T.R.
EGE UNIVERSITY
Graduate School of Applied and Natural Science

COMPARATIVE STUDY OF ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF PHARMACEUTICAL WASTEWATER

MSc THESIS

Özlem BERKÜN OLGUN

Chemical Engineering Department

İzmir
2019

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Özlem BERKÜN OLGUN tarafından yüksek lisans tezi olarak sunulan " İlaç Endüstrisi Atık Suyunun İleri Oksidasyon Yöntemleri ile Karşılaştırmalı Olarak Arıtımı" başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 02/12/2019 tarihinde yapılan tez savunma sınavında aday oybirliği/~~oyçokluğ~~u ile başarılı bulunmuştur.

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E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum "İlaç Endüstrisi Atık Suyunun İleri Oksidasyon Yöntemleri ile Karşılaştırmalı Olarak Arıtımı" başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

09/12/2019

İmza

Özlem BERKÜN OLGUN

ÖZET

İLAÇ ENDÜSTRİSİ ATIK SUYUNUN İLERİ OKSİDASYON YÖNTEMLERİ İLE KARŞILAŞTIRMALI OLARAK ARITIMI

OLGUN, Özlem BERKÜN

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Aralık 2019, 80 sayfa

Bu çalışmada İstanbul'da bulunan bir ilaç fabrikasından temin edilen atık suyun arıtılması, ileri oksidasyon yöntemlerinden foto-Fenton benzeri ve katalitik ıslak hava oksdasyonu yöntemleri ile karşılaştırılmalı olarak incelenmiş ve optimum reaksiyon koşulları belirlenmiştir. Her oksidasyon yönteminde de kütlece 1:10 oranında hazırlanan aktif karbon (AK) destekli Fe/AK ve $LaFeO_3$/AK katalizörleri test edilmiş ve uygun olduğu belirlenen katalizör ile optimizasyon deneyleri yapılmıştır. Hazırlanan katalizörler Taramalı Elektron Miroskopu, Brauner Emmett Teller yöntemleri ile karakterize edilmiştir.

İlk olarak katalizör seçimi deneyleri yapılmış ve Fe/AK katalizörünün her iki yöntemde de de daha uygun olduğu belirlenmiştir. Katalizör seçimi deneylerinin ardından her bir ileri oksidasyon yönteminde en yüksek performansı gösteren katalizör varlığında (Fe/AK), optimum reaksiyon koşullarının belirlendiği parametrik çalışmalar yürütülmüştür. Yapılan parametrik çalışma sonuçlarının ışığında Minitab Deneysel Dizayn programı kullanılarak yapılması gereken deneyler için deney planı oluşturulmuştur.

Bu deneylerin verileri de göz önüne alınarak, foto-Fenton benzeri yöntemi için optimum koşullar; 2.0 g/L katalizör yüklemesi, pH=4.5 değeri ve hidrojen peroksit konsantrasyonu 0.32mM olarak belirlenmiştir. Optimum koşullar altında foto-Fenton benzeri yöntemiyle yapılan çalışmalar sonucunda kimyasal oksijen ihtiyacı (KOİ) giderimi yaklaşık % 72.7 olarak gözlemlenmiştir.

Islak hava oksidasyonu yöntemi için optimum koşullar; 3.0 g/L katalizör yüklemesinde, 50 °C ve pH 3.0 olarak belirlenmiş olup; KOİ giderimi yaklaşık % 85 olarak bulunmuştur.

En yüksek kimyasal oksijen ihtiyacı değerlerinin sağlandığı Islak Hava Oksidasyonu için toksisite analizi ve kinetik çalışma yapılmıştır. *Lepidium sativum* tohumları ile gerçekleştirilen toksisite analizinde kök uzamasındaki inhibisyon % 4.2 olarak hesaplanmıştır.

Islak hava oksidasyonunda prosesin KOİ giderimi verilerinin iki adımdan oluşan birinci dereceden reaksiyon kinetiğine uyduğu ve aktivasyon enerjilerinin ilk adım ve ikinci adım için sırasıyla 25.7 kJ/mol ve 28.3 kJ/mol olduğu belirlenmiştir.

Anahtar kelimeler: aktif karbon, , atık su arıtımı, ilaç endüstrisi atıksu arıtımı, ileri oksidasyon yöntemleri, ıslak hava oksidasyonu, foto-Fenton benzeri oksidasyon

ABSTRACT

COMPARATIVE STUDY OF ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF PHARMACEUTICAL WASTEWATER

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MSc in Chemical Eng.
Supervisor: Assoc. Prof. Dr. Gülin ERSÖZ
December 2019, 80 pages

In this study, the treatment of pharmaceutical wastewater supplied from a pharmaceutical company in İstanbul has been investigated. The advanced oxidation methods comprising photo-Fenton like oxidation and catalytic wet air oxidation (CWAO) were applied to specify the optimum conditions. Both oxidation methods were performed in the presence of two different catalysts that were supported by Activated Carbon (AC) Fe/AC and $LaFeO_3$/AC, catalyst:1/10 by wt and with selection of the most effective catalyst type the optimization experiments were performed. The catalysts were characterized by Scanning electron Microscopy, and Brauner Emmett Teller methods.

Firstly, the catalyst screening experiments were applied, and Fe/AC catalyst was selected as most efficient catalyst for both methods. Then, the parametric studies were carried out in the presence Fe/AC to specify the optimum reaction conditions. Box Behnken statistical experiment design and the response surface methodology was used to investigate the effects of the independent variables on the response function and to determine the optimum conditions maximizing the percent removal of COD.

Accordance of the experiments data, the optimum conditions were determined as for catalyst loading 2.0 g/L, at pH 4.5 and hydrogen peroxide concentration was 0.32 mM. Under the optimum conditions, the degradation of the wastewater was observed as 72.7% for Photo-Fenton like oxidation study.

For the catalytic wet air oxidation method, the optimum conditions were determined as 3.0 g/L for catalyst loading at pH =3 and temperature of 50℃ and the degradation efficiency was found as around 85%.

Toxicity tests and kinetic study were performed for catalytic wet air oxidation which was determined to be the most efficient one among the advanced oxidation methods tested in this study. The toxicity tests with *Lepidium sativum* showed that the growth inhibition was 4.2.% after the treatment.

The COD degradation during the CWAO process followed two step first-order reaction kinetics. According to calculated parameters from linearized form of Arrhenius equation activation energies for first and second steps were approximately 25.7 kJ/mole and for slow step 28.3 kJ/mole, respectively.

Keyword: activated carbon, pharmaceutical industry wastewater treatment, treatment of wastewater, advanced oxidation methods, catalytic wet air oxidation, photo-Fenton like oxidation

PREFACE

As the world moves further into lack of water, trying new ways to rescue one of the part of the world is one of the best thing in my education and career life. Clear and pure water is the most important thing in the life. To keep the water in safe and clear must be the most important thing for all people from this point which is considered the beginning of the end for the world. In truth, I could not have achieved my current level of success without a strong support group. First of all, my parents and teachers who supported me with love and understanding. And secondly, my committee members and employer, each of whom has provided patient advice and guidance throughout the research process. Thank you all for your unwavering support.

İZMİR
09/12/2019

Özlem BERKÜN OLGUN

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1. INTRODUCTION

Nowadays pharmaceutical contaminants are considered as emerging environmental problems due to their continuous discharge to the aquatic ecosystem. The presence of pharmaceutical pollutants even at very low concentrations including chemical compounds and active pharmaceutical ingredients in the aquatic environment in the long term causes a potential risk for the environment and human health. Consequently, there is a continuously increasing attention for the treatment of this kind of wastewater (Klavarioti et al., 2009; Bredhult et al., 2007).

The most common routes by which pharmaceutical contaminants enter the environment are through domestic, industrial or hospital effluents or through the effluents from waste water treatment plants where pharmaceuticals are incompletely removed.

A wide range of methods including biological oxidation, photolysis, nano filtration, reverse osmosis, and adsorption have been used for the treatment of pharmaceutical wastewater. However, it is known that pharmaceuticals are persistence against biological degradation and most of the traditional treatment methods are not advanced to treat the water. Classic physical-chemical techniques and conventional microbiological techniques cannot totally treat micro pollutants. Many methods have been limited by sludge generation, inefficient removal, high costs (Chatzitakis et al., 2008).

Many kinds of conventional treatment techniques can be used to treat water containing pharmaceutical compounds. However, taking account into consideration of diverse nature of pollutant and low efficiencies of existing conventional methods, Advanced Oxidation Processes (AOPs) seem to be capable of giving more efficient treatment in better results.

Advanced oxidation processes are based on the intermediacy of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products.

Within the advanced oxidation processes, wet air oxidation, Fenton and photo-Fenton-like processes are the most effective methods for the treatment of pharmaceutical wastewater. AOPs can be used as pretreatment or post-treatment for biological systems, too.

In AOPs, the photo-Fenton-like oxidation method is a widely preferred method in order to reduce the various organic and inorganic components. Using the light source in the Fenton reaction leads the mineralization of organic compounds in a short time. Ultraviolet and visible light can be used in this method. In literature, there are various studies on photo-Fenton-like oxidation that have been employed to treat pharmaceutical containing wastewaters (Orak et a., 2017; Orak et al, 2016; Epold, 2015; Turbay, 2013).

Wet air oxidation is one of the important advanced oxidation processes due to the capability of destroying of complex organic and inorganic pollutants when compared to conventional physical, chemical and biological methods. Therefore, the method is very popular for removal of organic contaminants from wastewater. In literature, there are various studies on catalytic wet air oxidation that have been used to treat pharmaceutical containing wastewaters (Palas et al., 2019; Sun, 2013; Quesada-Peñate et al, 2012).

As mentioned above, the treatment of pharmaceuticals in the wastewater has been widely studied in literature, but due to the extremely diversified structure of pharmaceutical pollutants, their unsaturated/saturated character, the presence of various functional groups with different side chains, there is still need for further study of the fate and the removal mechanisms involved in industrial pharmaceutical waste waters.

The main objective of this study is to propose an eco-friendly, sustainable and innovative method for the treatment of pharmaceutical industry wastewater. For this purpose, two different advanced oxidation processes; photo-Fenton like and catalytic wet air oxidation processes were tested, and the efficiencies were compared in the presence of two prepared catalysts which are Fe/Activated Carbon and $LaFeO_3$/ Activated Carbon. The use of Fe/Activated Carbon and $LaFeO_3$/ Activated Carbon catalysts in advanced oxidation processes in the treatment of pharmaceutical wastewater and the comparison of the efficiencies of the two AOPs constitute the main innovative approaches of the present thesis.

2. THEORETICAL BACKGROUND

2.1. Pharmaceutical Wastewaters

Pharmaceuticals are a structurally diverse class of emerging contaminants that have been detected throughout the world, especially in wastewater impacted surface water, groundwater, and drinking water.

A large group of chemicals, such as pharmaceuticals, medicine compounds are used in the world for many years causing an increase in the amount pharmaceutical in the ecosystem and water. Pharmaceutical substances that are present in water are one of the important public and environment health problems.

Pharmaceutical wastewater has a complex composition and contains different kinds of organic pollutants such as, chemical oxygen demand (COD), Biochemical oxygen demand (BOD_5), NH_3-N, color, toxicity and other features (Li and Li, 2015).

To evaluate the effect of these pharmaceuticals in water. The World Health Organization has already researched scientific evidence to consider and evaluate this problem (Teixeira et al., 2016).

2.2 Water Quality Criteria

2.2.1 pH of Water

The pH value shows the presence of hydrogen (H^+) and hydroxyl ions (OH^-) in the water indicating if the medium is acidic, basic or neutral .pH highly affects the efficiency of processes. Water and wastewater can be classified as neutral, alkaline or acidic according to the following ranges:

$pH = 7$ neutral.

$pH > 7$ Alkaline.

$pH < 7$ Acidic.

(Arshad and Shakoor, 2017).

2.2.2 Electrical Conductivity (EC)

Conductivity is a measure of water’s capability to pass electrical flow. It depends on the dissolved ions in the water and their charge and movement. The more ions that are present, the higher the conductivity of water (Bauder et al., 2011).

2.2.3 Total Dissolved Solids (TDS)

Total dissolved solid is a measure of the combined total of organic and inorganic substances contained in a liquid. Presence of total dissolved solids in the water changes the properties of water. The amount of material dissolved in water including carbonate, chloride, bicarbonate, phosphate, sulfate, nitrate, sodium, calcium, magnesium, organic ions etc contributes to the TDS of water (Arshad and Shakoor, 2017).

The relationship between total dissolved solids and EC can be given as:

$$\text{TDS (mg/L)} = \text{EC (dS/m)} \times K$$

where, $K = 640$ in most cases (for EC: 0.5 -5 dS/m)

2.2.4 Total Suspended Solids (TSS)

Total suspended solids (TSS) are particles that are larger than 2 microns found in the water column. Anything smaller than 2 microns (average filter size) is considered as a dissolved solid. Total suspended solids are called as if there are existence of the particles in the water like as suspended. They can be microorganisms, algae, mineral particles and organic matter. Total suspended solids absorb heat from the water. So, the temperature of water getting higher, therefore dissolved oxygen level decreases in the water. All the suspended solids amount in the water is measured in milligrams per liter (mg/L) (Arshad and Shakoor, 2017).

2.2.5 Turbidity

Turbidity is defined as the degree to which light is scattered by particles suspended in a liquid. Turbidity can be caused by dissolved or total suspended solids. To adjust the water quality, turbidity is the most important parameter. It is very important risk for health to have high level of turbidity in drinking water. Because it causes diseases like gastrointestinal or digestion system. Turbid water will appear cloudy, murky, or otherwise colored, affecting the physical look of the water (Suarez and Lebron, 1993).

2.2.6 Color

The water color is an important decisive property to define water quality (whether the water consist pollutants or compounds or not) Water color is like a mirror to give a hint about the quality of water. Transparent water includes the dissolved solids at low level. To get the most accurate color, all suspended particles should be removed by filtration (Arshad and Shakoor, 2017).

2.2.7 Biochemical oxygen demand (BOD_5)

BOD_5 is the oxygen equivalent of organic matter. It is determined by measuring the dissolved oxygen used by microorganisms during the biochemical oxidation of organic matter in 5 days at 20℃.

2.2.8 Chemical oxygen demand (COD)

It is the oxygen equivalent of organic matter. It is determined by measuring the dissolved oxygen used during the chemical oxidation of organic matter in 2 hours.

2.3. Pharmaceutical Industry Wastewater Treatment

Wastewaters generated from the pharmaceutical industries vary not only in composition but also in quantity, by plant, season, depending on the raw materials and the processes used in the manufacturing of various pharmaceuticals. Pharmaceutical wastewaters are usually produced by chemical-synthetic process, and thus contain high levels of organic pollutants, bio-toxicity and salinity and thus usually a conventional treatment method cannot be not directly recommended.

The pharmaceutical industry employs a wide array of wastewater treatment and disposal methods. Most of the pollutant can be treated by chemical degradation and biodegradation. Many industrial wastewater treatment methods have been developed and applied for the treatment of pharmaceutical wastewater to get clean and reusable water for ground.

The wastewater treatment methods that can be applied are summarized in Table 2.1 (Gaehr et al., 2008).

Table 2.1. General Water Treatment Processes and Their Purposes

Water Treatment Process	Purpose
Conventional processes	
Coagulation/Flocculation	Form of large particles
Sedimentation	Particle settling and removal
Filtration	Removing algae, sediment, clay, organic/inorganic particles, and microorganisms Reducing the turbidity
Disinfection	Inactivate microorganisms
Air stripping	Remove volatile chemicals
Adsorption	Removing the taste and odor compounds, synthetic organic compounds, disinfection by-product precursors, and inorganic chemicals

Table 2.1. General Water Treatment Processes and Their Purposes- Continued

Other processes	
Advanced oxidation	Degradation of potentially remove organic chemicals, effective for disinfection
Ion exchange	Removing dissolved ionic constituents

2.3.1. Conventional Processes

The conventional processes are generally used to remove pollutants basically as preliminary treatment step.

Basically, adsorption is the physical process by performing as transfer from the liquid phase to the surface of a solid like a mass transfer. This transfer occurs on the boundary between the surfaces by chemical and physical coaction. Large surface area causes to get high adsorption level and high capacity of reactivity on the surface. Different types of materials with low cost such as tree bark, wood charcoal, saw dust, and other waste materials can be used as adsorbents (Chiban et al, 2011).

Disinfection methods can also be considered as conventional methods. Water disinfection causes removal of pollutants by deactivation or killing of pathogenic microorganisms. Disinfection methods can be applied by physically or chemically. Chemical disinfection methods are performed using chlorine, chlorine dioxide, ozone, halogens such as bromine, metals, phenols, alcohols etc. Disinfection methods can also be applied physically with ultraviolet light (UV), electronic radiation, gamma rays, sounds and heat.

Air stripping processes help to remove the chemicals which is called as volatile organic compounds. The air passes through the wastewater and volatile compounds are collected is been gas stream as these volatile compounds evaporate easily. This method usually has been used in treatment of ground water (National Service Center for Environmental Publications, 2012).

Coagulation/flocculation, wastewaters consist of negatively charged particles and with the addition of coagulants larger sludge forms from wastewaters in coagulatin/flocculation method, which allow us to remove pollutants. Coagulation is mostly in use for degradation of total suspended solids, biochemical oxygen demand, chemical oxygen demand and bacterial population (Semerjian and Ayoub, 2003).

The method in which the particles settle at the bottom of the solution due to gravity is called sedimentation and it is often used in combination with coagulation/ flocculation.

2.3.2. Advanced oxidation processes

The commonly employed treatment processes are not effective enough for complete removal of pharmaceuticals since they have low biodegradability.

Advanced oxidation processes (AOP) also have great interest for removal of pollutants from different industry wastewater. Treatment of pharmaceutical industry wastewater by advanced oxidation processes become very popular nowadays.

Advanced oxidation processes are defined as aqueous-phase oxidation processes based on the intermediacy of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms leading to the destruction of the target pollutant (Klavarioti et al., 2009).

Advanced oxidation processes are based on the oxidizing of pollutants into very small and harmless molecules by using hydroxyl radicals which have highly reactant with organic radicals. Although in the literature advanced oxidation processes have different classification, AOP’s are mainly classified according to production of hydroxyl radical’s mechanisms (Atalay and Ersöz, 2016; Sharma et al., 2011). There are many kinds of AOPs, such as wet air oxidation, supercritical water oxidation, Fenton reagent, photocatalytic oxidation, ultrasound oxidation, electrochemical oxidation and ozonation. The photochemical and the non-photochemical advanced oxidation processes are listed in Table 2.2.

