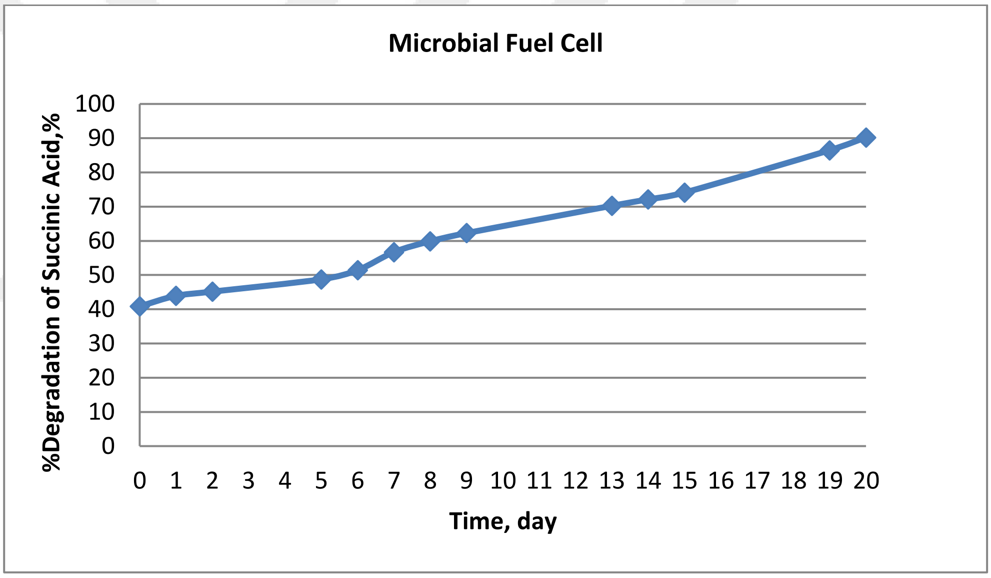


Figure 6. 29 Microbial Fuel Cell experimental results of succinic acid concentration degradation Reaction conditions: 25°C operation temperature, 150 ppm Organic Carbon Content of Succinic Acid for Microbial Fuel Cell starting point.

In this experiment, total organic carbon degradation was investigated by using microorganism’s activity in the Microbial Fuel Cell. For this experiment sodium acetate was added as a nutrient to the anodic cell as 50 % v/v and pH was adjusted to neutral condition (7.34). Total organic carbon content was decreased during the previous step of the hybrid system, adding acetate as a nutrient for microorganisms caused in increase total organic carbon content from 200 ppm to 400 ppm. When the degradation of total organic carbon was investigated during the microorganism's activity, TOC degradation value was around 35% (after sodium acetate addition, initial TOC value was evaluated as 40.02%) (Figure6.30).

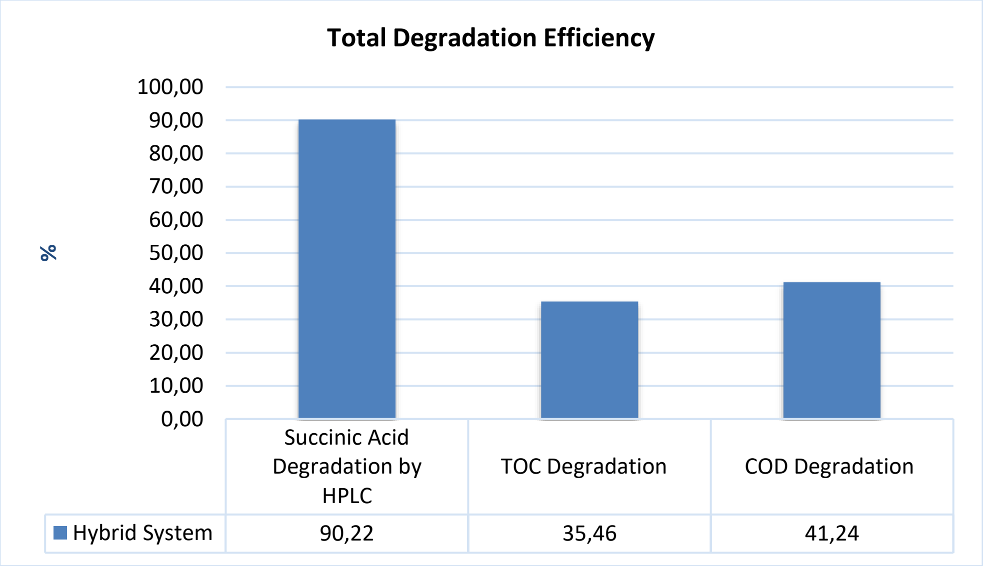


Figure 6. 30 Total Degradation Efficiency after Microbial Fuel Cell experimental results of TOC, COD and Succinic Acid Concentration Degradation on HPLC degradation. Reaction conditions: 25ºC operation temperature, 400 ppm Total Organic Carbon Content for Microbial Fuel Cell starting point.

Even though Total Organic Carbon content decreased with first step hybrid system around 32.02%, adding sodium acetate ($C_2H_3NaO_2$) increased total organic carbon according to previous step. After the Microbial Fuel Cell step total organic carbon content decreased around 35.46 % again. According to total succinic acid removal results, degradation was seen around 90%. These results showed that Microbial Fuel Cell step was successful as much as catalytic adsorption process. And it may lead to future work on the hypothesis that a hybrid system can be used to reduce the amount of carbon in the waste water that has higher total carbon content for any reason. Chemical Oxygen Demand decreasing was investigated for succinic acid with Microbial Fuel Cell. According to microorganism's activity, COD value decreased around 13 % (Figure 6.31).

When the Total COD decreasing was investigated for hybrid system, results showed that Chemical oxygen demand decreased totally around 41.24% according to starting COD value for succinic acid model solution. On the other hand, sodium acetate addition affected to starting concentration of COD value on MFC (Figure 6.31).

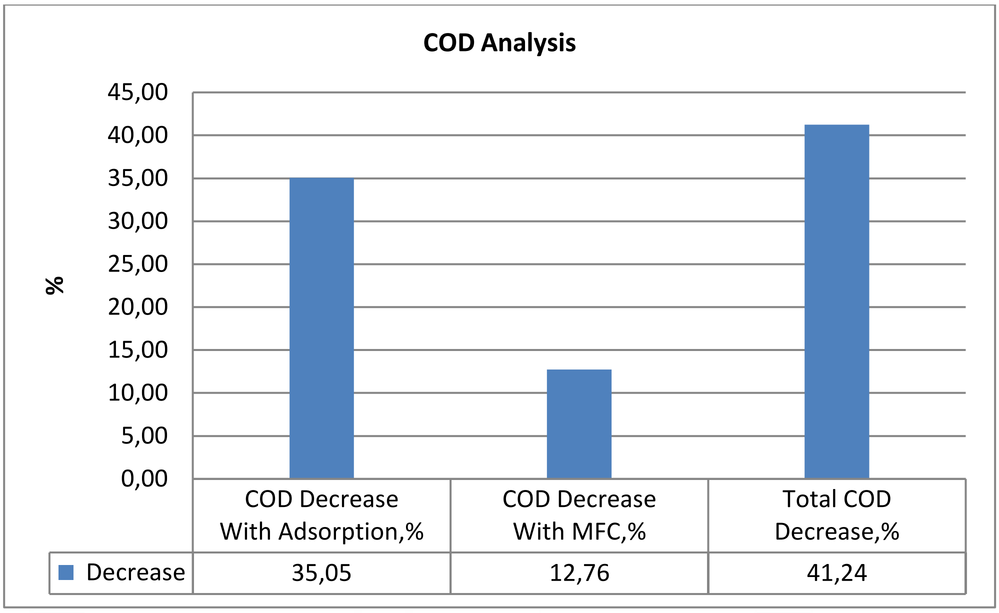


Figure 6. 31 Comparing of COD decreases for each steps of Hybrid system. Reaction conditions: 25°C operation temperature.

The pH trend during Microbial Fuel Cell was also monitored. Experiment occurred in neutral pH condition as 7.14 for succinic acid solution. Neutral pH trend is very important point for microorganism activity. Therefore, acidic output solution's pH which was obtained after adsorption was raised to 7.14 from 3.34 by using NaOH solution before the charging to MFC. When the pH trend was monitored for twenty days, pH trend did not show fluctuation during the experiment (Figure 6.32).

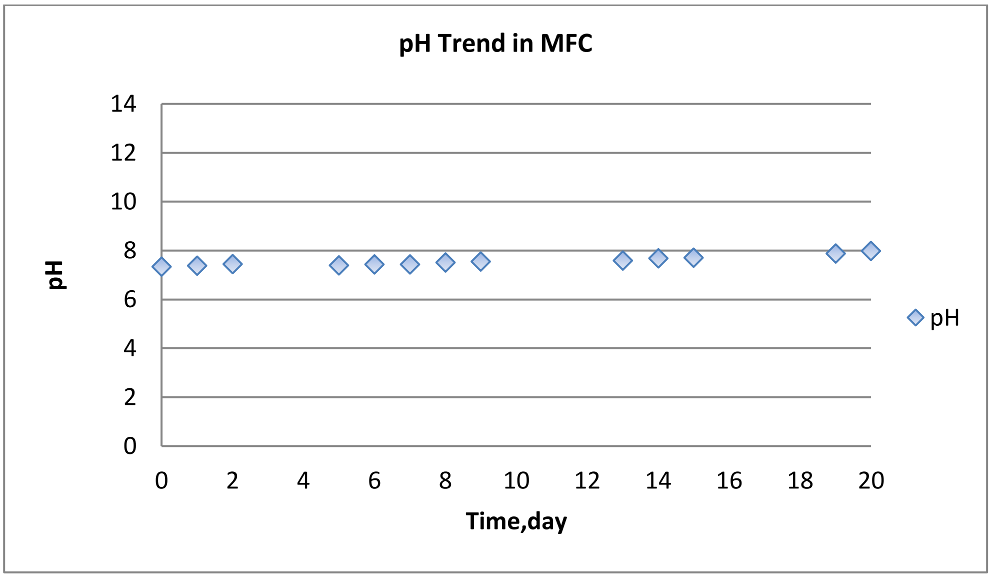


Figure 6. 32 Fe-TiO_2/AC catalyst adsorption experiment performed according to pH trend. Reaction conditions: 25°C operation temperature, 400 ppm Total Organic Carbon Content Microbial Fuel Cell starting point.

During the microbial fuel cell activity also open circuit voltage of succinic acid was investigated. The open circuit voltage was monitored daily. For this investigation 203.4 Ω external resistance was used and electrochemical performance was monitored. According to results, succinc acid electron donor capacity depends on Total Organic Carbon content. When the electron donor source presence, electrochemical activity was continued. Organic Carbon removal (35.45%) was achieved with good potential value (~0, 2 V) on neutral pH condition. The results provided that succinic acid was as electron donor.