Table 2.2. List of typical AOP systems

Non-photochemical	**Photochemical**
O_3/OH^-	H_2O_2/UV
O_3/H_2O_2	O_3/UV
O_3/US	O_3/H_2O_2/UV
O_3/GAC	H_2O_2/Fe^{2+} (photo-Fenton)
Fe^{2+}/H_2O_2 (Fenton system)	UV/TiO_2
Electro-Fenton	H_2O_2/TiO_2/UV
Electron Beam Irradiation	O_2/TiO_2/UV
Ultrasound (US)	UV/US
H_2O_2/US	
Wet air oxidation	

Advantages of Advanced Oxidation Processes (Sharma et al., 2011).

- Rapid reaction rates
- Small foot print
- Potential to reduce toxicity of organic compounds
- Mineralization of organics, i.e. conversion to salt and CO_2
- Does not concentrate waste for further treatment, such as membranes
- Easily Automated and Controlled
- Reduced Labor Input
- Does not create sludge as with physical chemical process or biological processes (wasted biological sludge)

Disadvantages of Advanced Oxidation Processes

- Capital intensive
- Complex chemistry must be tailored to specific application

- For some applications quenching of excess peroxide is required

Advanced oxidation processes are designed to both efficiently produce and use hydroxyl ions for these oxidation. They have a wide range of applications, mainly for oxidation of refractory compounds, TOC & COD reduction in:

- Gas effluent treatment
- Water reclaim / reuse / recycling
- Drinking water supplies
- Industrial & municipal wastewater
- Process water, ultra-pure water
- Electronic & pharmaceutical industry (Wang , 2012).

2.3.2.1. Photocatalytic Oxidation

Photocatalytic processes are also used for the degradation of the pollutants in recent years. In the process ultraviolet (UV) or visible light is used by a semiconductor. Photochemical oxidation, also known as ultraviolet photocatalytic oxidation, is a method combination of UV radiation and oxidant. Depending on the types of oxidants, photochemical oxidation can be categorized as UV/O_3, UV/H_2O, UV/H_2O_2/O_3 (Guo et al., 2017).

There are two different types of photocatalytic applications in water treatment: solar photocatalysis and photocatalytic systems equipped with artificial ultraviolet (UV) light. Both systems can be applied at ambient temperature to degrade various chemical and microbiological pollutants in water and air. As it utilizes of sunlight, solar photocatalysis technology is inexpensive, environmentally friendly, and universally applicable. The equipment needed is minimal and also appropriate for developing countries or remote sites with no access to electricity. Photocatalysis can be used to break down a wide variety of organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine resistant organisms), inorganic molecules such as nitrous oxides (NO_x) and, in combination with precipitation or filtration, can also remove metals (such as mercury). Due to this universal applicability, photocatalysis with nanoparticles as catalysts is used to reduce air pollution, in building materials for self-cleaning surfaces, in addition to water purification (Zhang et al., 2019).

2.3.2.2. Fenton Reagent Oxidation

Fenton's reagent involves the reaction between hydrogen peroxide and ferrous or ferric ions via a free radical chain reaction which produces hydroxyl radicals. The Fenton processed can eliminate the toxic compounds from the wastewater (Sharma et al., 2011).

During the Fenton Process side reactions are also possible. Hydroxyl radicals and hydrogen peroxide can give another oxidant radical such as HO_2*, which have also oxidizing ability of organic pollutants (Sharma et al., 2011).

$OH* + H_2O_2 \rightarrow H_2O + HO_2\boldsymbol{*}$

The general degradation mechanism of organic pollutants by Fenton reaction is shown below (Nidheesh et al. 2013):

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

$RH + HO* \rightarrow R* + H_2O$

$R* + Fe^{3+} \rightarrow R^+ + Fe^{2+}$

$Fe^{2+} + HO* \rightarrow Fe^{3+} + OH^-$

- **Photo-Fenton like oxidation**

Photo Fenton process is one of the advanced oxidation process. In this process of hydroxyl radicals are formed as a result of interaction of UV radiation and hydrogen peroxide or interaction of ferrous ions (or another catalyst), water and UV radiation (Sharma et al., 2011; Sahunin and Kaewboran, 2006):

$H_2O_2 + UV \rightarrow OH* + OH*$

$Fe^{3+} + H_2O + UV \rightarrow OH^* + Fe^{2+} + H^+$

$OH^* + \text{organic pollutants} \rightarrow \text{products}$

Electro-Fenton Process: Electrochemical Advanced Oxidation Processes (EAOPs) are a promising alternative because they are environmentally clean and can produce large amount of hydroxyl radicals under control of applied current. In these processes, the hydroxyl radicals can be produced by direct electrochemistry from water oxidation using high O_2 overvoltage anodes such as boron-doped diamond (BDD) or lead dioxide (PbO_2) anodes. Alternatively, hydroxyl radical production can take place in solution bulk through electrochemically assisted Fenton's reaction, where hydrogen peroxide is generated in situ from the two-electron reduction of O_2 on cathodes such as gas diffusion electrodes (GDEs), reticulated vitreous carbon (RVC) or graphite felt.

2.3.2.3. Catalytic Wet Air Oxidation

The wet air oxidation (WAO) method can be used to remove high levels of toxic and harmful compounds from wastewater. Wet air oxidation is a thermochemical process where hydroxyl radicals and other active oxygen species are formed at elevated temperatures and pressures (Luck, 1999). Due to the presence of a catalyst, high oxidation rates are achieved and consequently, one can use less severe reaction conditions (low temperature and pressure) to reduce chemical oxygen demand to the same degree as in the case of non-catalytic process.

The degradation mechanisms by WSO is complex, however, the general consensus is that the chemical reaction stage occurs mostly via free-radical reactions typically including initiation, propagation and termination reactions. Numerous reactions have been proposed, and the main reactions in the presence of organic compounds (RH) are listed as follows (Zhou and He, 2006).

$RH + O_2 \rightarrow HO_2^{\bullet} + R^{\bullet}$

$H_2O + O_2 \rightarrow HO_2^{\bullet} + {}^{\bullet}OH$

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

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

${}^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O$

$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2$

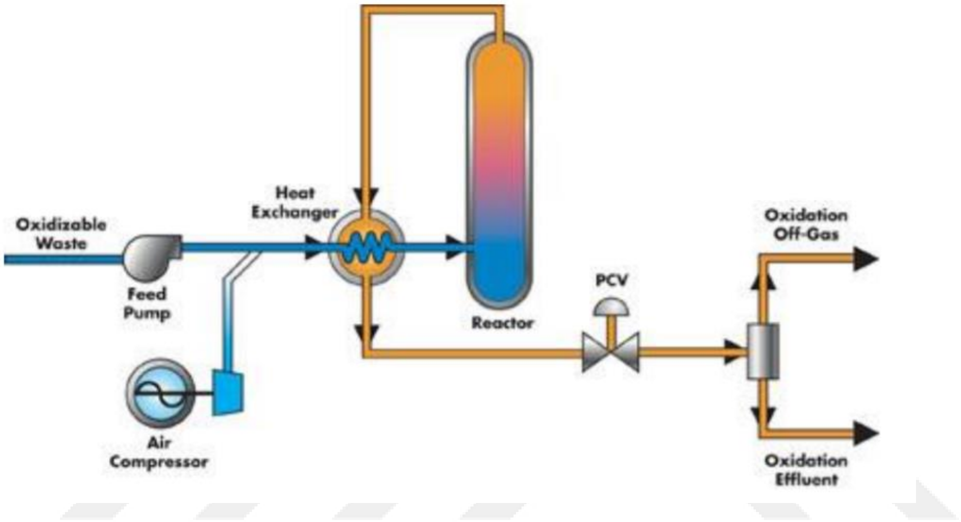


Figure 2.1. Catalytic Wet Air Oxidation Processes

2.3.2.4. Ozonation

Ozone is mostly a decolorization agent due to its high reactivity toward carbon-carbon double bonds. Although the ozonation assists to decrease the foaming ability and discoloration, a large amount of organic loading can stand as high chemical oxygen demand (COD) and total organic carbon (TOC) residuals.

2.3.2.5. Ion Exchange

Ion exchange is a common technique which is applied with using synthetic resins for treating the wastewater. The polymeric resins are commonly used in the ion exchange systems. Because the ions are transferred between the solid and liquid phases. The main disadvantage is the cost for the ion exchange processes (Rengaraj et al., 2001).

3. LITERATURE SURVEY

The studies in literature related with pharmaceutical wastewater treatment by photo-Fenton like oxidations, photocatalytic oxidations, and catalytic wet air oxidation with using mainly activated carbon catalysts were examined.

Some of these studies are explained below.

Yujie He et. al, performed a study on investigation of the effects of solar irradiation on degradation of pharmaceutical active compounds (PhACs) in wastewater. The study has been performed using immobilized TiO_2 as a catalyst. Experiments were planned in two main parts: photocatalytic oxidationt using TiO_2 and photolysis (no catalyst). They investigated the effect of solar irradiation on PhACs in wastewater using immobilized TiO_2, and to study the potential of this photocatalysis technique as a post-treatment process for wastewater effluent. Using sol gel method TiO_2 was immobilized on 200–500 m sand. In the presence of catalyst, the removal yield of the PhACs in pharmaceutical wastewater was reached to 100% for propranolol diclofenac active ingredient, and for carbamazepine approximately to 76%. The photodegradation pattern followed pseudo-first order kinetics. Photodegradation of PhACs followed pseudo-first-order kinetics, and the kinetic constant of photocatalysis was much higher than that of photolysis in the absence of a catalyst. They concluded that technique is a promising post-treatment process to improve water quality (Yujie He et al., 2016).

Alalm et. al, had a study on the treatment of the pharmaceuticals wastewater. They evaluated the photocatalytic activity of bare TiO_2 and TiO_2 immobilized on activated carbon (TiO_2/AC) for degradation of pharmaceuticals. namely amoxicillin, ampicillin, diclofenac, and paracetamol using solar irradiation. Amoxicillin and ampicillin were completely degraded by TiO_2/AC, while 89% of amoxicillin and 83% of ampicillin were removed by bare TiO_2. Similarly with TiO_2/AC higher removal of diclofenac (85%) and paracetamol (70%) were attained as compared to bare TiO_2. They concluded that photocatalytic degradation efficiency of pharmaceuticals was strongly dependent on the pH values and catalyst loading (Alalm et al., 2016).

Tokumura et al, applied the simple semi-theoretical models in the light of advanced oxidation processes (AOPs) in order to degrade the pharmaceutical compounds form the water. The application of advanced oxidation processes were performed in three different ways. First one was photo-Fenton process with a liquid-liquid reaction, the second one was TiO_2 photocatalytic oxidation process as a solid-liquid reaction, and the third way was a gas-liquid reaction which was pieced together ozone and hydrogen peroxide such as an oxidation. The best effective result of degradation efficiency was observed with the third type of application which is combination of ozone and hydrogen peroxide (Tokumura et al., 2016).

In 2015, Magureanu et al. studied on pharmaceutical wastewater treatment by using coagulation, Photocatalysis and Photo Fenton methods. FeCl3 as a coagulating agent was used as a pre-treatment step prior to in-situ dual process. The parametric optimization in case of in-situ dual process was carried out in batch mode under artificial UV-A irradiations. The biodegradability index (BOD5/COD) of wastewater increased from 0.172 to 0.71 after 5h of treatment via in-situ dual process. The field-scale applications of fixed-bed in-situ dual process using Fe-TiO_2 composite beads were validated from successful treatment (~80% COD reduction) of real wastewater in less than 120 min in a pilot-scale once-though cascade reactor under natural solar irradiations. Moreover, Fe-TiO_2 composite beads represented an outstanding recyclability efficiency (>70 recycles) without depicting any significant reduction in their activity as confirmed through various characterization techniques (Magureanu et al., 2015).

The degradation of chlorhexidine digluconate (CHD) that is used in antibiotic as an active ingredient in aqueous solution, was performed by applying the heterogeneous photocatalysis. The most important aim of the study with supporting of calcium alginate beads was application of immobilized TiO_2. Immobilization is selected to decrease the limitations of heterogeneous photocatalysis. By XRD TiO_2 nano particle characterization was determined by scanning electron microscopy cand X-ray spectroscopy (SEM/EDAX). The evaluation of the performance of free TiO_2

suspension has been done. And additionally, the degradation efficiency of TiO_2 which was produced by impregnation method on the alginate beads (TIAB) had been observed. Even though, the study shows the degradation efficiency decreases while using TIAB, while recycling of the catalyst is good in terms. In this study the kinetic parameters were also determined (Sarkar et al., 2015).

In 2006 R. Molinari a et. al, had a study on the photo degradation of different pharmaceuticals which include furosemide, hydrochloride, ofloxacine, phenazone, naproxen, carbamazepine and clofibric acid in aqueous medium at various pH values by using a batch photo reactor and a photocatalytic membrane reactor. The catalyst was selected as Polycrystalline TiO_2. In this study different membranes were tested also. Due the characterization properties of the catalyst, several amounts of adsorption rates on the substrate surface are observed while changing the pH value. For membrane system the pharmaceutical removal ingredients were selected as Furosemide and ranitidine. In this section, the hybrid membrane system was decided as a treatment method. The degradation efficiency level indicated that applying hybrid membrane photo reactor system was not adequate for the chemical treatment of the wastewater. (Molinari et al., 2006).

Yuan et al. had been carried out the study on the catalytic wet oxidation of pharmaceutical wastewater. The pollutant sludge of the water was removed by Cu/Ce catalyst in a batch reactor. According to the experimental results, the catalyst shows good catalytic performance which was generated by co-precipitating with nitrate. With the presence of the catalyst and getting higher concentration of the catalyst, increased the COD removal. COD degradation rate was found to be 75% at 260 ◦C for 60 min with an initial oxygen pressure at 1.0 MPa and the catalyst loading of 10 g/L. These results show that applying the catalytic wet oxidation of pharmaceutical pollutants with the catalyst of Cu/Ce is aneffective method degradation (Yaun et al., 2018).

Szabados et al, investigated the catalytic wet oxidation processes for the removal of paracetamol. The study was tested with Pt, Ru, Ir containing Ti monoliths. The monometallic Pt and Ru/Ti catalysts were the most active, even below 150 °C. RuO_2/Ti had the highest specific activity. They concluded that the wet oxidation of paracetamol could be successfully performed at 150 °C and ~30 bar total pressure during two hours with commercial precious metal coated Ti mesh, used as monolith catalysts (Szabados et al., 2017).

Zhan et al. investigated the pretreatment of a high concentration pharmaceutical wastewater by catalytic wet air oxidation process. Parametric studies were performed to examine the effects of catalyst type, temperature of the reaction medium, pH value of water and partial pressure of oxygen for the reaction on the degradation efficiencies. According to the effect of catalyst type experiments, the best efficiency had been observed with the catalysts that had been prepared by co-precipitation method. They concluded that the biodegradability of the wastewater improved greatly after CWAO, the ratio of BOD5/COD increased less than 0.1-0.75 when treated at 220 °C (Zhan et al., 2013).

Benitez et. al, investigated wet air oxidation method on four selected pharmaceuticals (metoprolol, naproxen, amoxicillin, and phenacetin) individually dissolved in ultra-pure water, at varying the temperature and oxygen pressure. Due to the moderate (amoxicillin) or low (metoprolol, naproxen, and phenacetin) efficiency found in the oxidation of these pollutants, a catalytic wet air oxidation (CWAO) process was then tested using a platinum catalyst supported on multi-walled carbon nanotubes (CNT). In most experiments, the removals were in the sequence: amoxicillin > naproxen > phenacetin (Benitez et al., 2011).

4. EXPERIMENTAL

In this thesis, treatment of pharmaceutical industry wastewater by two different advanced oxidation methods was realized. The experimental study can be investigated in two steps;

- Preparation and characterization of catalysts
- Application of advanced oxidation methods

The schematic presentation of experimental study is shown in Figure 4.1

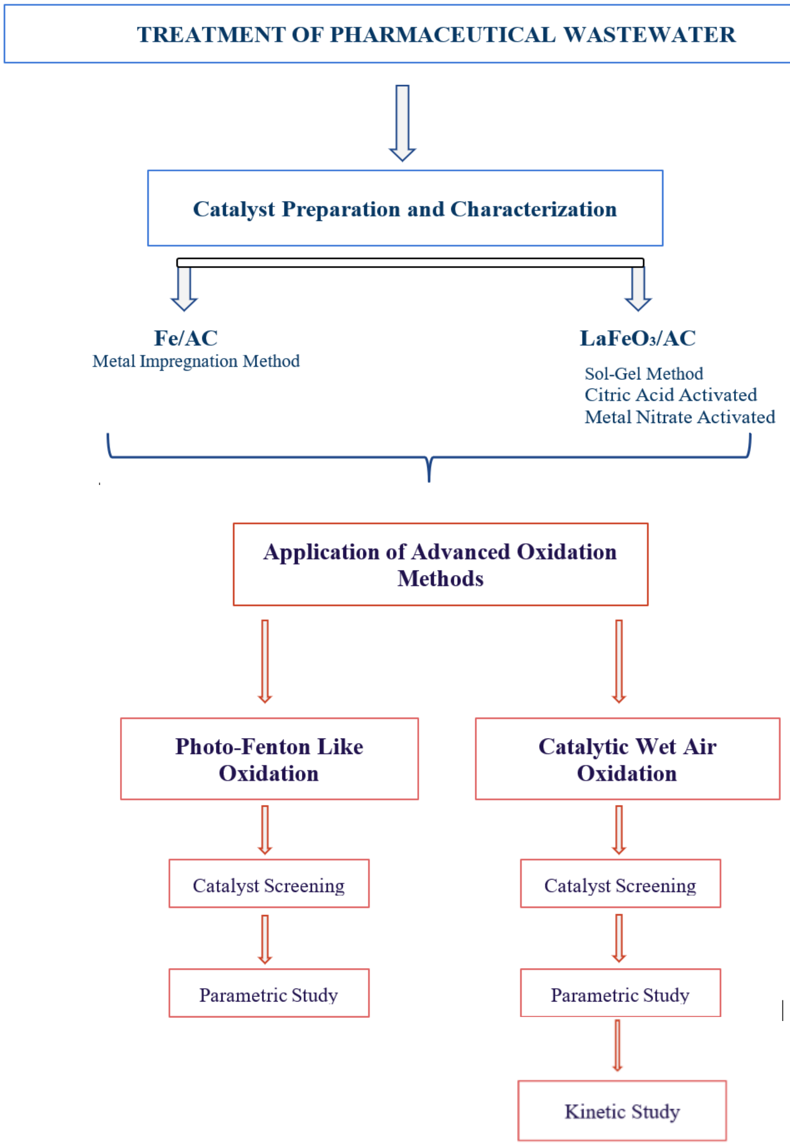


Figure 4.1. Schematic presentation of experimental study

4.1 Properties of Pharmaceutical Wastewater

The pharmaceutical wastewater which had been used in this study obtained from a pharmaceutical company in İstanbul. The company has the largest product portfolio in the sector, approximately 350 products by developing its own products. The product range includes antianemic, antibacterial/antiviral, dermatology, endocrine, metabolism, gastrointestinal, cardiovascular, as well as food supplements, vitamins and etc. Wastewater was collected from the factory in different periods. Since different batches were obtained, the initial characteristic properties of the wastewater were varied.