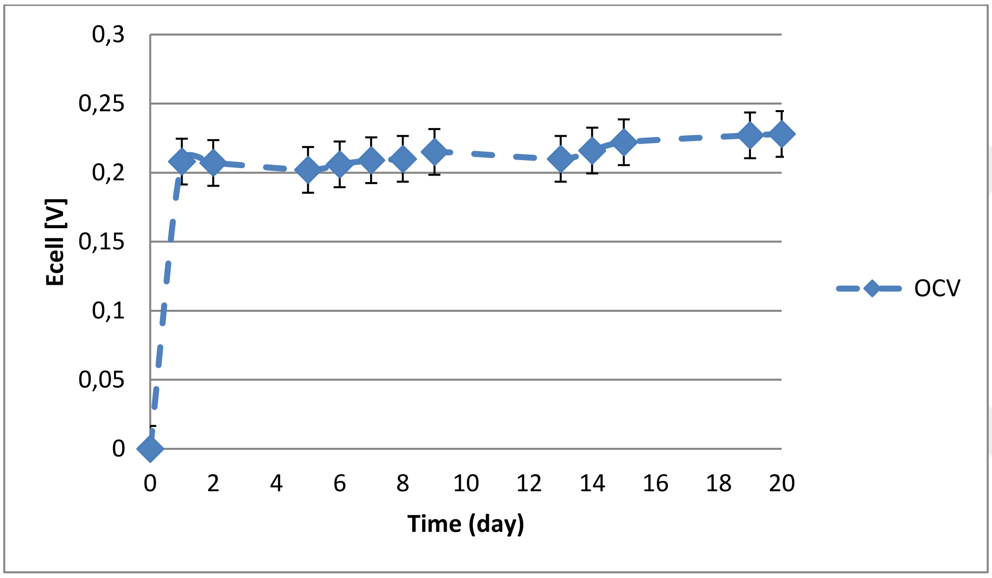


Figure 6. 33 Open circuit voltage experiments performed according to cell potential. Reaction conditions: 25°C operation temperature, 400 ppm Total Organic Carbon Content Microbial Fuel Cell starting point.

6.3 General Considerations on Hybrid System

For the first step of the hybrid system, Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ and $Fe\text{-}TiO_2/AC$ catalysts were prepared. Firstly, Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts were prepared by using Sol-Gel method. ZrO_2 which used as catalyst support for these catalysts was prepared by neutral activation. Secondly, activated carbon was used as catalyst support for $Fe\text{-}TiO_2/AC$ catalysts was prepared by chemical activation methods such neutral activation and $Fe\text{-}TiO_2/AC$ catalysts were prepared by Sol-gel method.

As the first step of the hybrid system two AOP methods such as catalytic wet air oxidation, and photo-Fenton-like catalytic oxidation were tested for target compound Succinic acid.

The effluent which was obtained from Fenton-like oxidation treatment was charged to Microbial Fuel Cell for hybrid system second step treatment.

Degradation experiments for succinic acid were carried out in two main steps and explained in detail below.

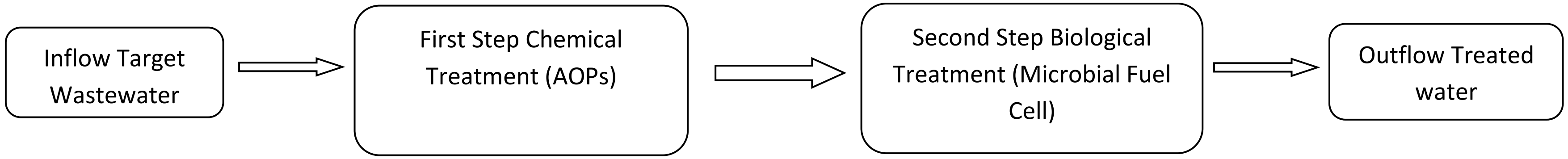
In catalyst screenings for AOPs for succinic acid target compound, Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts were tested for catalytic wet air oxidation by varying several operation conditions. Even though succinic acid degradation with Bi catalysts did not show remarkable efficiency for wet air oxidation system, Co/ZrO_2 catalyst showed remarkable performance. For this reason, Co/ZrO_2 catalyst and $Fe\text{-}TiO_2/AC$ catalyst were tested in photo-Fenton-like catalytic oxidation. The most successful catalyst was determined as $Fe\text{-}TiO_2/AC$ catalyst and it was used for further parametric studies after catalyst screening.

In the first step of the hybrid treatment, the optimum operation conditions were determined as 25°C temperature and 4 g/L $Fe\text{-}TiO_2/AC$ catalyst loading, 5mM H_2O_2 under UV light irradiation for succinic acid degradation.

For the second tep of the hybrid system (For Microbial Fuel Cell), the effluent which was obtained from first step was charged into the MFC system and the effect of reaction parameters on succinic acid degradation was investigated. Neutral pH condition and 203.4 Ω external resistance was used. 1ml supernatant and 50%v/v sodium acetate were added. Under this operation conditions, succinic acid electrochemical performance was monitored.

Optimum operating conditions for succinic acid with maximum degradation efficiencies achieved are shown in Figure7.1 in detail.

Figure7. 1. Hybrid System Optimum Values of the Operation Conditions for Succinic Acid Degradation.