Table 4.1. The characteristics of wastewater from the pharmaceutical industry

Parameter		**Initial**
COD (ppm)		1400-1900
TOC (ppm)		230
pH		6
Dissolved Oxygen (mg/L)		0.50
Turbidity (NTU)		215
Color (m^{-1})	436 nm (yellow)	6.1
	525 nm (red)	3.1
	620 nm (blue)	1.8

At the factory, biological treatment is applied to the waste water. Approximetly, the effluent of the system has COD value around 250 ppm.

4.2. Preparation of Catalysts

Fe/AC and $LaFeO_3$/AC (AC: Activated Carbon) catalysts were prepared and used in the advanced oxidation processes. The catalysts were prepared according to the procedures in literature (Zazo et al., 2009). The main steps of the catalyst preparation are presented in Figure 4.2.

4.2.1 Fe/AC Catalysts Preparation

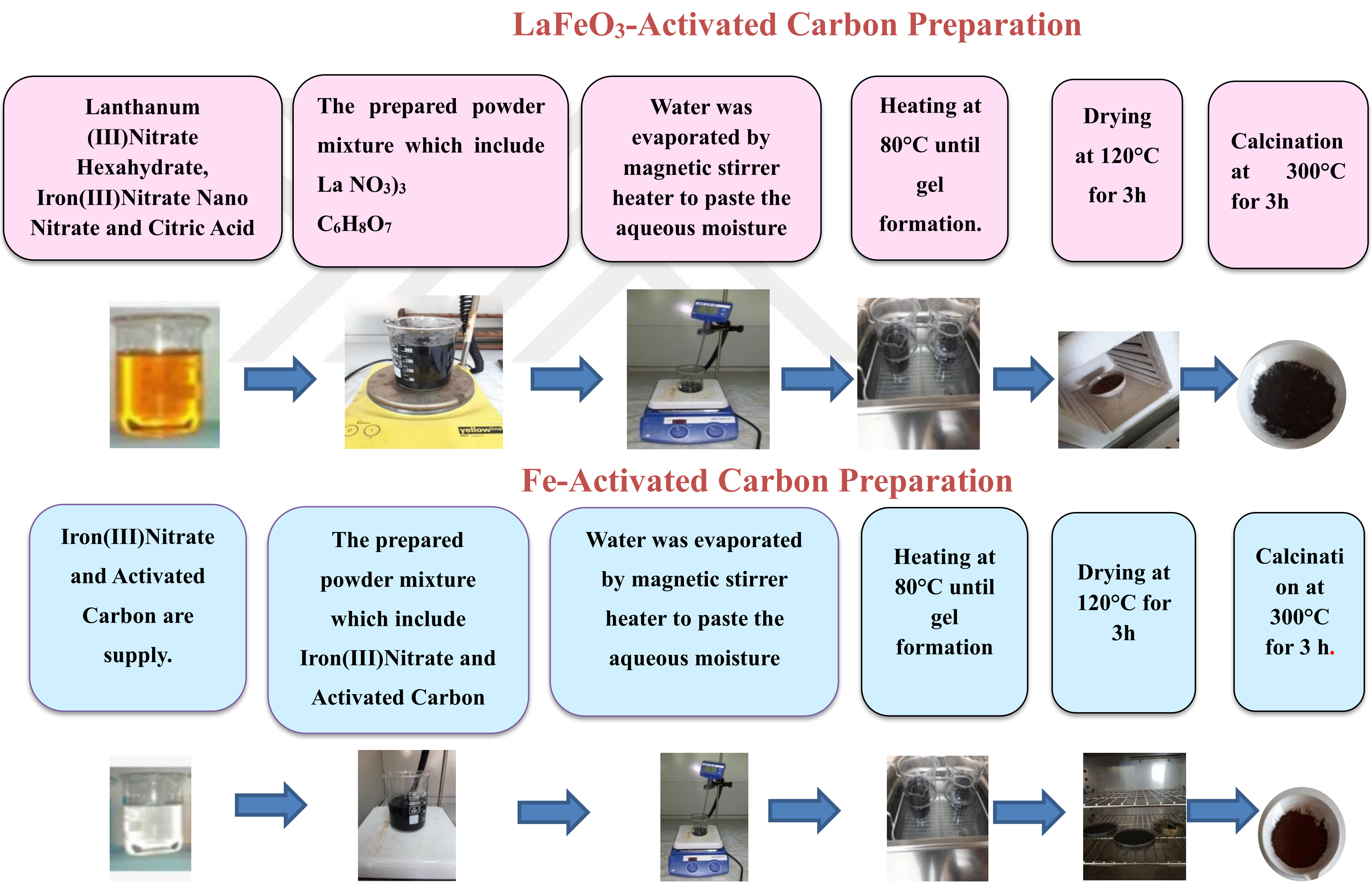
The general procedure for the preparation of 5 grams of Fe/AC catalyst is as follows:

- 3.62 g of Fe $(NO_3)_3.9H_2O$ is dissolved 100 ml of water.
- 4.5 grams activated carbon is added into the solution.
- The mixture is heated at 80°C under stirring to evaporate the water.
- The catalysts are dried in oven.
- The catalysts are calcined at 300°C for 3 hours.

4.2.2 $LaFeO_3$ /AC Catalysts Preparation

The general procedure for the preparation of 2 grams of $LaFeO_3$/AC catalyst is as follows:

- 0.346 g of $La(NO_3)_3.6H_2O$, 0.3232 g of $Fe(NO_3)_3.9H_2O$, and 0.504 g of $C_6H_8O_7$ are dissolved in 100 ml of water.
- 1.8 grams of activated carbon is added into the solution.
- The mixture is heated at 80°C under stirring until gel formation is observed.
- The catalysts are dried in oven.
- The catalysts are calcined at 300°C for 3 hours.



LaFeO$_3$-Activated Carbon Preparation

Lanthanum (III)Nitrate Hexahydrate, Iron(III)Nitrate Nano Nitrate and Citric Acid

The prepared powder mixture which include La NO$_3$)$_3$ $C_6H_8O_7$

Water was evaporated by magnetic stirrer heater to paste the aqueous moisture

Heating at 80°C until gel formation.

Drying at 120°C for 3h

Calcination at 300°C for 3h

Fe-Activated Carbon Preparation

Iron(III)Nitrate and Activated Carbon are supply.

The prepared powder mixture which include Iron(III)Nitrate and Activated Carbon

Water was evaporated by magnetic stirrer heater to paste the aqueous moisture

Heating at 80°C until gel formation

Drying at 120°C for 3h

Calcination at 300°C for 3 h.

Figure 4.2. LaFeO$_3$/AC and Fe/AC catalyst preparation steps

4.3 Characterization

The surface morphologies of the catalysts were investigated by Scanning Electron Microscopy with Energy Dispersive Spectrometry in EGE-MATAL (Ege University Application and Research Center for Testing and Analysis) by using a Thermo Scientific Apreo scanning electron microscope. The elemental distribution on the catalyst surface was monitored by the mapping mode of the scanning electron microscope.

Brunauer–Emmett–Teller, BET, surface area of the catalyst which showed the highest performances in AOPs was determined by using AUTOSORB-6B Surface area analyzer in Middle East Technical University Central Laboratory.

4.4. Application of Advanced Oxidation Processes

4.4.1. Photo-Fenton Like Oxidation

4.4.1.1. Experimental Setup and Procedure

The Photo-Fenton like batch experiments were carried out in 250 mL glass beaker using a magnetic stirrer in a UV cabin (Camag brand and Long-wave UV light 366 nm) for 2 hours (30 minutes in the dark side, 90 minutes in UV light). The experimental system is illustrated in Figure 4.3.

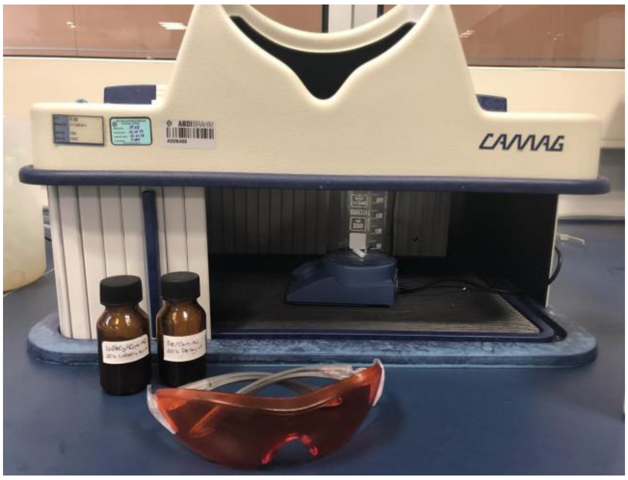


Figure 4.3. Experimental set up of Photo-Fenton like Oxidation

For a typical run following procedure is applied:

- 250 ml of pharmaceutical wastewater is filtered and filled into beaker
- pH is adjusted to the desired value
- the required amount of catalyst is added into the reaction medium and continuous mixing is maintained for 30 minutes in darkness (without UV light).
- at the end of 30 minutes, required amount of H_2O_2 is added and UV light is turned on for 90 minutes.
- 5 ml samples are taken to analyze

4.4.1.2. Experiments

In order to select the most efficient catalyst for Photo-Fenton Like Oxidation experiments, the following experiment series (Figure 4.4) were performed as catalyst screening experiments.

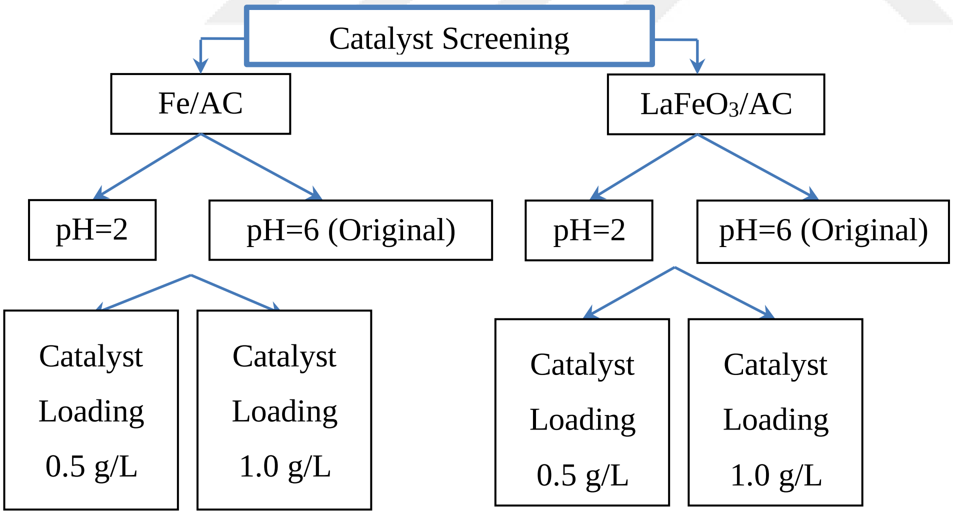


Figure 4.4. Summary of Catalyst Screening Experiments for Photo-Fenton Like Oxidation

After selection of most suitable catalyst a parametric study was planned according to response surface method, Box–Behnken design. This methodology permits estimating not only the effect of the operating parameters on the treatment efficiency but also the interaction between them, reducing the number of experiments (Diez et al, 2018; Asaithambi et al. 2016). Three factors (pH, catalyst loading and initial hydrogen peroxide concentration) were defined. The proposed reaction conditions are given in results and discussion section.

4.4.2. Catalytic Wet Air Oxidation

4.4.2.1. Experimental Setup and Procedure

The catalytic wet air oxidation experiments are performed as a semi batch reactor with a bubble column which is 500 ml as volume (*h*=0.5 m; *D=0.*35 m). The reactor material is stainless steel. The system had a PID controller (1/32DIN temperature controller) to heat to the desired temperature by electrical wires wrapped around the reactor and to set the temperature. In order to restrain the heat loss from the reactor, it was insulated with glass wool. At top of the reactor, there is a condenser. And in the system, there is a compressed dry air tube. The air pressure and air flow are adjusted with a valve which is connected to the air tube.

For a typical run, 300 mL of wastewater is charged and heated to the desired temperature by heating elements around the reactor and the reaction temperature is controlled by a PID controller. Air is fed continuously and distributed into the reactor via a sparger placed at the bottom of the reactor. There is no need to have a stirrer to mix the reaction mixture and catalyst particles. The samples are taken and analyzed at the end of experiment.

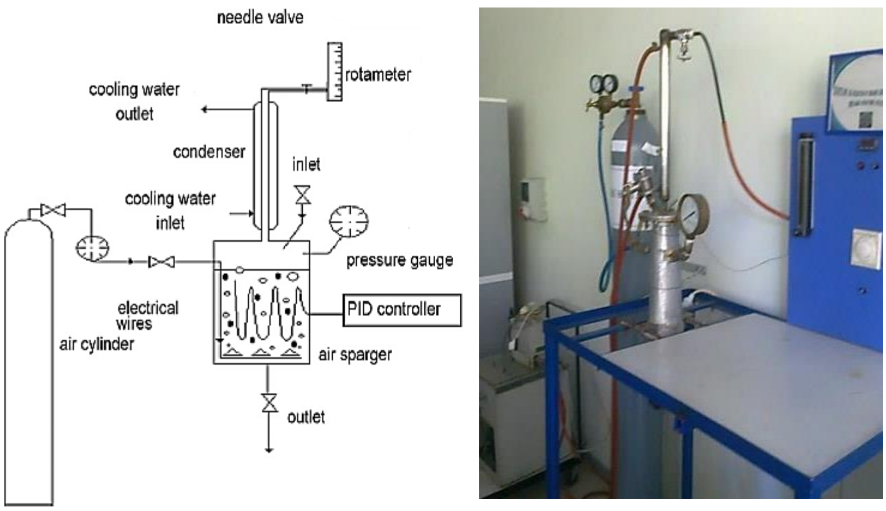


Figure 4.5. Experimental setup of CWAO process.

4.4.2.2. Experiments

Preliminary experiments were performed to evaluate the most suitable catalyst Fe/AC and $LaFeO_3$/AC catalysts' activities were tested and compared according to the experimental plan shown in Figure 4.6.

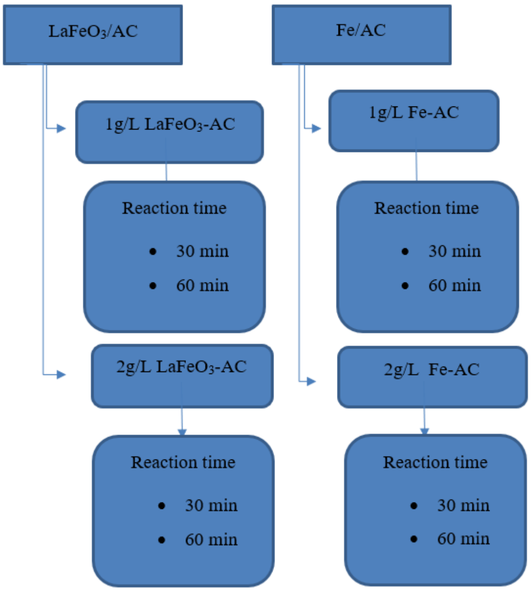


Figure 4.6. Experimental plan for the catalytic wet air oxidation screening study (T=50°C, pH=6)

After selection of most suitable catalyst a parametric study was planned according to response surface method, Box–Behnken design. Three factors (pH, Catalyst loading and temperature) were defined. The proposed reactions conditions are given in results and discussion section.

After summarizing and evaluating the achievements made by the studies, with the most appropriate catalyst the kinetic study was realized in order to derive the kinetic model of the reaction. In the first set, experiments were performed to demonstrate the absence of external mass transfer limitations. In the following sets, in order to obtain kinetic data at different reaction temperatures, tests were performed.

4.5. Analysis

4.5.1. Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) analysis was performed by using Spectro quant Merck COD Cell Test (15-300 mg/L), NOVA 400 spectrophotometer, and WTW Thermo-reactor. COD removal efficiencies are calculated using the following equation:

$$Degradation\ Efficiency\ = \frac{COD_0 - COD_t}{COD_0}$$

Where, COD_0 is the initial chemical oxygen demand in mg/L and COD_t is the chemical oxygen demand at time t.

4.5.2. Total Organic Carbon (TOC)

TOC-L Shimadzu analyser was used to determine the total organic carbon. TOC Removal % formula is:

$$TOC\ Removal\,\% = \frac{TOC_0 -\ TOC_t}{TOC_0}\ x\ 100$$

which TOC_0 represents initial TOC and TOC_t represents TOC at time t.

4.5.3. Turbidity

The turbidity of initial and final pretreated pharmaceutical wastewater samples are analyzed in a WTW Turbo 550I R turbidimeter.

4.5.4. Toxicity

The toxicity was evaluated according to the procedures and formulas in literature (Almeida and Corso, 2014; Hoekstra et al., 2002). The seeds of the *Lepidium sativum* were purchased from a local market. 5 mL of untreated wastewater solution and distilled water (as the control group) pipetted onto filter papers fitted into separate. A certain number of undamaged seeds were distributed uniformly on each of the dish. All dishes were incubated in the dark at room temperature. At the end of the 4 days, the length of the *L. sativum* roots was measured and the average root lengths were determined for each group of seed growing in untreated and treated wastewater solutions and distilled water. The relative root growth and the toxicity in terms of root growth inhibition were calculated according to the following formula:

Root Growth Inhibition, % = $[\frac{L_C-L_D}{L_C}] \times 100$

Relative Root Growth, % = $[\frac{L_D}{L_C}] \times 100$

L_C: Average root length growing in the control medium (distilled water), cm

L_D: Average root length growing in the untreated or treated waste water, cm

4.5.5. Color

Colour removal was measured by UV/VIS spectrophotometer at 436, 525 and 620 nm respectively by using Thermo Genesis 10S UV-VIS Spectrophotometer.

Colour removal efficiencies were calculated by using following equation:

$$\text{Color Removal Efficiency } \% = \frac{A_0 - A_F}{A_0} \times 100$$

where A_0 is initial absorbance value of wastewater and A_F is final absorbance value after treatment

4.5.6. Conductivity

The conductivity of initial and final pre-treated pharmaceutical wastewater samples were analysed in a WTW Multi 340i multi meter.

5. RESULTS AND DISCUSSION

5.1. Characterization of the catalyst supports and catalysts

The textural properties of the catalysts were investigated by Scanning Electron Microscopy (SEM) analysis. The micrographs of the catalyst samples were detected at 10000- and 25000-times magnifications. The micrographs of the Fe/AC and $LaFeO_3$/AC catalysts are shown in Figures 5.1 and 5.2, respectively.

SEM-EDS analysis was performed to determine the weight and atomic percentages of the elements in the catalyst structures, and the results are presented in Figure 5.3 and Table 5.1 for Fe-AC catalyst whereas Figure 5.4 and Table 5.2 show the distribution of various elements on $LaFeO_3$-AC catalyst surface. In addition, the distribution of lanthanum, iron and oxygen on the catalyst support material was investigated by SEM/mapping method. The SEM/mapping images of Fe-AC and $LaFeO_3$-AC catalysts are presented in Figures 5.5 and 5.6, respectively.

It is evident from the micrographs of the Fe-AC and $LaFeO_3$-AC catalyst samples that the catalysts had heterogeneous structures. The catalyst textures were full of cavities and crevices. The micrographs of the catalysts also showed that the catalysts were constituted by the aggregation of small cornered particles with different shapes and sizes. Typical EDS spectrum correspond to the various elements in the sample was obtained by X-Rays generated by emmision from energy level shell K. EDS analysis demonstrates that the target weight ratio (10%) of iron to activated carbon support material was accomplished successfully with a negligible deviation since 10.12% by wt. Fe content was detected in the Fe/AC catalyst (according to Table 5.1). EDS analysis of $LaFeO_3$/AC catalyst confirmed that the elements present in the catalyst structure were lanthanum, iron, oxygen, and carbon. According to Table 5.2, the quantitative analysis showed that the weight percentages of La (5.49%) and Fe (3.07%) in $LaFeO_3$/AC catalyst structure are close to the target weight percentages which were calculated as 5.72% and 2.3% for La and Fe, respectively. In Figure 5.3, the detected Fe and C atoms are signed in pink and blue, respectively, whereas La, Fe, O, and C atoms are shown as yellow, pink, green, and blue points, respectively, in Figure 5.4. The mapping micrographs demonstrate that the active part of the Fe/AC and $LaFeO_3$/AC catalyst were distributed homogeneously on the activated carbon surface.

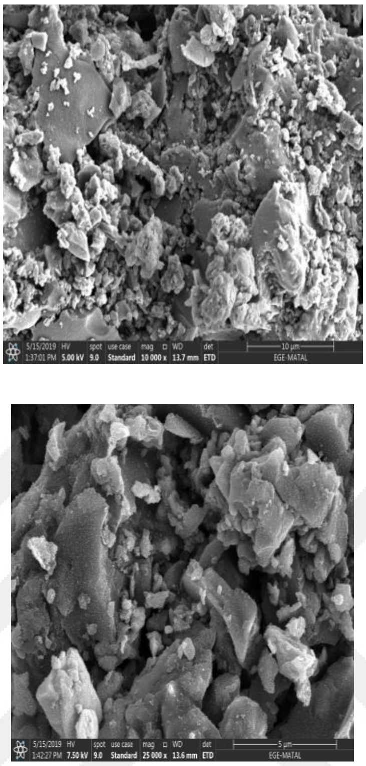


Figure 5.1. SEM micrographs of Fe/AC catalyst

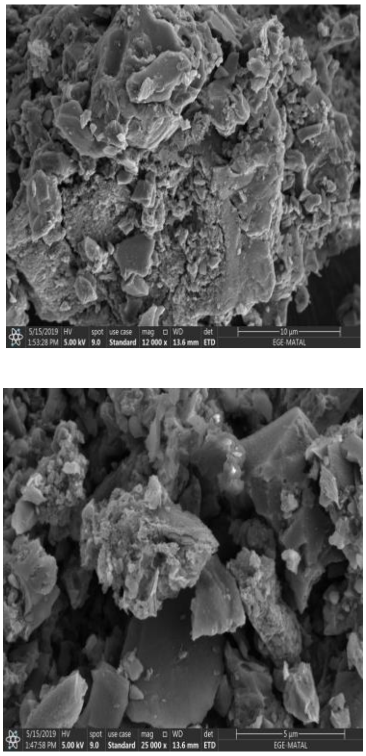


Figure 5.2. SEM micrographs of $LaFeO_3$/AC catalyst

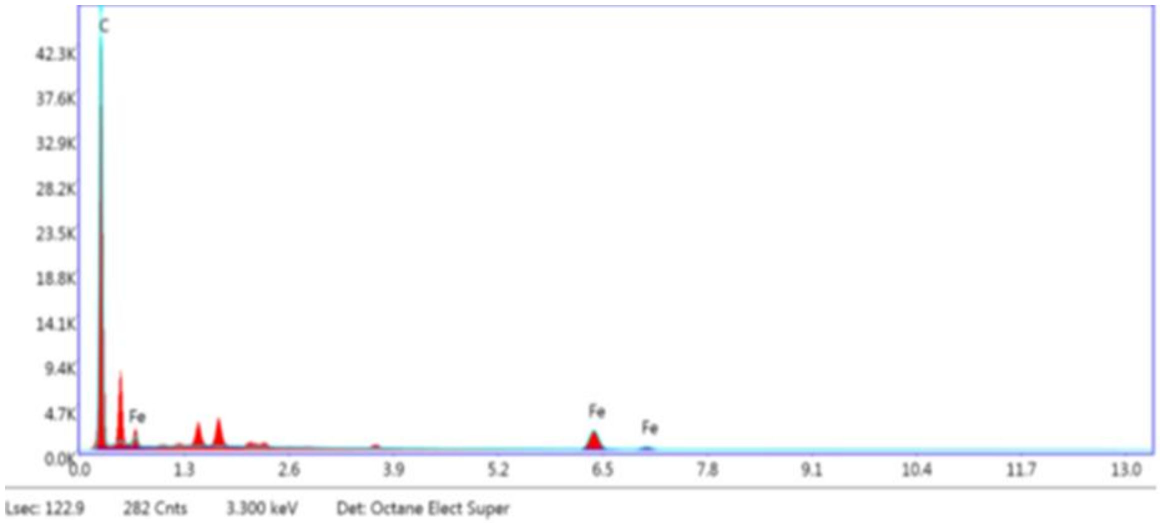


Figure 5.3. SEM-EDS Analysis of Fe-AC Catalyst

Table 5.1 Elemental distribution of Fe and C elements on Fe-AC catalyst surface

Element	Weight (%)	Atomic (%)
C K	89.88	97.64
Fe K	10.12	2.36

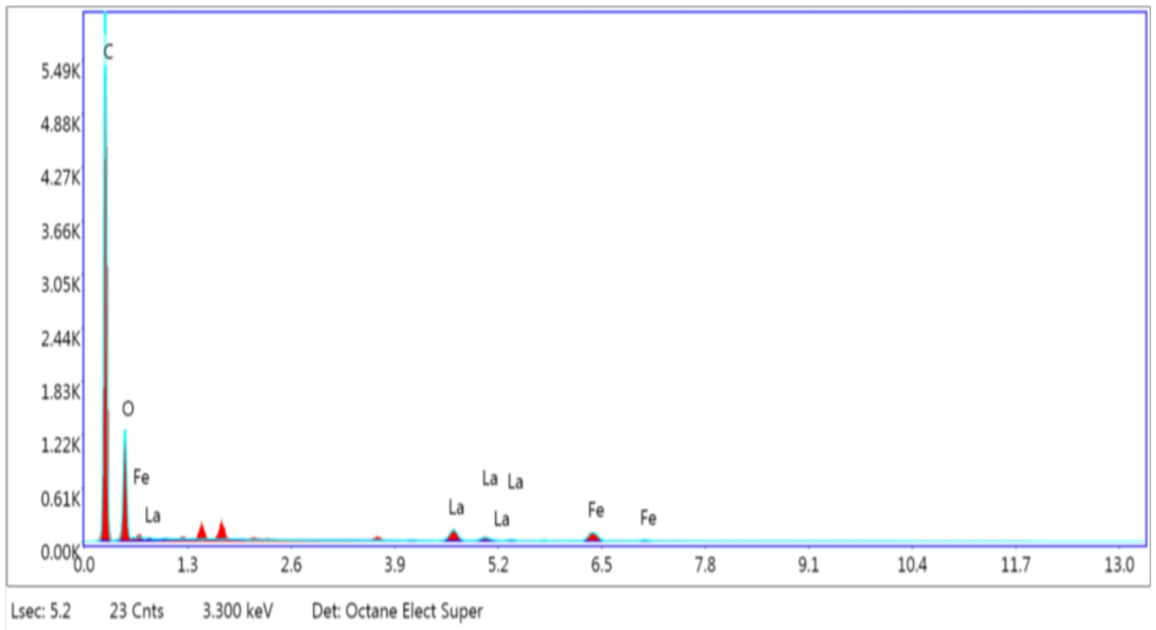


Figure 5.4. SEM-EDS Analysis of $LaFeO_3$-AC Catalyst

Table 5.2. Elemental distribution of C, O, La, and Fe elements on $LaFeO_3$/AC catalyst surface

Element	Weight (%)	Atomic (%)
C K	66.65	77.15
O K	24.78	21.53
La L	5.49	0.55
Fe K	3.07	0.76

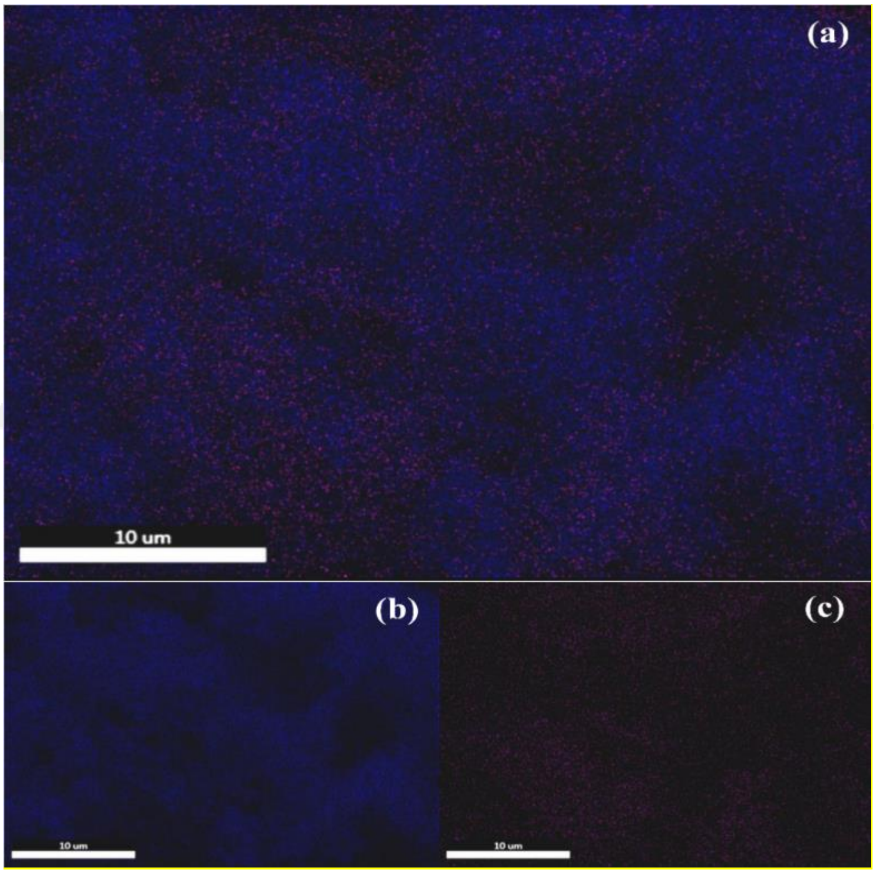


Figure 5.5 SEM Mapping Micrographs Analysis for Fe-AC, distribution of all of the elements (a), distribution of Carbon element (b), and distribution of Fe element (c).

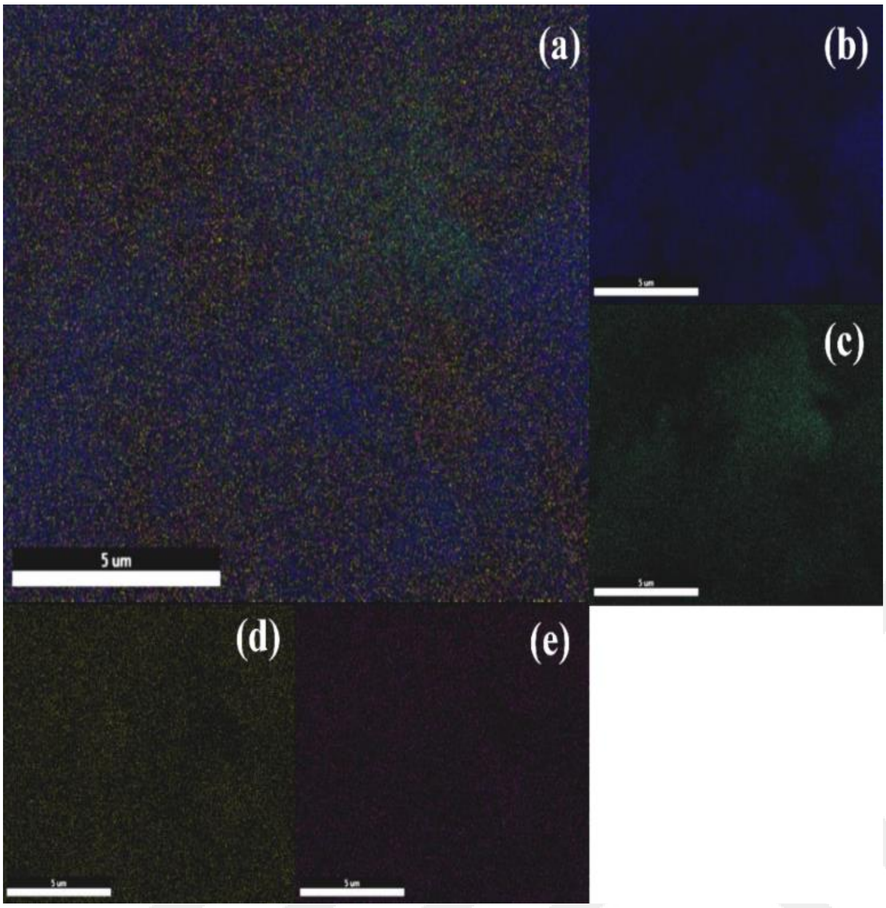


Figure 5.6. SEM Mapping Micrographs Analysis for $LaFeO_3$-AC, distribution of all of the elements (a), distribution of Carbon element (b), distribution of Oxygen element (c), distribution of Lanthanum element (d), and distribution of Fe element (e).

BET analysis measurements of surface area based on the Brunauer–Emmett–Teller (BET) method was performed only for Fe/AC catalyst. According to the results Fe/AC catalyst has a surface area of 654.04 m^2/g. When Fe/AC catalyst surface areas reported in the literature are compared, this BET surface area has found to be good agreement with literature. For example Meselle et al reported that Fe (.~9 wt)/AC had a surface area of 577 m^2/g (Meselle et al., 2012).

5.2. Photo-Fenton Like Oxidation Results

5.2.1. Catalyst screening

The heterogeneous oxidative degradation of pharmaceutical wastewater by photo-Fenton like oxidation was performed under isothermal conditions (room temperature) in a 250 mL glass beaker using a magnetic stirrer in a UV cabin in order to compare the efficiencies of commercial activated carbon (90wt%) supported (Fe/AC and $LaFeO_3$/AC) catalysts.

The efficiency of the catalysts were tested and compared in the absence of H_2O_2 changing the catalyst loading from 0.5 to 1.0 g/L and at two different pH values, 2 and 6 (original value) in two hours (30 minutes in dark, 90 minutes under UV light)

The results are given in Table 5.3 for both catalysts.

Table 5.3. Results of catalyst screening experiments

COD Removal (%)				
Catalyst Type	**$LaFeO_3$/Commercial AC**		**Fe/Commercial AC**	
Catalyst Loading(g/L)	0.5	1.0	0.5	1.0
pH=2	46.1	46.9	67.4	73.6
pH=6 (original)	50.2	49.1	53.3	61.2

No noticeable COD removal by adsorption (in the first 30 minutes dark period) was obtained during heterogeneous Fenton-like oxidation experiments with the both catalysts used.

In general, the experimental results indicated that, Fe/AC catalyst is more effective than $LaFeO_3$/AC catalyst. Especially, at the acidic conditions the performance of Fe/AC is considerably higher. Hence, Fe/AC catalyst was found to be more promising and the parametric studies for photo-Fenton like oxidation were realized in the presence of this catalyst.

5.2.2. Parametric Study

The experiments for the parametric study were carried out in the presence of the best promising catalyst, Fe/AC, which was determined by catalyst screening experiments. The parametric study experiments were also performed in the darkness for 30 minutes and then, continued in UV light irradiation for 90 minutes to investigate both the adsorption and the UV light effect.

The experimental plan to optimize the parameters affecting the COD removal efficiency was formed by using response surface method- Box–Behnken design. Three factors (pH, catalyst loading and initial hydrogen peroxide concentration) were defined. The proposed reactions conditions are tabulated in Table 5.4.

Table 5.4. Box-Behnken set of experiments for the optimization ([COD]o=1900 mg/L)

Experiment No	pH	Catalyst Loading (g/L)	H_2O_2 (mM)
1	3	0.5	1
2	9	0.5	1
3	3	2.0	1
4	9	2.0	1
5	3	1.25	0
6	9	1.25	0
7	3	1.25	2
8	9	1.25	2
9	6	0.5	0
10	6	2.0	0
11	6	0.5	2
12	6	2.0	2
13	6	1.25	1
14	6	1.25	1
15	6	1.25	1
16	6	1.25	0

Table 5.4. Continued

17	6	1.25	2
18	6	2.0	1
19	6	0.5	1
20	3	1.25	1
21	9	1.25	1

Effect of the parameters on the photo-Fenton-like process

Box-Behnken set of experiments for the optimization were performed and the effects of the independent variables on the response function are given and discussed in the following sections.

In each set, as observed in the screening study, only a negligible COD removal efficiency (<5%) was obtained in the dark period.

Catalyst loading and pH

The catalyst loading was varied between 0.5- 2.0 g/L along the increase in the pH range from 3 to 9, at fixed initial hydrogen peroxide concentration of 1mM.