<table>
<tr><th colspan="8">Hybrid System Optimum Values of the Operation Conditions for Succinic Acid Degradation</th></tr>
<tr><td colspan="8">
</td></tr>
<tr><td colspan="4">Photo-Fenton Like Oxidation (Adsorption)</td><td colspan="4">Microbial Fuel Cell</td></tr>
<tr><td>Catalyst</td><td>[Catalyst] (g/L)</td><td>Temperature (ºC)</td><td>Degradation (%)</td><td>Supernatant (ml)</td><td>Temperature (ºC)</td><td>External Resistance (Ω)</td><td>Degradation (%)</td></tr>
<tr><td>Fe-TiO_2/AC</td><td>4</td><td>25</td><td>40.84</td><td>1</td><td>25</td><td>203.4</td><td>90.2</td></tr>
</table>

7.0 CONCLUSIONS

This study aimed at investigation of the treatment of the organic pollutants (fumaric acid and succinic acid), which was generated during the olive oil production process, by applying hybrid system which includes chemical and biological treatment methods subsequently. For this purpose, AOPs and Microbial Fuel Cell implementation to hybrid system was investigated as chemical and biological treatments. In addition, environmentally friendly green catalysts (for chemical treatment) and the supernatant which was obtained from animal digestate were used in the chemical and biological treatment methods.

Pre-study which was carried out in La Sapienza Di Roma University, synthetic wastewater consisting of fumaric acid was treated by using H-type MFC system. In this study it was demonstrated that this kind of system can be used also with waste containing intermediate or phenolic by-product of chemical oxidation as fumaric acid. This kind of organic matter showed the same electron donor capacity as sodium acetate. Moreover, their combination was demonstrated to be an incentive for microbial activity. High organic carbon removal (97%) with good potential value (0,2 V) with neutral pH condition was achieved. The results proved the benefit to use fumaric acid as nutrient and electron donor because it is already present in waste and avoid the addition of external substrate.

For the chemical treatment step of hybrid the Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts were synthesized by using Sol-Gel method and for these catalysts, ZrO_2 which used as catalyst support for these catalysts were prepared by neutral activation as chemical activation method. Secondly, activated carbon used as catalyst support for $Fe\text{-}TiO_2/AC$ catalysts was prepared by chemical activation methods such neutral activation and $Fe\text{-}TiO_2/AC$ catalysts were prepared by Sol-gel method. The performences of these catalysts were investigated during the catalyst screening experiments for catalytic wet air oxidation and photo-Fenton like oxidation.

Co/ZrO_2, Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalysts were used on catalytic wet air oxidation method for succinic acid degradation step. Even though Bi/ZrO_2, $Co\text{-}Bi/ZrO_2$ catalyst did not show a performance for catalytic wet air oxidation for succinic acid degradation, Co/ZrO_2 showed remarkable effect according to Bi/ZrO_2, Co-Bi/ZrO_2 Wet air oxidation catalyst screening experiments which were carried out with Co/ZrO_2 showed 8.21% succinic acid degradation efficiency by using 0.1 g/L Co/ZrO_2 catalyst under 100^oC, 20 bar operation condition. However, 8.21% degradation efficiency of succinic acid was not sufficient for first step of hybrid system. According to these results, the Co/ZrO_2 catalyst having better perfomance was used in photo-Fenton like oxidation of succinic acid.

Following by the wet air oxidation experiments results, Co/ZrO_2, Fe-TiO_2/AC catalysts were tested in catalyst screening experiments of photo-Fenton like catalytic oxidation. For this purpose, two different light sources and two different operation temperatures were used for each catalyst by using 1 g/L of catalyst loading. The highest degradation was obtained under 60^oC operation temperature for both of two catalysts by using UV light sources. When the experimental results are compared, Fe-TiO_2/AC was more effective than Co/ZrO_2. Additionally, optimization of the reaction condition was investigated, and there was insignificant difference in the degradation efficiencies for25^oC and 60^oC operation temperature with UV light source. These results showed that succinic acid degradation efficiency was obtained as 22.2% with 1g/L Fe-TiO_2/AC catalyst under optimum operation condition which is 25^oC temperature, 5mM H_2O_2 and UV light.

The effects of operational parameters such as catalyst loading ([Catalyst]), hydrogen peroxide concentration ([H_2O_2]), and UV light effect after darkness period on degradation efficiency were investigated. During the photo-Fenton oxidation process, first 30 minute was kept stable under darkness for investigation of adsorption on Fe-TiO_2/AC in each experiment. After thirty-minute UV light was opened and hydrogen peroxide was added. The, results showed that Fe-TiO_2/AC adsorption properties on succinic acid degradation had important role in photo-Fenton catalytic oxidation. The synergic effect between catalyst, UV light ant hydrogen perxide was remarkable. Succinic acid was degraded around 40% during the adsorption with 4 g/L of Fe-TiO_2/AC at pH = 3.34. When TOC and COD values were investigated, 32.02% TOC and 35% COD degradation was achieved for succinic acid. According to this study for first step of hybrid system, adequate treated waste water was achieved for Microbial Fuel Cell that is hybrid system second step.

For Microbial Fuel Cell, outflow water of adsorption was fed to the system after the adding sodium acetate (50% v/v) and NaOH by adjusting pH condition as neutral. Sodium acetate was used as nutrient for microorganisms. In this study digestate was centrifuged for obtaining supernatant which was used as microorganism sources. 1ml supernatant was added to intermediate waste water which was obtained from adsorption, 203.4 Ω external resistant was used in this system and 25^{o}C temperature was adjusted as operation conditions. Succinic acid degradation efficiency, TOC and COD values, pH trend and electrochemical performance has been monitored during the 20 days in Microbial Fuel Cell. After twenty days, succinic acid degradation around 90%, TOC degradation around 35.45%, COD degradation around 41.24% and electrical potential around 0.2 V were achieved successfully.

General Conclusions:

For general conclusions extracted from this study can be expressed as:

- Pre-study experiments showed that Fumaric acid is good electron donor for Microbial Fuel Cell. In additionally, it can be used as a nutrient for microorganisms like sodium acetate.
- Microbial Fuel Cell is successful method for degradation of organic acid compound degradation.
- Fe-TiO_2/AC is more successful catalyst for succinic acid degradation according to Co/ZrO_2, Bi/ZrO_2, Co-Bi/ZrO_2 catalysts.
- Wet air oxidation method was not useful for succinic acid degradation during the first step of hybrid system. When the photo-Fenton like catalytic oxidation method was investigated as other AOPs, Fe-TiO_2/AC catalyst adsorption is more effectively according to photo catalytic property. Presence of hydrogen peroxide and UV light show that Fenton like oxidation is effectively on succinic acid.
- According to hybrid system first treatment step outflow water is important for second step treatment condition. For this reason, presence of hydrogen

peroxide is not suitable for microbial activity for second treatment step Microbial Fuel Cell.

- The Microbial Fuel Cell Method is a successful treatment method that produces electricity at the same time as it purifies the waste water.
  Hybrid systems which can be combined with different treatment method are innovatively and successful treatment methods for treated wastewaters which include strong decompose compounds such as phenolic compounds and organic acids.

The main goal of this study was the development of innovative eco-friendly methods for degradation pollutant present in Olive Oil Mill Wastewater. In this study, it has been proved that new methods can be developed in waste water where only one treatment method is not enough. Hybrid system which was combined with Microbial Fuel Cell produced electrical power during the treated of wastewater. Additionally, walnut shells were also successfully reused as green catalyst which was applied to hybrid system and decreasing operating costs and prevented generation of secondary wastes. It is thought that this will lead a great interest for application of hybrid system which include chemical treatment and biological treatment method together such as AOPs and Microbial Fuel Cell in industrial scale especially for treatment of organic compounds such as succinic acid and its derivatives which still have been a great challenge for industry from both economic and environmental point of views.

Future Study

As the future study removal of Phenolic compounds of olive oil mill wastewater on chemical step of hybrid system analysis can be recommended. After the treated of Phenolic compounds, effluent can be charged to Microbial Fuel Cell directly.

REFERENCES

Abo-Farha, S.A., 2010, Comparative study of oxidation of some azo dyes by different advanced oxidation processes: Fenton, Fenton-Like, Photo-Fenton and Photo-Fenton-Like, Journal of American Science, 6(10):128-142pp.

Ahmed M.J. and Dhedan S.K., 2012, Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons, Fluid Phase Equilibria, 317:9-14pp.

Ahmadpour A. and Do D.D., 1997, The preparation of activated carbon from macadamia nutshell by chemical activation, Carbon, 35:1723-1732pp.

Ammary B., 2004, Nutrients requirements in biological industrial wastewater treatment, African Journal of Biotechnology, 3(4): 236-38pp.

Andreozzi, R., Caprio V., Insola, A. And Marotta, R., 1999, Advanced oxidation processes (AOP) for water purification and recovery, Catalysis Today, 53: 51–59pp.

Arienzo, M. And Capasso, R., 2000, Analysis of metal cations and inorganic anions in olive oil mill wastewaters by atomic absorption spectroscopy and ion chromatography. Detection of metals bound to the organic polymeric fraction., J. Agric. Food Chem., 48:1405–1410pp.

Asiltürk M. and Şener Ş., 2012, TiO_2-Activated carbon photocatalyst: Preparation, characterization and photocatalytic activities, Chemical Engineering Journal, 180:354-363pp.

Aworn A., Thiravetyan P., and Nakbanpote W., 2008, Preparation and characteristics of agricultural waste activated carbon by physical activation having micro- and mesopores, J. Anal. Appl. Pyrolysis, 82(2):279–285pp.

Azbar, N., Bayram, A.,Filibeli, A., Müezzinoğlu,A., Şengül,F. and Özer, A., 2004, A review of waste management options in olive oil production, Critical Reviews in environmental Science and Technology,34: 209 – 247pp.

REFERENCES(continued)

Azzam M.O.J., Al-Malah K.I., and Abu-Lail N.I., 2004, Dynamic post-treatment response of olive mill effluent wastewater using activated carbon,Journal of Environmental Science and Health,39:269-280pp.

Banic N., Abramovic B., Krstic J., Sojic D., Loncarevic D., Cherkezova Z., and Guzsvany V., 2011, Photodegradation of thiacloprid using Fe-TiO_2 as a heterogenous photofenton catalyst, Applied Catalysts B:Environmental, 107:363–371pp.

Barreto R. D., Gray K. A. and Anders K., 1995, Photocatalytic degradation of methyl tert-butyl ether in TiO_2 slurries: a proposed reaction scheme. Water Res.,29:1243-1248pp.

Bavasso I., Di Palma L. and Petrucci E., 2016, Treatment of wastewater in H-Type MFC with protonic exchange membrane: experiental study of organic carbon and ammonium reduction with electrochemical characterization, Chemical Engineering Transaction, 47: 223-228.

Benitez J., Beltran-Heredia J., Torregrosa J., Acero J. L. and Cercas V., 1997, Aerobic degradation of olive oil mill wastewaters, Appl Microbiol Biotechnol, 47: 185-188pp.