As seen in Figure 5.7, at each pH value, as the loading was increased, the COD removal efficiencies were enhanced slightly. For example, at pH =3, increasing the catalyst loading from 0.5 to 2.0 g/L raised the degradation efficiency from 67.9% to 71.9% or at pH =6, increasing the catalyst loading from 0.5 to 2.0 g/L raised the degradation efficiencies from 58.2% to 69.0%. The increase in degradation with increasing catalyst loading can be attributed to the availability of active sites on catalyst surface (Rastkari et al., 2017).

It is well known that, in a heterogeneous photocatalytic processes, pH is one of the most important parameters affecting the process efficiency. Because the medium pH can directly affect the electrostatic interactions between the catalyst surface and substrate molecules and hence the adsorption behavior of substrate molecules on the photocatalyst surface, as well as the formation of hydroxyl radicals by the reaction between hydroxide ions/H_2O (An et al., 2011).

The impacts of pH on the photocatalytic degradation were assessed with the initial pH at three diverse values of 3, 6 and 9, as illustrated in Figure 5.7. The removal of COD increased as the pH of solution decreased from 9 to 3. If the pH effect is considered, it is obvious that at alkali medium, the catalytic effect was less compared to the acidic and neutral conditions.

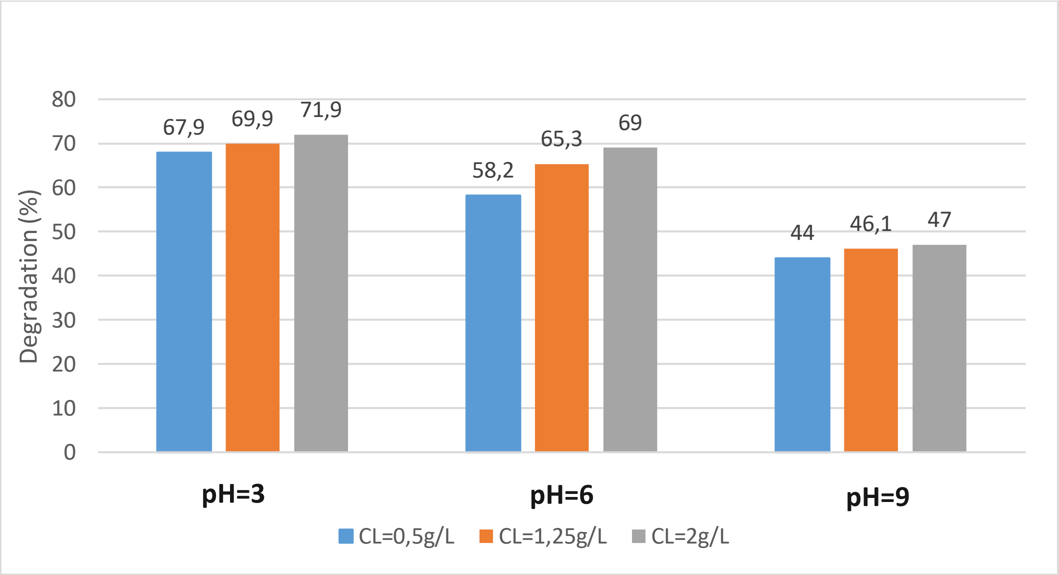


Figure 5.7. Effect of catalyst loading and pH value on COD removal in the presence of Fe/AC catalysts.
(Reaction conditions: [COD]o=1900mg/L, 366nm UV light intensity, 120 min, room temperature, $[H_2O_2]_o$=1 mM.)

The interactive effect of the catalyst loading and pH on COD removal efficiency in the process can also be seen in the surface diagram in Figure 5.8

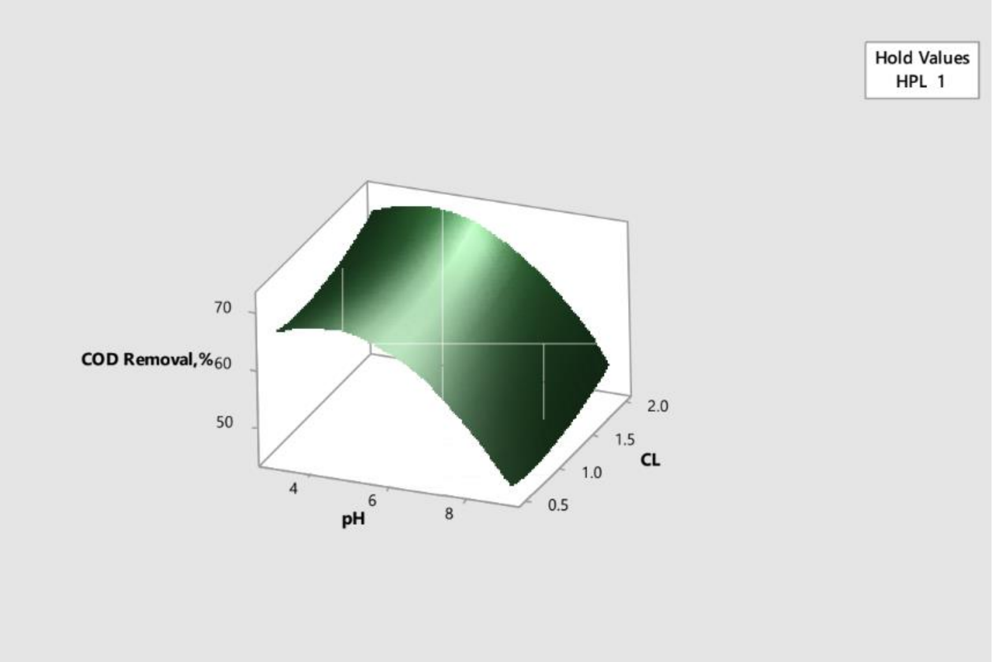


Figure 5.8. Surface diagram for COD removal showing interaction between catalyst loading and pH.
(Reaction conditions: [COD]o=1900 mg/L, 366nm UV light intensity, 120 min, room temperature.)

In Figure 5.9 the predicted values of COD removal are given in contour graph. According to the figure, in order to obtain COD removals above 70%, it is recommended to use catalyst loading values higher than 1.75 g/L. It is not recommended to operate at pH values higher than 8 since the predicted efficiencies were below 50%. According to figure, maximum COD removal efficiencies were observed at acidic conditions.

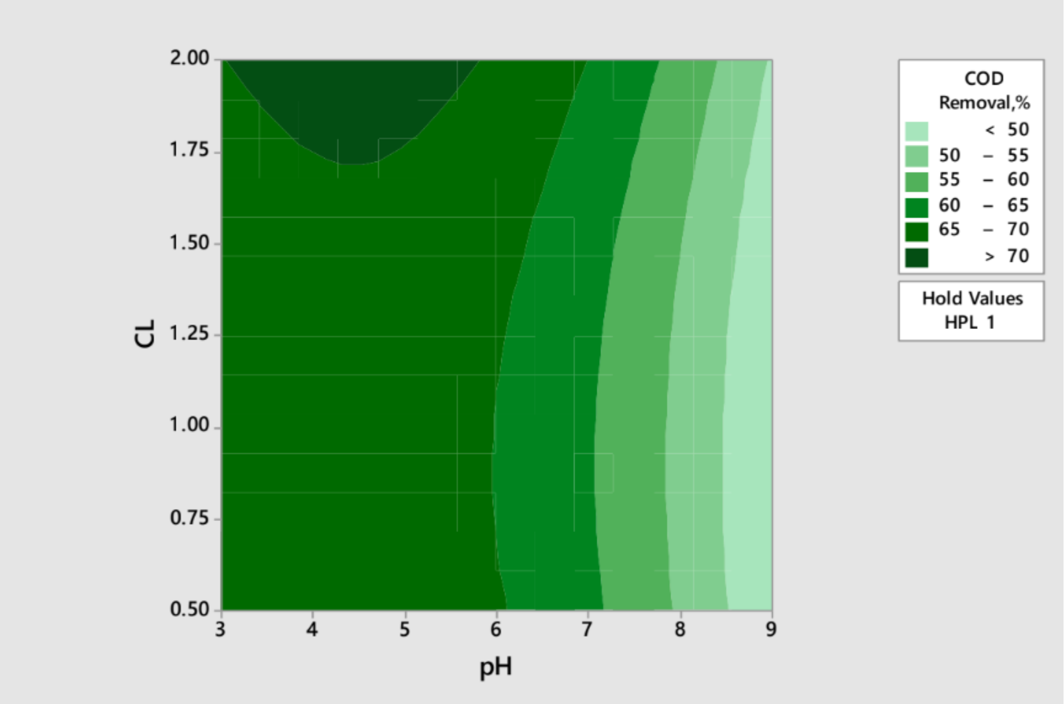


Figure 5.9. Contour diagram -Effect of catalyst loading and pH on COD removal (Reaction conditions: [COD]o=1900 mg/L, 366nm UV light intensity, 120 min, room temperature.)

Catalyst Loading and Initial Hydrogen Peroxide Concentration

1 and 2 mM of initial hydrogen peroxide concentration were tested at catalyst loading of 0.5, 1.25 g/L, 2 g/L and pH value at 6. In addition, an experiment without addition of hydrogen peroxide was performed. The influence of the initial hydrogen peroxide concentration and catalyst loading on degradation efficiency are plotted in Figures 5.10 and 5.11.

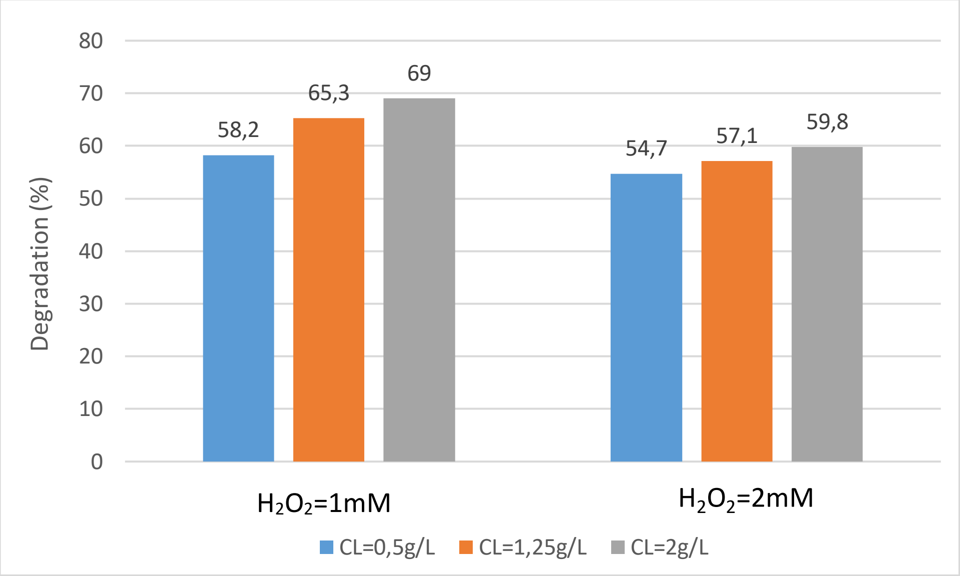


Figure 5.10. Degradation results with different hydrogen peroxide concentration (Reaction conditions: $[COD]_o$=1900 mg/L, 366nm UV light intensity, pH=6, 120 min, room temperature)

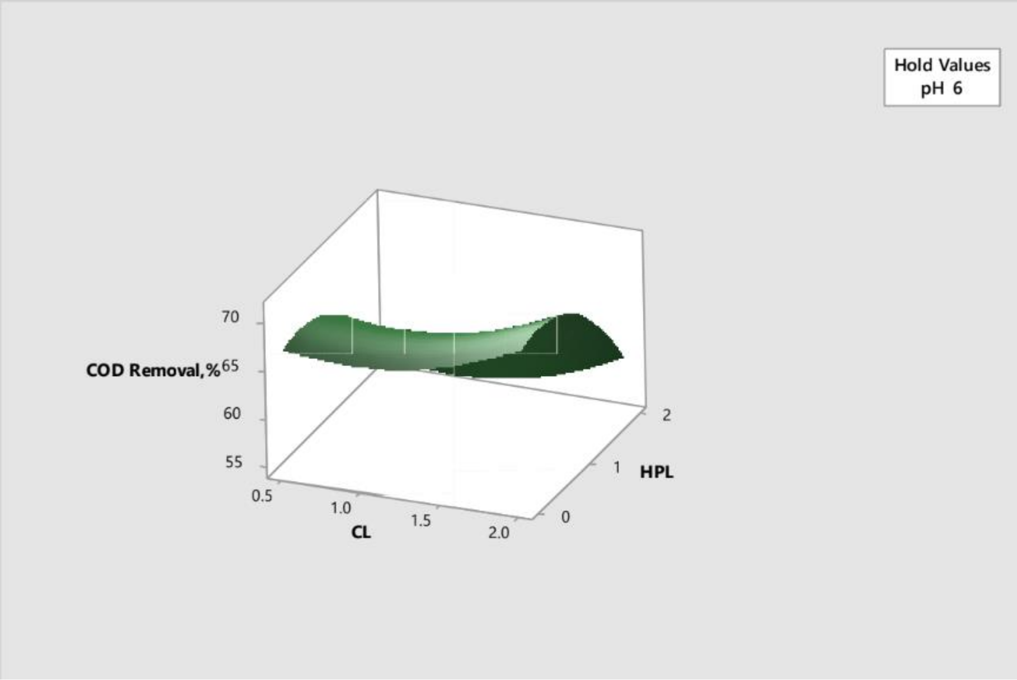


Figure 5.11. Surface diagram of Effect of catalyst loading and Hydrogen Peroxide concentration on COD removal in the presence of Fe/AC catalysts.
(Reaction conditions: [COD]o=1900 mg/L, 366nm UV light intensity, 120 min, room temperature.)

The results demonstrate an enhancement of COD removal when the H_2O_2 concentration was increased up to 1mM. By increasing the amount of hydrogen peroxide up to this value, the COD removal percentage increases due to the increase in the concentration of hydroxyl radicals. Above this value, the removal decreases because the hydroxyl radicals are scavenged by the excess H_2O_2 molecules. It is well known that the excess amount of hydroxyl radicals may react with H_2O_2 to form less effective hydroperoxyl radicals (Shemer et al., 2006). This trend (the decline of % COD removal with H_2O_2 concentrations) is more evident when the catalyst loading is high. As catalyst loading is increased the COD removal efficiencies increased. Especially, at low concentration of oxidant, catalyst loading is more effective.

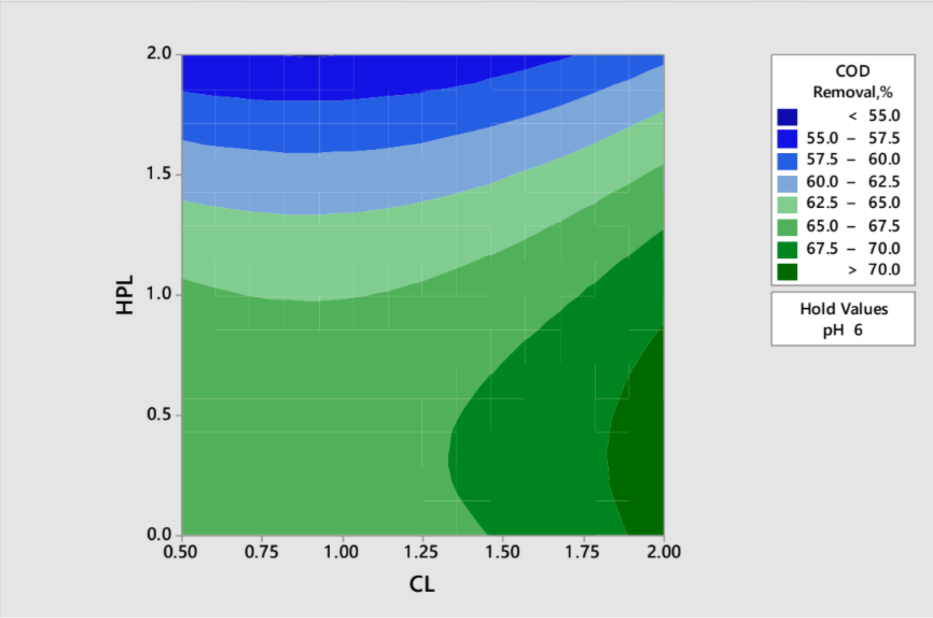


Figure 5.12. Contour diagram -Effect of catalyst loading and Hydrogen Peroxide concentration on COD removal.

(Reaction conditions: $[COD]_o$=1900 mg/L, 366nm UV light intensity, 120 min, room temperature.)

Considering the contour diagram shown in Figure 5.12, it can be concluded that studying above 1.5 g/L catalyst loading and below 1mM H_2O_2 results in the higher COD removals.

Optimization Study

According to the considered experimental design, a model was derived experimentally for fitting data. This model is represented by the following equation:

COD Removal (%)=

50.67+9.56*pH-6.55*CL+2.77*HPL-1.077*pH*pH+3.68*CL*CL-4.23 HPL*HPL

[catalyst loading (CL), pH and amount of hydrogen peroxide (HPL)]

The coefficient of determination (R^2) of the model is 0.95. The insignificant lack of fit also shows that the model is suitable for studying the parameters and optimization of the process.

According to the optimization graph in Figure 5.13, it can be concluded that increasing the catalyst loading, increases the degradation efficiency. At the same time, decreasing the pH value in the reaction medium, enhances the degradation efficiency.

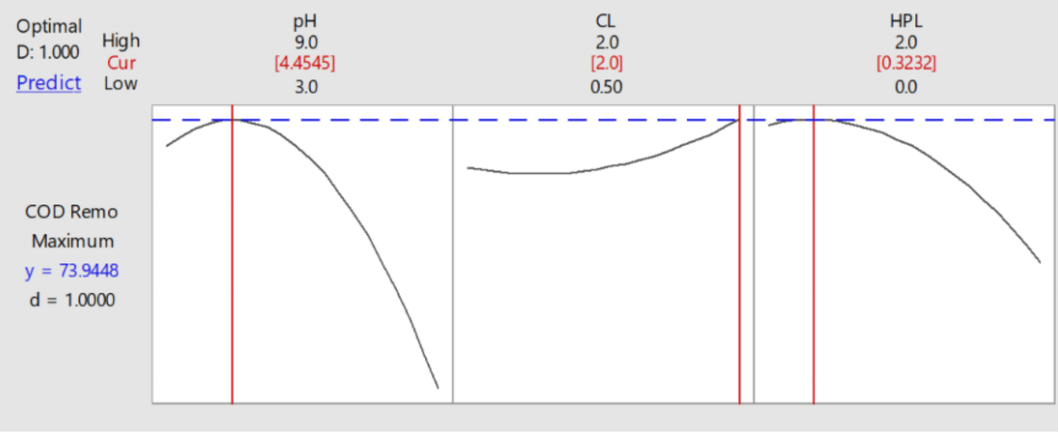


Figure 5.13. Graphs of Minitab Design of Experiments program results

The optimization results show that, the most suitable conditions for catalyst loading, pH and hydrogen peroxide concentration value are 2.0 g/L, 4.5 and 0.32 mM, respectively.

Furthermore, a closer analysis of the results in Figure 5.14 reveals that:

- increasing the catalyst loading, increases the degradation efficiency.
- above the optimum oxidant concentration (0.32 mM) COD efficiencies were influenced negatively.
- The COD removal efficiency curve approaches a plateau at pH=4.5.

At the optimum conditions an experiment is performed and the COD removal profile was derived for photo-Fenton like oxidation. The profile is presented in Figure 5.14.

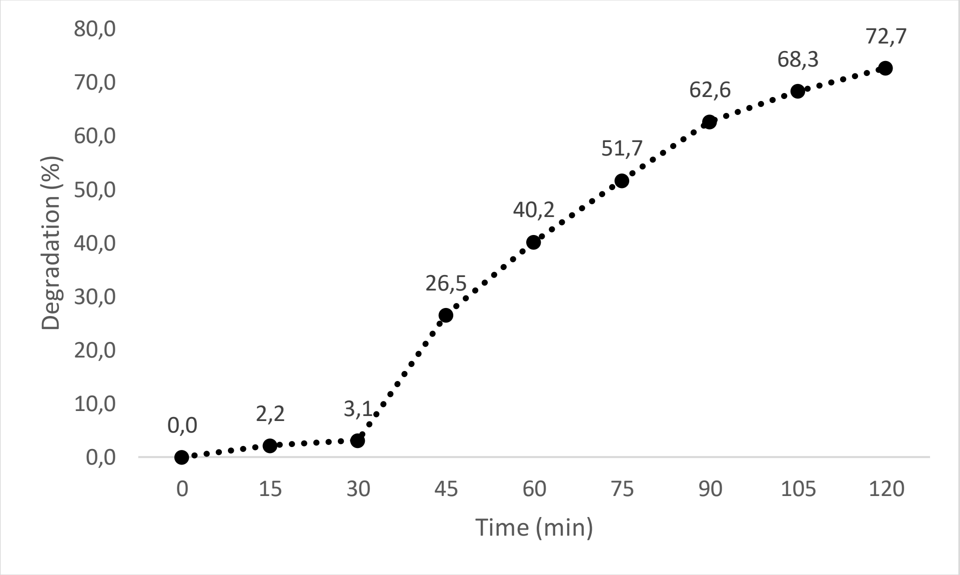


Figure 5.14. Graph of Applying optimum conditions for the experiment pH=4.5, Catalyst Loading= 2.0 g/L,[H_2O_2]$_o$= 0.32mM

At the first 30 minutes, since the test was performed in dark conditions, COD removal efficiencies were very low (~3%) and were achieved by just adsorption. After the dark period, the efficiencies increased considerably due to the effective oxidation process. The COD removal obtained (72.7%) shows the good accuracy of the model. Since the predicted removal value by the model is 73.95%.

5.3. Catalytic Wet Air Oxidation Results

5.3.1. Catalyst screening experiments

Preliminary experiments were performed to determine the most effective catalyst for the catalytic wet air oxidation of the pharmaceutical industry wastewater. The catalytic performances of Fe/AC and $LaFeO_3$/AC catalysts were compared at two different catalyst loading values (1 and 2 g/L), at 1 atm air pressure and at 50°C reaction temperature.

The catalyst screening experiments were previously carried out for 30 and 60 minutes. According to the results, COD removal efficiencies obtained at 30 min and 60 min were nearly the same. For example with 2 g/L of $LaFeO_3$/AC catalyst 70.1% and 69.7% COD removal efficiencies were obtained at 30 min and 60 min, respectively. Hence all the subsequent experiments were lasted for 30 minutes.

COD removal efficiencies obtained with the two catalysts at various catalyst loadings in 30 min are shown in Figure 5.15.

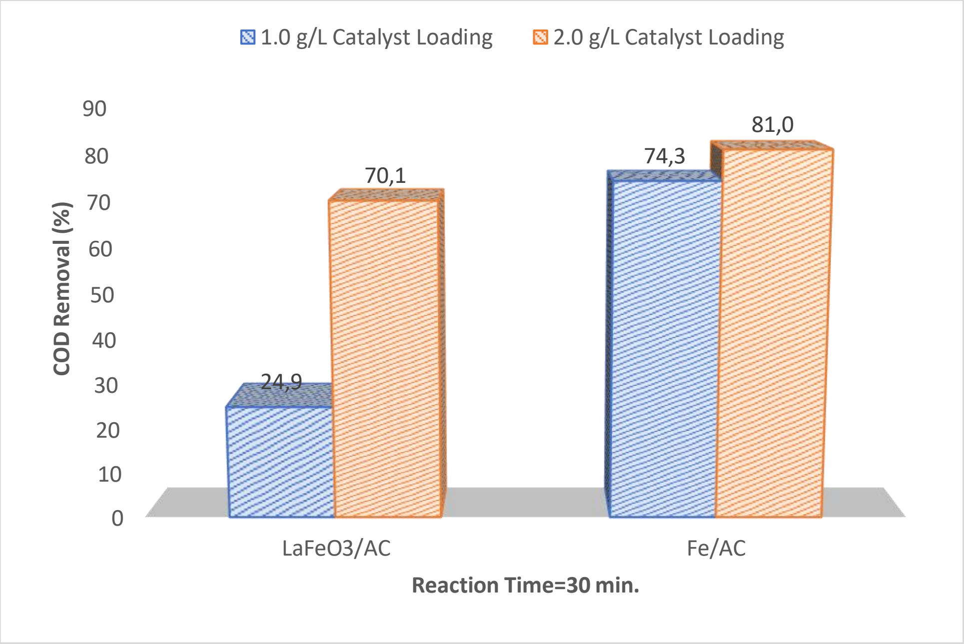


Figure 5.15. Catalytic wet air oxidation of pharmaceutical industry wastewater in the presence of Fe/AC and $LaFeO_3$/AC catalysts.
(Reaction conditions: [COD]o=1499mg/L, 50°C, 1 atm, original pH =6, 30 min.)

According to Figure 5.15, the first point to note is that, Fe/AC catalyst was more effective in COD removal in comparison with $LaFeO_3$/AC catalyst.

Furthermore, the results proved that the catalyst loading is quite important parameter for the tests performed in the presence of $LaFeO_3$/AC catalyst in the COD removal. At 1 g/L of $LaFeO_3$/AC , the removal was only 24.9% whereas at 2.0 g/L of loading, COD removal was improved considerably to 70.1%

However, for Fe/AC catalyst, although there was a change in the COD removal while increasing the catalyst loading from 1.0 g/L to 2.0 g/L, the change was not as much as the change observed with $LaFeO_3$/AC. The highest COD removal efficiency was evaluated as 81 % in the presence of Fe/AC at 2.0 g/L of catalyst loading.

From these results, it can be concluded that the catalyst is more active as the iron content in the catalyst structure is increased. The iron contents of catalysts were determined by EDS analysis (Tables 5.1 and 5.2). The perovskite catalyst ($LaFeO_3$/AC) was not effective as much as Fe/AC since the iron content (~3 wt %) of perovskite based catalyst is considerable lower than the iron content of Fe/AC(~10wt%). Hence probably, higher iron content led to a significant improvement in COD removal.

The stability and the reusability of the catalyst was also evaluated by applying the cycle runs. In the repeated runs approximately 3-5% decrease in COD removal were achieved.

The above results indicate that Fe/AC catalyst is much more promising to be used in CWAO parametric study.

5.3.2. Parametric Study

The activity of the Fe/AC catalysts in catalytic wet air oxidation was studied by testing various catalyst loading values, pH values and reaction temperature. The experimental plan was formed by using response surface method- Box–Behnken design. Three factors (pH, Catalyst loading and reaction temperature) were defined. Table 5.5 presents the set of trials needed to be done by following the Box-Behnken model.

Table 5.5. Box-Behnken set of experiments for the optimization **(**[COD]o=1499 mg/L)

Experiment No	Catalyst Loading (g/L)	Temperature (℃)	pH
1	1	30	6
2	3	30	6
3	0	50	6
4	1	50	6
5	2	50	6
6	3	50	6
7	1	40	3
8	3	40	3
9	1	40	9
10	3	40	9
11	2	30	3
12	2	50	3
13	2	30	9
14	2	50	9
15	2	40	6
16	2	40	6
17	1	40	6

Effect of the parameters on catalytic wet air oxidation process

The effect of interaction between the independent variables (catalyst loading and pH; temperature and pH; catalyst loading and temperature) and its impact on COD removal efficiency has been the key feature of the thesis study and is presented by using surface diagrams and contour plots.

Catalyst loading and pH

The amount of catalyst used is an important factor for the degradation of pollutants. To evaluate the optimum catalyst loading, this quantity was varied from 0 to 3 g/L, keeping the pH at 6 (original pH value) and the temperature at 50°C. The results of these experiments are shown in Figure 5.16. In general, the presence of catalyst seems crucial since in the absence of catalyst very low COD removal efficiency (24.7%) was achieved whereas increasing loading to 1 g/L increased the removal remarkably (74.3%). It can be seen that COD removal efficiency enhances by increasing the catalyst amount. This increase in the removal efficiency may be attributed to the increase in the number of catalyst active surface sites.

However further increase in the loading was found to be less effective. The increasing of the catalyst loading from 1.0 g/L to 3.0 g/L, raised the degradation efficiencies to 81.3%.

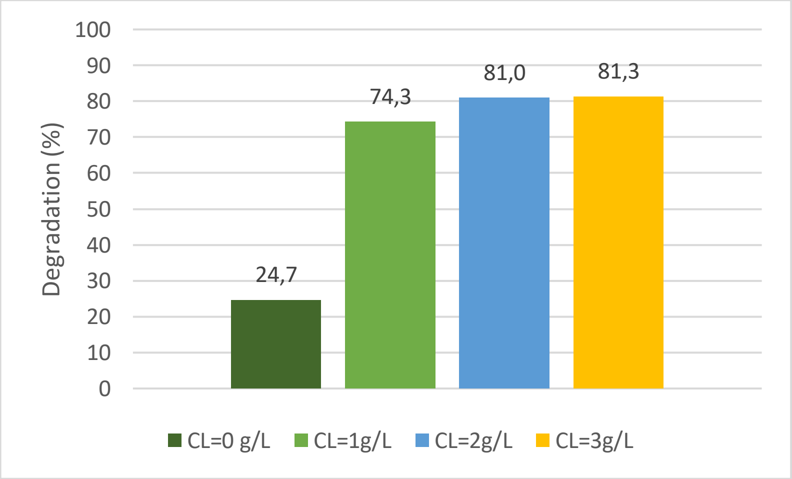


Figure 5.16. Effect of catalyst loading value on COD removal in the presence of Fe/AC catalysts. Reaction conditions: [COD]o=1499mg/L, pH=6, Reaction Run Time=30 min, T=50°C, Air Flow Rate=0.62 L/min.

In order to investigate the effect of pH, this parameter was varied from 3 to 9. The temperature was set at 50°C, and the catalyst loading was 2 g/L. The results obtained are shown in Figure 5.17. The degradations were determined as 84%, 81

% and 80.3%, at pH 3, 6 and 9, respectively. The results show that although acidic medium favors COD removal, generally pH is not very effective.

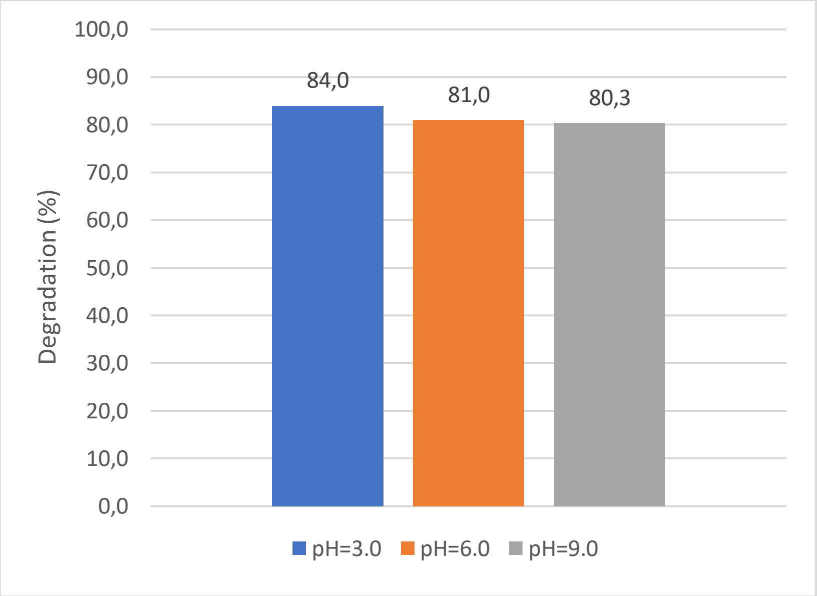


Figure 5.17. Degradation results of varied pH value in the presence of Fe/AC catalysts. (Reaction conditions [COD]o=1499mg/L, Catalyst Loading= 2.0 g/L, Reaction Run Time=30 min, T=50℃, Air Flow Rate=0.62 L/min.)

To investigate the integrated effect of catalyst loading and pH, response surface model was used and the results were given in the form of surface plot as in Figure 5.18. As mentioned before, COD removal efficiency increases by increasing catalyst loading. And at acidic medium, the higher efficiency values are obtained.

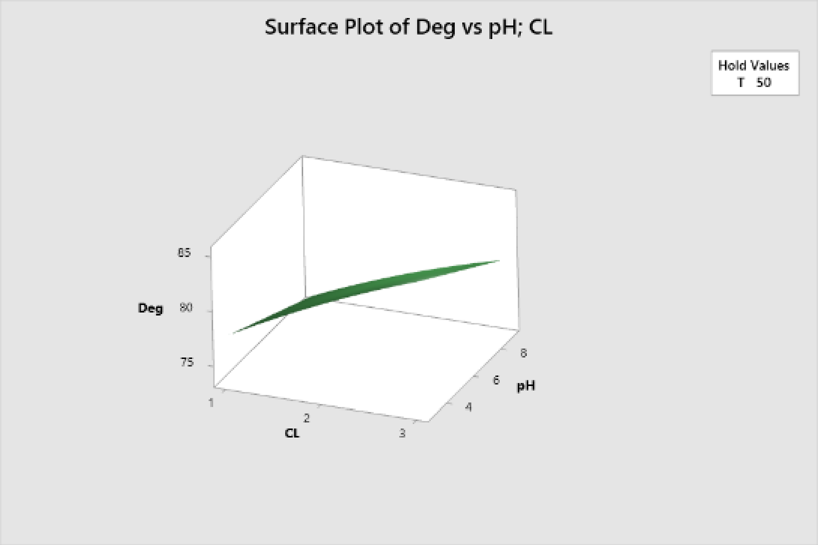


Figure 5.18. Surface diagram of Effect of catalyst loading and pH value on COD removal in the presence of Fe/AC catalysts.

(Reaction conditions: [COD]o=1499mg/L, Reaction Run Time=30 min, T=50°C, Air Flow Rate=0.62 L/min.)

If the contour plot (Figure 5.19) is investigated, it is recommended to operate at catalyst loading near to upper limit (2-3 g/L) and pH value approaching lower limits if COD removals higher than 85% is required. But even at lower catalyst loading values efficiencies around 70% can be obtained.

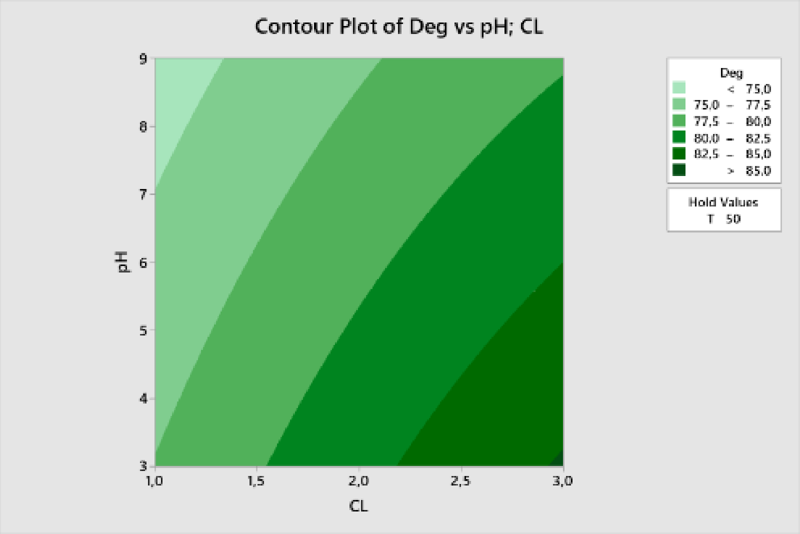


Figure 5.19. Contour diagram- Effect of catalyst loading and pH value on COD removal in the presence of Fe/AC catalysts.

(Reaction conditions: [COD]o=1499, Reaction Run Time=30 min, T=50℃, Air Flow Rate=0.62 L/min.)

Temperature and pH

To investigate the effect of temperature on the degradation, the experiments were performed at catalyst loading of 1.0 g/L and at pH= 6. The temperature values increasing from 30 to 50 °C were tested. In Figure 5.20, the temperature effect was shown as bar graph.

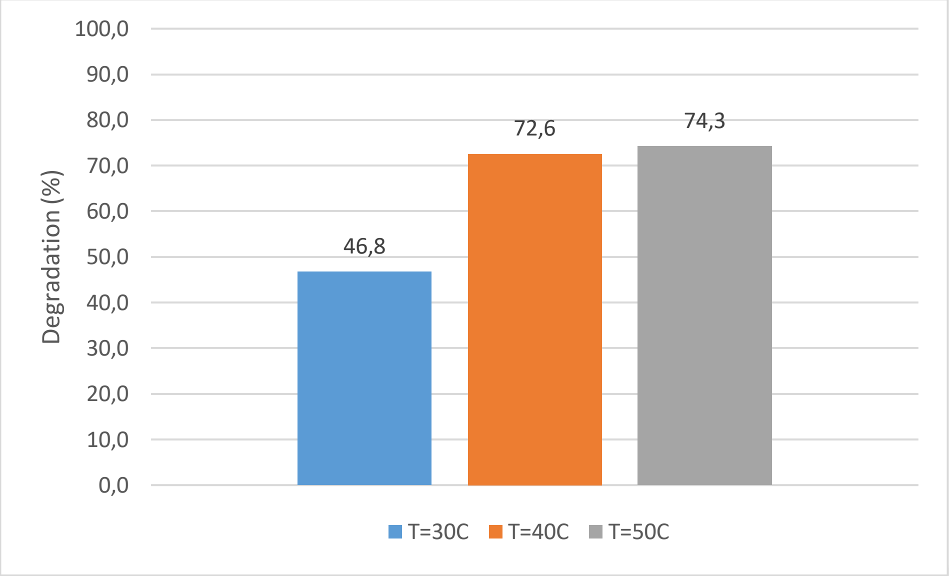


Figure 5.20. Degradation results of varied Temperature and pH=6 value in the presence of Fe/AC catalysts.
(Reaction conditions: [COD]o=1499 mg/L, Catalyst Loading= 1.0 g/L, Reaction Run Time=30 min. Air Flow Rate=0.62 L/min.)