Canizares, P., Lobato, J., Paz,R., Rodrigo, M.A. and Saez,C., 2007, Advanced oxidation processes for the treatment of olive-oil mills wastewater, Chemosphere, 67:832–838pp.

Carpio E., Zúñiga P., Ponce S., Solis J., Rodriguez J. and Estrada W., 2005, Photocatalytic degradation of phenol using TiO_2 nanocrystals supported on activated carbon, Journal of Molecular Catalysis A: Chemical, 228:293–298pp.

Cassono, J.J., Higgins, M.E. and Seefeldt, M.W., 2011, Performance of the weather research and forecasting model for Month-Long Pan-Arctic Simulations, American Meteorological Society, 139:3469-3488pp**.**

Clarke N. and Knowles G.,1982, High purity water using H_2O_2 and UV radiation, Effluent and Water Treatment Journal, 22:335-341pp.

REFERENCES(continued)

Cukalovic, A., and Stevens, C.V., 2008, Feasibility of production methods for succinic acid derivatives: a marriage of renewable resources and chemical technology, Biofuels, Bioprod. Bioref., 2:505–529pp.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., and Tchobanoglous, G., 2012, Water Treatment, Principles and Design, Part 18: Advanced Oxidation, John Wiley & Sons, Inc

Chang P.B.L. and Young T.M., 2000, Kinetics of methyl tert-butyl ether degradation and by-product formation during uv/hydrogen peroxide water treatment, Wat. Res., 34(8):2233±2240pp.

Chen, S., Sun, D., and Chung, J.S., 2007, Anaerobic treatment of highly concentrated aniline wastewater using packed-bed biofilm reactor, Process Biochemisstry, 42:1666–1670pp.

Childs S.L., Chyall L.J., Dunlap J.T., Smolenskaya V.N., Stahly B.C.and Stahly G.P., 2004, Crystal engineering approach to forming cocrystals of amine hydrochlorides with organic acids. Molecular complexes of Fluoxetine Hydrochloride with Benzoic, Succinic, and Fumaric Acids,AM. CHEM. SOC.,126: 13335-13342pp.

Choi W., Shim W., Ryu D., Hwang M., and Moon H., 2012, Effect of ball milling on electrochemical characteristics of walnut shell-based carbon electrodes for EDLCs, Microporous and Mesoporous Materials, 155:274–280pp.

Daud, N.K. and Hameed, B.H., 2010, Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst, Journal of Hazardous Materials, 176:938–944pp.

Della Greca, M., Fiorentino, A., Monaco, P., Previtera, L. and Temussi, F., 2000, Phenolic components of olive mill wastewaters. Nat.Prod. Lett.,14: 429–434pp**.**

REFERENCES(continued)

Debellefontaine, H., Chakchouk, M., Foussard, J.N., Tissot, D. and Striolo, P., 1996, Treatment of organic aqueous wastes: Wet air oxidation and wet Peroxide oxidation, Environmental Pollution, 92(2):155-164pp.

Du Z., Li H. and Gu T., 2007, A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy, Biotechnology Advances, 25:464–482pp.

Duarte F., Maldonado-Hódar F.J., and Madeira L.M., 2011, Influence of the characteristics of carbon materials on their behaviour as heterogeneous Fenton catalysts for the elimination of the azo dye Orange II from aqueous solutions, Applied Catalysis B: Environmental, 103 (1-2):109–115pp.

Drouiche M., Le Mignot V., Lounici H., Belhocine D., Grib H., Pauss A. and Mameri N., 2004, A compact process for the treatment of olive mill wastewater by combining UF and UV/H_20_2 techniques, Desalination, 169:81-88pp.

Ekpete O.A. and Horsfall M., 2011, Preparation and characterization of activated carbon derived from fluted pumpkin stem waste, Research Journal of Chemical Sciences, 1(3):10–17pp.

El-Abbassia, A., Kiai,H., Hafidi, A., Garcia-Payo, M.C. and Khayet,M., 2012**,** Treatment of olive mill wastewater by membrane distillation using polytetrafluoroethylene membranes, Separation and Purification Technology, 98: 55–61pp.

El-Sheikh. A. H., Al-Degs Y. S, Nevman A. P., and Lynch D. E., 2007, Oxidized activated carbon as support for titanium dioxide in UV-assisted degradation of 3-chlorophenol, Separation and Purification Technology, 54:117–123pp.

Foo K.Y. and Hameed B.H., 2010, Decontamination of textile wastewater via TiO_2/activated carbon composite materials, Advances in Colloid and Interface Science, 159:130–143pp.

REFERENCES(continued)

Fu L., You S.L., Zhang G.Q., Yang F.L. and Fang X.H., 2010, Degradation of azo dyes using in-situ Fenton reaction incorporated into H_2O_2-producing microbial fuel cell, Chemical Engineering Journal, 60:164–169pp.

Galiatsatou P., Metaxas M., Arapoglou D. and Kasselouri-Rigopoulou V., 2002, Treatment of olive mill waste water with activated carbons from agricultural by-products, Waste Management, 22:803–812pp.

Glaze W.H., Yiishyan L. and Joon-WunK.,1995, Advanced oxidation processes. A kinetic model for the oxidation of 1,2-Dibromo-3-chloropropane in water by the combination of Hydrogen Peroxide and UV Radiation, Ind. Eng. Chem. Res., 34: 2314—2323pp.

Gray N. F., 2005, Water Technology: An Introduction for Environmental Scientists and Engineers (2nd Edition), Elsevier Science & Technology Books, ISBN 0750666331, Amsterdam, The Netherlands.