At 30°C, the COD removal was rather low. As temperature was increased from 30ºC to 40°C, the removal raised to 72.6%. But, further increase in temperature did not cause a significant effect.

In Figure 5.21, the interactive effect between T and pH can be investigated. Temperature is more effective since sharper decline in COD removal occurs when the temperature decreased. pH is not effective as much as T.

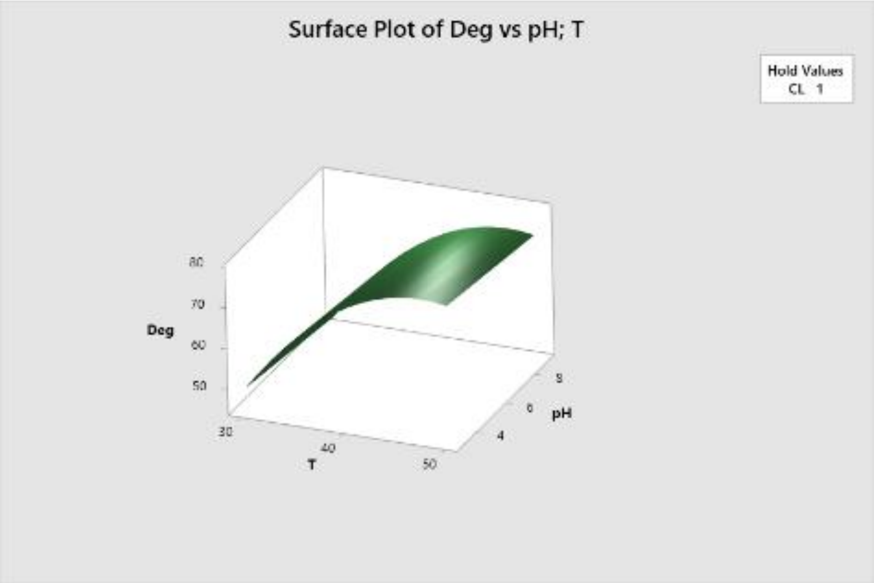


Figure 5.21. Surface diagram of Effect of Temperature and pH value on COD removal in the presence of Fe/AC catalyst.
(Reaction conditions: [COD]o=1499 mg/L, Catalyst Loading= 1.0 g/L, Reaction Run Time=30 min. Air Flow Rate=0.62 L/min)

Predicted COD values changing with respect to pH and temperature are given in Figure 5.22. When the T is around or above 40°C, COD removal efficiency is higher than 70% in a wide range of pH(3-9).

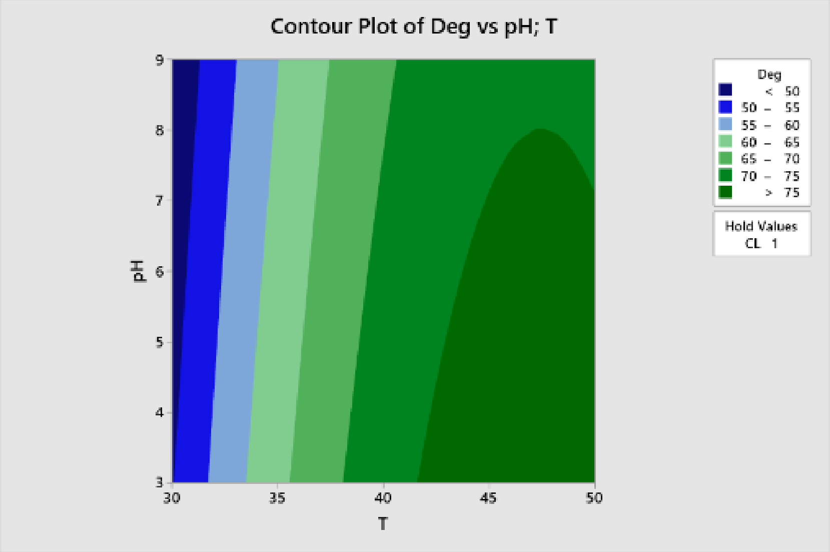


Figure 5.22. Contour diagram of Effect of Temperature and pH value on COD removal in the presence of Fe/AC catalysts.
(Reaction conditions: [COD]o=1499, Catalyst Loading= 1.0 g/L, Reaction Run Time=30 min. Air Flow Rate=0.62 L/min)

Catalsyt loading and temperature

Interactive effect of catalyst loading and temperature was investigated in Figures 5.23 and 5.24. Temperature is much more effective for COD removal in comparison to catalyst loading. For example at pH=6, at catalyst loading of 1 g/L, when the temperature is increased from is 30°C to 50°C , COD removal efficiency increased from 46.8 to 74.3%, respectively (62% increment). But at the same pH value and at 30°C, increasing loading three times, increased the COD by approximately just 7%.

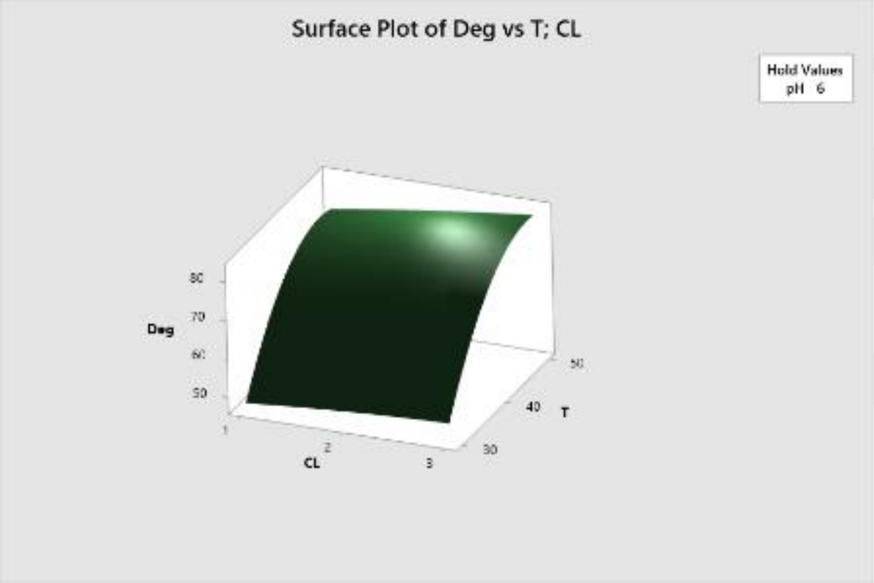


Figure 5.23. Surface diagram of Effect of Temperature and catalyst loading on COD removal in the presence of Fe/AC catalyst.
(Reaction conditions: [COD]o=1499 mg/L, pH=6, Reaction Run Time=30 min. Air Flow Rate=0.62 L/min)

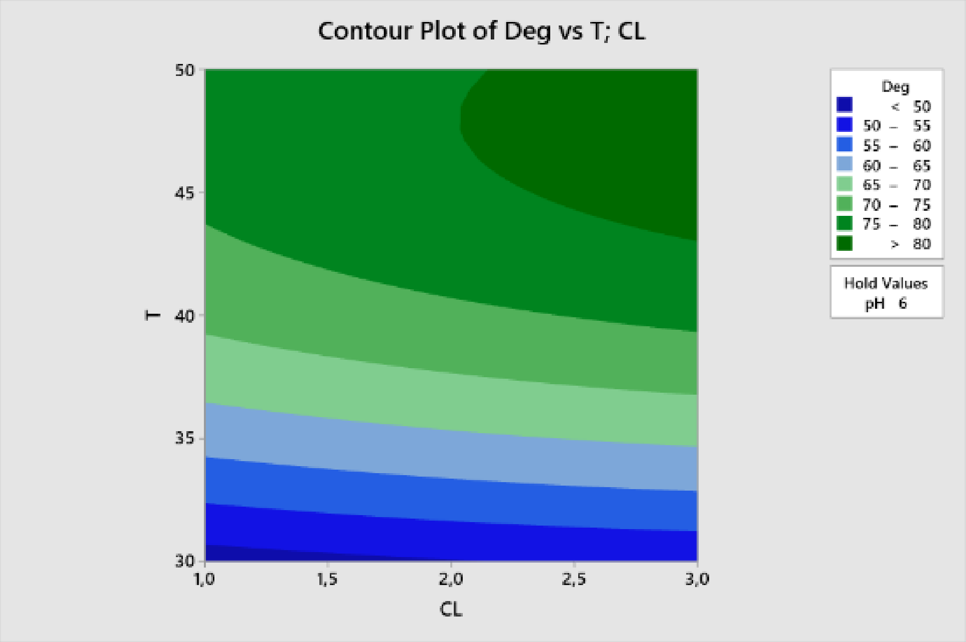


Figure 5.24. Contour diagram of Effect of Temperature and catalyst loading on COD removal in the presence of Fe/AC catalysts.
(Reaction conditions: [COD]o=1499mg/L, pH=6, Reaction Run Time=30 min. Air Flow Rate=0.62 L/min)

- **Optimization Study**

According to the considered experimental design, a model is derived experimentally for percentage COD removal. This model is represented by the following expression as a function of catalyst loading (CL), pH and temperature (T):

COD Removal (%)=

-131,6 + 1,19* CL + 8,80* T - 0,508 *pH - 0,40 CL*CL - 0,0938 T*T +0,092CL*T- 0,133 CL*pH

Using the optimization function of the Minitab DOE software program, response surface method can predict the optimal combination of parameters to obtain the highest percentage of COD removal. The highest removal (~85%) can be achieved using catalyst loading was 3.0 g/L, at temperature of ~50°C and at pH =3 at air flow rate of 0.62 L/min (Figure 5.25).

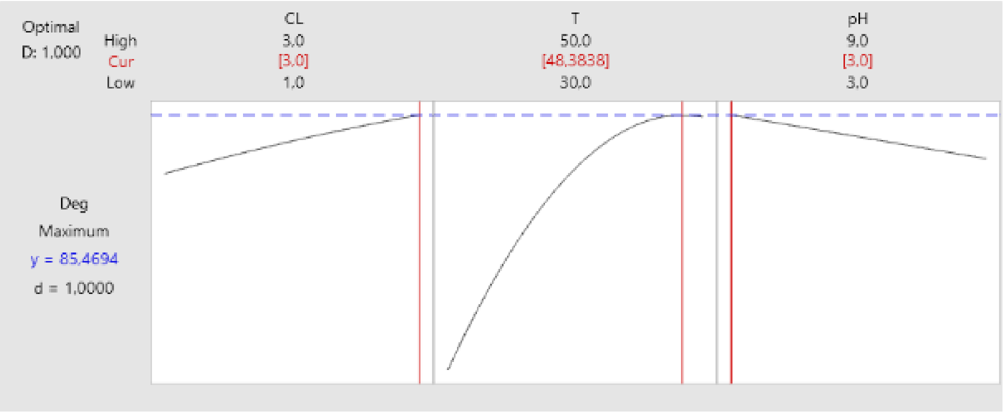


Figure 5.25. Graphs of Minitab Design of Experiments program results

The treated wastewater properties at these optimized conditions are given in the following Table 5.6.

Table 5.6. The treated wastewater properties at these optimized conditions

Parameter		**Initial**	**After treatment**
COD (ppm)		1499	254
TOC (ppm)		230	11
pH		6	4.3
Dissolved Oxygen (mg/L)		0.5	0.5
Turbidity (NTU)		215	33.6
Color (m^{-1})	436 nm (yellow)	6.1	0.145
	525 nm (red)	3.1	0.1
	620 nm (blue)	1.8	0.075

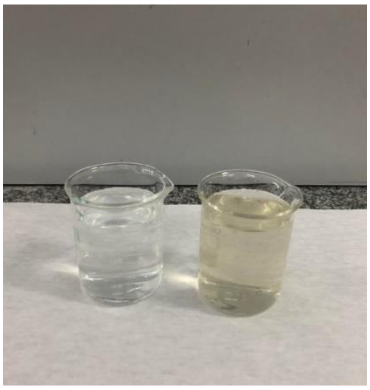


Figure 5.26. The treated water and wastewater samples

In addition the toxicity test was performed at these conditions. The average root lengths in the control medium and the treated solution after 96 hours were evaluated as 4.15 cm and 3.95 cm, respectively. The root growth inhibition was calculated as 4.82% indicating that the treated solution had low toxicity.

According to the treated waste water discharge regulations limits for pharmaceutical waste water treatment; COD must be lower than 150 ppm (Su Kirliliği Kontrolü Yönetmeliği, 2004). Although toxicity, turbidity, color, TOC standards were satisfied, the methods applied in wastewater treatment were not very enough to achieve the discharge water standards of wastewater in terms of chemical oxygen demand. Probably, instead of a single method, multiple methods can be applied as a hybrid process by improving the conditions.

Kinetic Study

The kinetic study was carried out with the best promising catalyst at the optimum conditions (pH=3, 0.3 g/L catalyst loading) at three different temperatures as 30 °C, 40 °C and 50 °C. A kinetic model was determined for the degradation of and reaction rate constants and activation energy were determined according to these data.

The collected kinetic data are given in Figure 5.27.

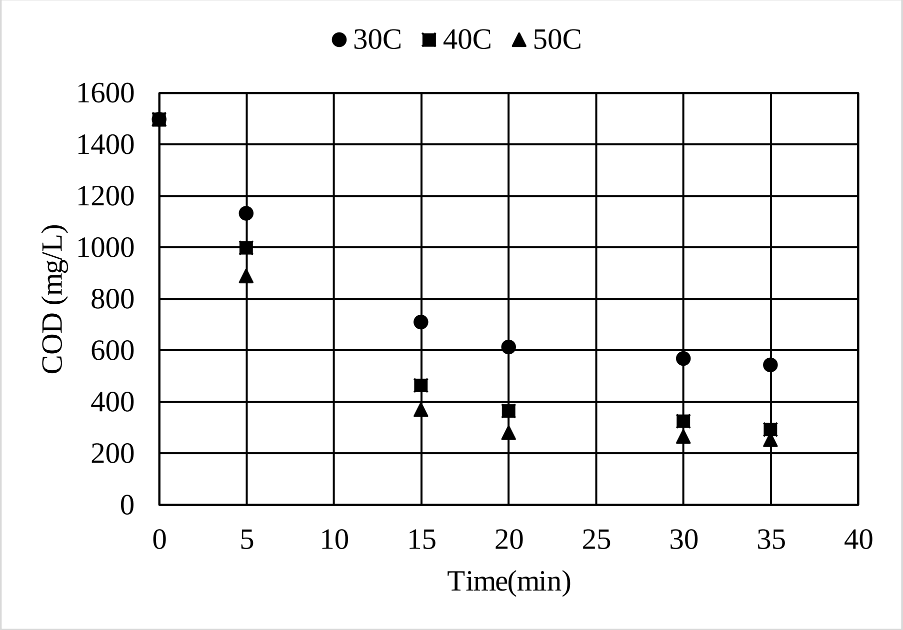


Figure 5.27. Kinetic Data

In literature, there are many studies that organic compound destruction is described using a simple power law expression Therefore, it seemed reasonable to extend the kinetic modelling to the reaction network in terms of power law kinetics.

In developing this kinetic model, the following assumptions are made:

- Heterogeneous reaction follows Power law mechanism
- Surface reaction is dependent on just COD concentration
- both diffusional resistances (internal and external) are eliminated (catalysts were in powder form and the kinetic tests were performed at above air flow rate which COD removal did not change)

Single Step Model

The kinetic behaviour of the pharmaceutical wastewaters degradation was studied with first order and second order kinetics.

$$-\frac{d[COD]}{dt} = k_1\,[COD]^n$$

where [COD] is the chemical oxygen demand concentration, k is the reaction rate constant, and n is the reaction order with respect to the chemical oxygen demand concentration.

First-order kinetic model equation:

To obtain the first order kinetic model, n is taken as 1 and integrated and the following equation was obtained.

$$\ln[COD] = ln[COD]_0 - k_1 t$$

where, $[COD]_0$, is the initial chemical oxygen demand concentration, $k_1(min^{-1})$ is the first order reaction rate constant.

Plotting $\ln\frac{COD_0}{COD}$ vs reaction time, the slope will give the reaction rate constant (Figure 5.28).

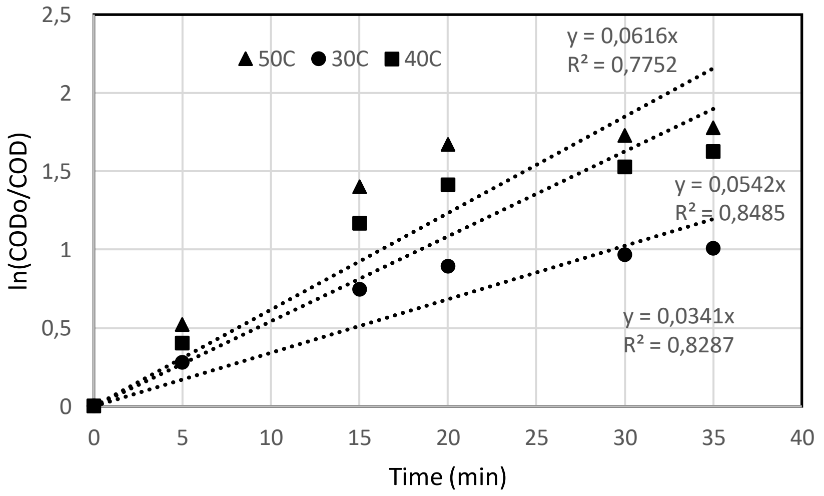


Figure 5.28. The 1^{st} order reaction kinetics

Second-order kinetic model

To obtain the second order kinetic model, n is taken as 2 and integrated and the following equation was obtained.

$$\frac{1}{[COD]} = \frac{1}{[COD]_0} + k_2 t$$

where, k_2 (L mol^{-1} min^{-1}) is the second order reaction rate constant.

Plotting 1/COD-1/COD$_o$ vs reaction time, the slope will give the reaction rate constant (Figure 5.29).