Gupta, V.K., Ali, I., Saleh, T.A., Nayaka, A. and Agarwal, S., 2012, Chemical treatment technologies for waste-water recycling, The Royal Society of Chemistry, 2: 6380–6388pp.

Gu L. , Chen Z., Sun., C., Wei B. and Yu X., 2010, Photocatalytic degradation of 2, 4-dichlorophenol using granular activated carbon supported TiO_2, Desalination, 263:107–112pp.

Hamdi, M., 1991, Effects of agitation and pretreatment on the batch anaerobic digestion of olive mill wastewater. Biores. Technol.,36:173–178pp.

Huang D., Miyamoto Y., Matsumoto T., Tojo T.,Fan T., Ding J.,Guo Q., and Zhang D., 2011, Preparation and characterization of high surface area TiO2/activated carbon by low temperature impregnation, Separation and Purification Technology, 78:9–15pp.

Hsin-Tsung, C., Jee-Gong, C., Djamaladdin, G.M. and Lin, M.C., 2008, Computational study on kinetics and mechanisms of unimolecular decomposition of succinic acid and its anhydride, J. Phys. Chem., 112: 6621–6629pp.

REFERENCES(continued)

İnan, H., Dimoglo, A., Şimşek, H. and Karpuzcu, M., 2004, Olive oil mill wastewater treatment by means of electro-coagulation, Separation and Purification Technology 36: 23–31pp.

Kalderis D., Bethanis S., Paraskeva P., and Diamadopoulos E., 2008, Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times, Bioresource Technology, 99:6809–6816pp.

Khoufi S., Aloui F. and Sayadi S., 2006, Treatment of olive oil millwastewater by combined process electro-Fenton reaction and anaerobic digestion, Water Research,40:2007-2016pp.

Kim, K. and Ihm, S., 2011, Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review, Journal of Hazardous Materials, 186:16–34pp.

Kim J.R., Cheng S., Oh S.-E. and Logan B.E., 2007, Power generation using different cation, anion, and ultrafiltration membrane in microbial fuel cells. Environ. Sci. Tech.,41: 1004-1009pp.

Kim, J. Sohn, M., Kim, D., Sohn, S., and Kwon, Y., 2001, Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu^{2+} ion, Journal of Hazardous Materials, 85(3):301–315pp

Lafia W.K., Shannak B., Al-Shannag M., Al-Anber Z. and Al-Hasan M., 2009, Treatment of olive mill wastewater by combined advanced oxidation and biodegradation, Separation and Purification Technology,70:141–146pp.

Levec, J., and Pintar, **A.**, 2007, Catalytic wet-air oxidation processes: A review, Catalysis Today, 124: 172–184pp.

REFERENCES(continued)

Li Y., Lu A., Ding H., Wang X., Wang C., Zeng C. and Yan Y., 2010, Microbial fuel cells using natural pyrrhotite as the cathodic heterogeneous Fenton catalyst towards the degradation of biorefractory organics in landfill leachate, Electrochemistry Communications,12:944–947pp.

Liu S., Sun S., and Huang Z., 2010, Carbon spheres/activated carbon composite materials with high Cr (VI) adsorption capacity prepared by a hydrothermal method, Journal of Hazardous Materials, 173(1-3):377-383pp.

Logan B.E., Hamelers B., Rozendal R.A., Schroder U., Keller J., Freguia S., Aelterman P., Verstraete W. and Rabaey K., 2006, Microbial fuel cells: methodology and technology. Environ.Sci. Technol. 40: 5181-5192pp.

Lvovich, M. I., 1979, World water resources, present and future, GeoJournal, (5)3: 423–43pp.

Maity S.K, Rana M.S., Srinivas B.N., Bej S.K., Murali Dhar G. and Prasada Rao T.S.T., 2000, Characterization and evaluation of ZrO_2 supported hydrotreating catalysts, Journal of Molecular Catalysis A: Chemical, 153:121–127pp.

Malaeb L., Katuri K. P., Logan B.E., Maab H., Nunes S.P. and Saikaly P.E., 2013, A hybrid Microbial Fuel Cell Membrane bioreactor with a conductive Ultrafiltration Membrane biocathode for wastewater treatment, Environ. Sci. Technol., 47:11821−11828pp.

Minh D.P., Gallezot P. and Besson M., 2006, Degradation of olive oil mill effluents by catalytic wet air oxidation:1. Reactivity of p-coumaric acid over Pt and Ru supported catalysts, Applied Catalysis B: Environmental, 63:68–75pp.

Nowicki, P., Pietrzak, R., and Wachowska, H., 2010, Sorption properties of active carbons obtained from walnut shells by chemical and physical activation, Catalysis Today, 150(1-2):107–114pp.

REFERENCES(continued)

Ovejero, G., Rodriguez A., Vallet, A., and Garcia, J., 2013, Catalytic wet air oxidation of a non-azodye with Ni/MgAlO catalyst, Chemical Engineering Journal, 215-216:168–173pp.

Pariente M.I., Martinez F., Melero J.A., Botas J.A., Velegraki T., Xekoukoulotakis N., and Mantzavinos D., 2008, Heterogeneous photo-Fenton oxidation of benzoic acid in water: Effect of operating conditions, reaction by-products and coupling with biological treatment, Applied Catalysis B: Environmental, 85(1- 2):2–32pp.

Puma G.L., Bono A., Krishnaiah D., and Collin J.G., 2008, Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: A review paper, Journal of Hazardous Materials, 157(2-3):209–219pp.

Rambabu R., Azargohar R., Dalai A.K., and Adjaye J., 2013, Evaluation and comparison of enrichment efficiency of physical/chemical activations and functionalized activated carbons derived from fluid petroleum coke for environmental applications, Fuel Processing Technology, 106:501–510pp.

Ramos-Cormenzana, A., Juarez-Jimenez, B. and Garcia-Pareja, M.P., 1996, Antimicrobial activity of olive mill waste-waters (alpechin) and biotransformed olive oil mill wastewater, International Biodeterioration & Biodegradation 38: 283–290.

Rashed, M.N., 2013, Adsorption technique for the removal of organic pollutants from water and wastewater, organic pollutants monitoring, Risk and Treatment, 7:167-194.

Rabaey K. and Verstraete W., 2005, Microbial fuel cells: novel biotechnology for energy generation, Trends Biotechnol, 23:291–298pp.

Ramirez J. H., Maldonado-Hodar F. J., Perez-Cadenas A. F., Moreno-Castilla C., Costa C. A., and Madeira L. M., 2007, Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts. Applied Catalysis B: Environmental 75:312–323pp.

REFERENCES(continued)

Rey A., Faraldos M. , Casas J.A., Zazo J.A., Bahamonde A., and Rodriguez J.J., 2009, Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, Applied Catalysis B: Environmental, 86:69–77pp.

Ricciardi, M., 2006, Wastewater treatment by high efficiency heterogeneous photo-fenton process, The Third European Conference on Oxidation and Reduction Technologies for ex-Situ Treatment of Water, Air and Soil and in-Situ Treatment of Soil and Groundwater (ECOR-3), 90–91pp.

Rohr F.,Lindvag O.A., Holmen A. and Blekkan E.A.,2002, Fischer–Tropsch synthesis over cobalt catalysts supported on zirconia-modified alumina, Catalysis Today, 58:247–254pp.

Russell D. L., 2006, Practical Wastewater Treatment, John Wiley & Sons, Inc., ISBN-13: 978-0-471-78044-1, Hoboken, New Jersey, USA

Spuhler D. , Andrés J., and Pulgarin R.H.C., 2010, The effect of Fe^{2+}, Fe^{3+}, H_2O_2 and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing Escherichia coli K12, Applied Catalysis B: Environmental, 96(1-2):126–141pp.

Sciarria T. P., Tenca A., D'Epifanio A., Mecheri B.,Merlino G., 2013, Using olive mill wastewater to improve performance in producing electricity from domestic wastewater by using single-chamber microbial fuel cell, Bioresource Technology,147:246–253pp

Samer M., 2015, Biological and Chemical Wastewater Treatment Processes /1st Edition), InTech Europe, DOI: 10.5772/61250, Rijeka, Croatia.

Song H. and Lee S.Y., (2006) Production of succinic acid by bacterial fermentation. Enzyme Microb. Tech., 39: 352.-361pp.

Sonune, A. and Ghate, R., 2004, Developments in wastewater treatment methods, Desalination, 167: 55-63pp.

REFERENCES(continued)

Tang K. S., Teng T. T., Alkarkhi A. F. M., and Li Z., 2011, Sonocatalytic degradation of rhodamine B in aqueous solution in the presence of TiO2 coated activated carbon, APCBEE Procedia 1:110-115pp.

Tichit D., Coq B., Armendariz H. and Figueras F.,1996, One step sol-gel synthesis of sulfated zirconia catalyst,Catalysis Letters,38:109-113pp

Teh C. M. and Mohamed A.R., 2011, Roles of titanium dioxide and ion-doped titanium dioxide photocatalytic degradation of organic pollutants (phenolic compounds and dyes) in aqueous solution, Journal of Alloys and Compounds, 509:1648–1660pp.

Umar, M., Abdul, H., and Yusoff, M., 2010, Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate, Waste Management, 30-11:2113–2121pp.

Ward D.A. and Ko E.I., 1995, Prepering catalyst materials by the Sol-Gel Method, Ind.Eng.Chem.Res.,34:421-433pp.

Wang X., Cheng S.A., Feng Y.J., Merrill M.D., Saito T. and Logan B. E., 2009, Use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells. Environ. Sci. Technol. 43, 6870-6874pp.

Wu X., Tan M., Tian S., Song F., Ma Q., He Y., Yang G., Tsubaki N.and Tan Y., 2019, Designing ZrO_2-based catalysts for the direct synthesis of isobutene from syngas: The studies on Zn promoter role, Fuel, 243: 34-40pp.

Yang T., and Lua A., 2003, Characteristics of activated carbons prepared from pistachio-nut shells by physical activation., Journal of Colloid and Interface Science, 267:408–417pp.

Yang, M., 2011, A current global view of environmental and occupational cancers, Journal of Environmental Science and Health, Part C, 29:223–249pp.

REFERENCES(continued)

Yanbiao L., Jinhua L., Baoxue Z., Xuejin L., Hongchong C.,Quanpeng C., Zhongsheng W., Lei L., Jiulin W. and Weimin C., 2011, Efficient electricity production and simultaneously wastewater treatment via a high-performance photocatalytic fuel cell., Water Research., 45:991 -3998pp.

Zeikus, J.G., Jain, M.K., Elankovan, P., 1999, Biotechnology of succinic acid production and markets for derived industrial products, Appl Microbiol Biotechnol 51: 545-552pp.

Zhu X. and Logan B.E., 2013, Using single-chamber microbial fuel cells as renewable power sources of electro-Fenton reactors for organic pollutant treatment, Journal of Hazardous Materials 252– 253: 198– 203pp.

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