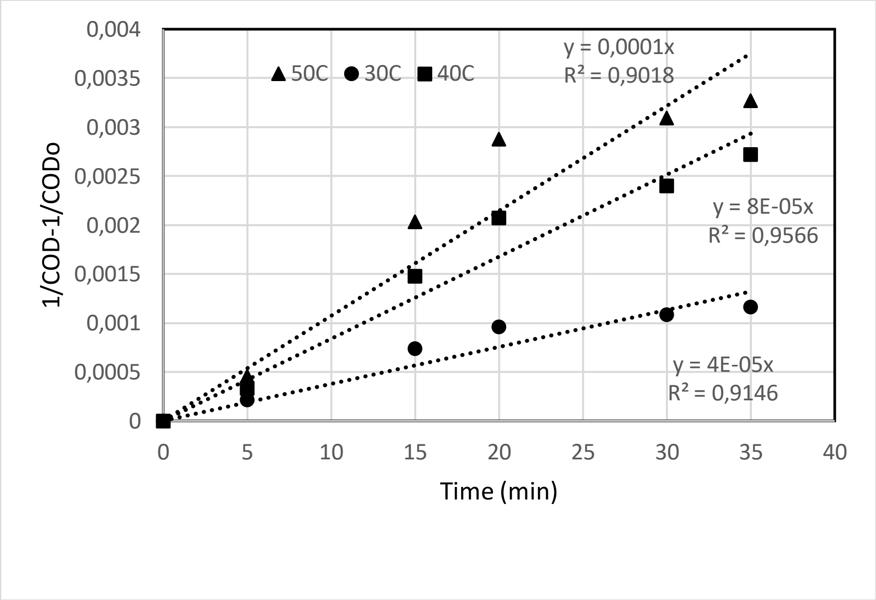


Figure 5.29. The 2nd order reaction kinetics

When the collected kinetic data applied to first and second order kinetic models, correlation coefficients of the two models were not satisfactory. Therefore, two step mechanism was tested.

Two Step Model

In the recent literature, due to the complexity of mechanism of reaction for catalytic wet air oxidation multisteps reaction mechanisms have been proposed in the presence of various catalysts. According to this recommended model; COD removal tested in following two-stage mechanism. The fast first step may involve the removal of weak pollutants; the slow step may evaluate strong pollutants' bonds breakage.

According to the results removal of COD has found to have two step reaction mechanism. It can be clearly understood from Figure 5.30, the first step of reaction is very fast and after 20 minutes, reaction behaviour was slow. And it was suitable for first order two step reaction mechanism.

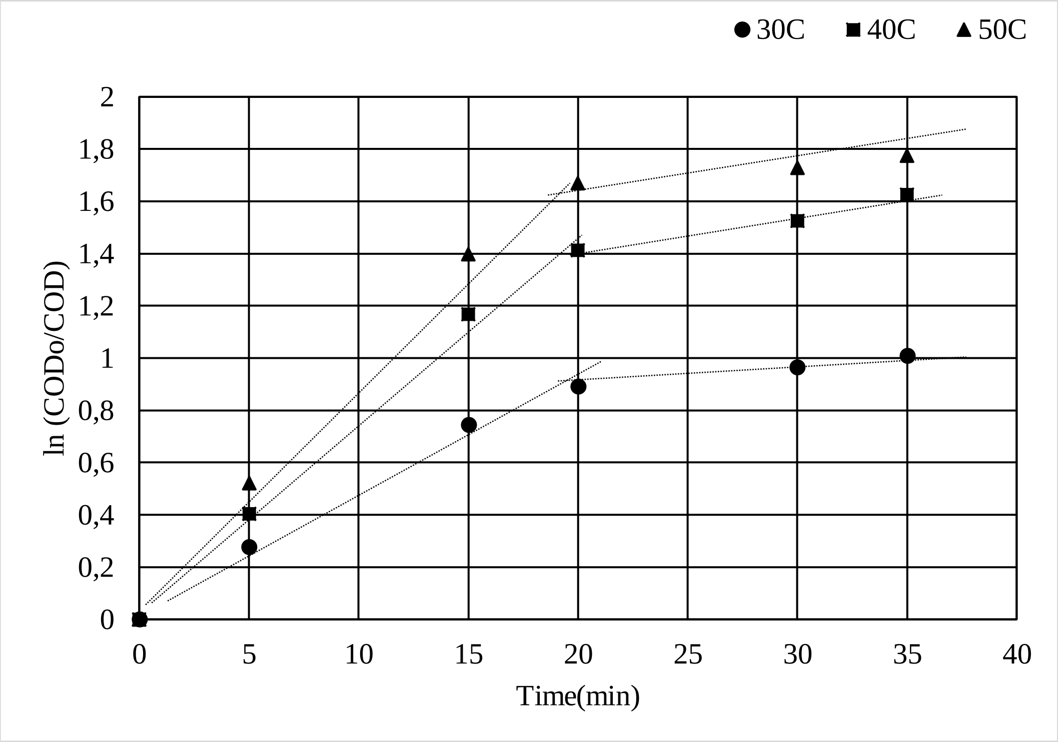


Figure 5.30. First order kinetic plot in two steps at various temperatures

As seen in Figure 5.30, the data fit into two straight lines for a given temperature, indicating that oxidation proceeds in two distinct steps: a fast initial reaction of large molecules decomposed into intermediate products followed by a slow reaction of further oxidizing the intermediate products.

Reaction rate equation for two steps can be predicted as follows for both first order reaction kinetics :

Initial step: fast reaction

$$-\frac{d[COD]}{dt} = k_{fast}[COD]$$

$$\ln\frac{COD_0}{COD_1} = k_{fast}t_1$$

Second step: slow reaction

$$-\frac{d[COD]}{dt} = k_{slow}[COD]$$

$$\ln\frac{COD_1}{COD} = k_{slow}(t - t_1)$$

According to figure mentioned above the reaction rate constants for both steps were calculated for 30, 40 and 50 °C temperatures and showed in following Table.5.7.

Table 5.7. Results of kinetic model

Temperature (˚C)	**k_{Fast}(1/min)**	**k_{Slow}(1/min)**	**R^2 Fast**	**R^2 Slow**
30	0.0468	0.0066	0.99	0.97
40	0.0735	0.0077	0.99	0.99
50	0.0877	0.0133	0.99	0.97

Determining the activation energy

The Arrhenius equation,

$$k = Ae^{-E/RT}$$

can be written in linear form

$$lnk = \frac{-E}{RT} + lnA$$

Where k represents the rate constant, E is the activation energy, R is the gas constant (8.3145 J/K mol), and T is the temperature expressed in Kelvin.

Plotting $\ln(k)$ vs. $1/T$ will yield a straight line of slope $-E/R$ and intercept of $\ln(A)$.

In Figure 5.31, the Arrhenius plots for the both two steps are given.

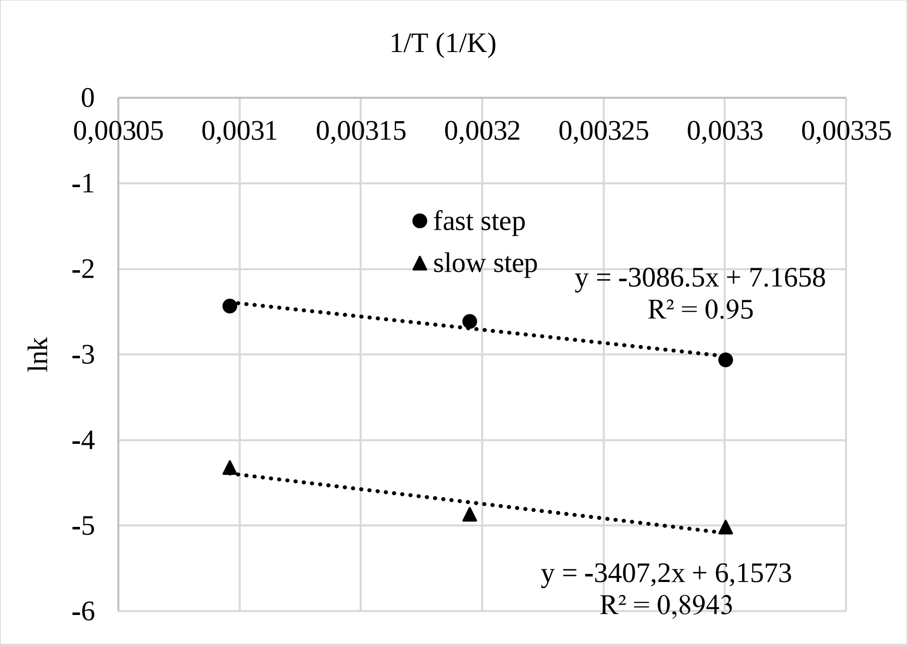


Figure 5.31. Arrhenius plots

According to figure mentioned above the Arrhenius constant and activation energies for fast and slow steps were calculated and showed in following Table 5.8.

Table 5.8. Arrhenius constant and Activation energies for fast and slow step

	Fast Step	**Slow Step**
E (J/mole)	25661.16	28327.46
A (min^{-1})	1294	472
R^2	0.95	0.89

According to calculated parameters from linearized form of Arrhenius equation activation energy for fast step was approximately 25.7 kJ/mole and for slow step 28.3 kJ/mole as expected.

For fast step of first order reaction kinetics for removal of COD is given by following equation.

$$-\frac{d[COD]}{dt} = 1294e^{\frac{-25661.16}{RT}}[COD]$$

For slow step first order reaction kinetics for removal of COD is given by following equation.

$$-\frac{d[COD]}{dt} = 472e^{\frac{-28327.46}{RT}}[COD]$$

6. CONCLUSIONS

The growing industrial development is leading to the production of contaminants that are seriously threatening the ecosystems. Especially pharmaceutical industry that produces residual waters containing high complexity compounds, causing aquatic toxicity has received considerable attention by the researchers

In this context, in this thesis two types of advanced oxidation processes were applied to pharmaceutical wastewater and the evaluated efficiencies were compared in the presence of Fe/Commercial AC and $LaFeO_3$/Commercial AC catalysts.

The following terms are concluded:

Characterization of Catalysts

- The Fe-AC and $LaFeO_3$-AC catalyst had heterogeneous structures with the textures full of cavities and crevices.

- For Fe-AC catalyst, EDS analysis demonstrates that the target weight ratio (10%) of iron to activated carbon support material was accomplished successfully. EDS analysis of $LaFeO_3$/AC catalyst confirmed that the elements present in the catalyst structure were lanthanum, iron, oxygen, and carbon. With the weight percentages of La (5.49%) and Fe (3.07%) in $LaFeO_3$/AC catalyst structure were close to the target weight percentages

- The mapping micrographs demonstrate that the active part of the Fe/AC and $LaFeO_3$/AC catalyst were distributed homogeneously on the activated carbon surface.

- According to BET analysis measurements Fe/AC catalyst had a surface area of 654.04 m²/g.

Photo-Fenton-Like Oxidation

- The performances of Fe/AC and $LaFeO_3$/AC catalysts were compared and the highest degradation efficiency was found as 73.7% for Fe/AC.

- Box Behnken statistical experiment design and the response surface methodology was used to investigate the effects of the independent variables on the response function and to determine the optimum conditions maximizing the percent removal of COD.

- Applying the Minitab Design of Experiment program and considering all the parametric studies results, the optimum reaction conditions were determined as 2.0 g/L for catalyst loading, 0.32 mM for initial H_2O_2 concentration and 4.5 of pH in the presence of commercial activated carbon supported catalyst (Fe/AC). The degradation efficiencies were evaluated as 72.7% at these optimum conditions.

Catalytic Wet Air Oxidation

- The catalytic performances of Fe/AC and $LaFeO_3$/AC catalysts were tested. Based on the results, Fe/AC catalyst was determined as the most suitable catalyst for the treatment of pharmaceutical industry wastewater since the highest COD removal efficiency was evaluated as 76.8% at 30 minutes.

- For catalytic wet air oxidation, the parametric study conditions were designed in the presence of Fe/AC catalyst type to specify the optimum conditions to get maximum efficiency for pharmaceutical wastewater treatment.

- Box Behnken statistical experiment design and the response surface methodology was used to investigate the effects of the independent variables.

- The optimum conditions were specified for degradation of pharmaceutical wastewater as 3.0 g/L Fe/AC catalyst loading, at pH 3 and at temperature of 50℃ with air flow rate is 0.62 L/min. At these conditions COD removal percentage was around 85%.

- In the light of determination of optimum conditions, the kinetic study was performed. According to the kinetic studies it was observed that the removal of chemical oxygen demand by CWAO process follows two steps first order reaction.

General

Although toxicity, turbidity, color, TOC standards were satisfied, the methods applied in wastewater treatment were not very enough to achieve the discharge water standards of wastewater in terms of chemical oxygen demand. Thus, hybrid process is required. As an hybrid process combination of adsorption with the AOPs used in the study can be recommended as a future set.

REFERENCES

Alalm M. G., Tawfik A., Ookawara S., 2016, Enhancement of photocatalytic activity of TiO_2 by immobilization on activated carbon for degradation of pharmaceuticals, Environmetal Chemical Engineering, 4:1929-1937pp.

Almeida E. J. R., Corso C.R., 2014, Comparative study of toxicity of azo dye Procion Red MX-5B following biosorption and biodegradation treatments with the fungi Aspergillus niger and Aspergillus terreus, Chemosphere 112:317–322pp.

An, T., An, J., Yang, H., Li, G., Feng, H., Nie, X., 2011, Photocatalytic degradation kinetics and mechanism of antivirus drug-lamivudine in TiO_2 dispersion. Journal of hazardous materials, 197: 229-236pp.

Arshad M., Shakoor A., 2017, Irrigation Water Quality, Chapter 7:147-150pp.

Asaithambi P., Ara A., Daud WMABW, 2016, Integrated ozone-electrocoagulation process for the removal of pollutant from industrial effluent, Optimization Through Response Surface Methodology, Chem Eng Process, 105:92–102pp.

Atalay, S, Ersöz G. 2016**,** Novel Catalysts in Advanced Oxidation of Organic Pollutants Springer Briefs in Molecular, Gülin Ersöz, Editör: Sanjay K. Sharma, Springer, ISBN:978-3-319-28948-9.

Bauder T.A., Waskom R.M., Sutherland P.L. and Davis J. G., 2011, Irrigation Water Quality Criteria, Colorado State University.

Benitez F. J., García J., Aceroa J. L., Real F. J., Roldan G., 2011**,** Non-catalytic and catalytic wet air oxidation of pharmaceuticals in ultra-pure and natural waters, Universidad de Extremadura, Spain.

Bredhult C, Bäcklin BM, Olovsson M., 2007, Effects of some endocrine disruptors on the proliferation and viability of human endometrial endothelial cells in vitro. Reprod Toxicol 9:23-550pp.

Chatzitakis A., Berberidou C., Paspaltsis I., Kyriakou G., Sklaviadis T., Poulios I., 2008, Photocatalytic degradation and drug activity reduction of chloramphenicol. Water Res 42:386–94pp.

Chiban M., Zerbet M. , Carja G. and Sinana F.; 2011, application of low-cost adsorbents for arsenic removal, Journal of Environmental Chemistry and Ecotoxicology, 4(5): 91-102pp.

Díez A. M., Ribeiro A. S., Sanromán M. A., Pazo M., 2018, Optimization of photo-Fenton process for the treatment of prednisolone, Environmental Science and Pollution Research, 25: 27768–27782pp.

Epold I.; 2015, Degradation of Pharmaceuticals by Advanced Oxidation Technologies in Aqueous Matrices, Tallinn University of Technology, Faculty of Chemical and Materials Technology Department of Chemical Engineering.

Ersöz G., 2014, Fenton-like oxidation of Reactive Black 5 using rice husk ash based catalyst, Applied Catalysis B: Environmental, 147p, 353–358pp.

Gaehr F., Hermanuts F., Oppermann W., 2008, Ozonation- an important technique to comply with new German laws for textile waste water treatment, Water Sci Technol, 30(3):255-263pp.

Guo Y., Qi P. S. and Liu Y. Z., 2017, A Review on Advanced Treatment of Pharmaceutical Wastewater IOP Conf. Series: Earth and Environmental Science, 63.

Hoekstra P. F., , Dehn L. A., , George J. C., , Solomon K. R., Muir D. C.G., O'Hara T. M., 2002, rophic ecology of bowhead whales (Balaena mysticetus) compared with that of other arctic marine biota as interpreted from carbon-, nitrogen-, and sulfur-isotope signatures, Canadian Journal of Zoology, 80(2): 223-231pp.

Klavarioti M., Mantzavinos D., Kassinos D., 2009, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Department of Civil and Environmental Engineering, University of Cyprus, Greece, 35: 402-417pp.

Li, X. and Li. G., 2015, A Review: Pharmaceutical Wastewater Treatment Technology and Research in China ,Asia-Pacific Energy Equipment Engineering Research Conference.

Luck, F., 1999, Wet air oxidation: past, present, and future, 53p, 81–91pp.

Magureanu M., Mandache N., Parvulescu V., 2015, Degradation of pharmaceutical compounds in water by non-thermal 90(7):129-134pp.

Meselle S. A., Stüber F., Bengoa C., Fortuny A., Febregat A., Font J.; 2012, Phenol degradation by heterogenous Fenton Like reaction using Fe supported over activated carbon, Prague.

Molinari R., Pirillo F., Loddo V., Palmisano L.; 2006, Dipartimento di Ingegneria Chimica e dei Materiali, Universita` della Calabria, Via Pietro Bucci, Cosenza, Italy and Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Universita` di Palermo, Palermo, Italy.

Nidheesh P.V., Gandhimathi R., Ramesh S.T., 2013, Degradation of dyes from aqueous solution by Fenton processes: a review, Environ SciPollut Res 20: 2099–2132pp.

NSCEP, National Service Center for Environmental Publications, 2012, A Citizen’s Guide to Air Stripping.

Orak, C. Atalay, S. Ersöz, G. 2017. Photocatalytic and photo-Fenton-like degradation of methylparaben on monolith-supported perovskite-type catalysts, Separation Science and Technology, 52(7), 1310-1320,

Orak, C. Atalay, S. Ersöz, G. 2016, Degradation of Ethylparaben using Photo-Fenton-Like Oxidation over BiFeO3, Anadolu Üniversitesi Bilim ve Teknoloji Dergisi A- Uygulamalı Bilimler ve Mühendislik, 17(5), 915-925

Palas, B. Ersöz, G. Atalay, S. 2019, Bioinspired metal oxide particles as efficient wet air oxidation and photocatalytic oxidation catalysts for the degradation of acetaminophen in aqueous phase, Ecotoxicology and Environmental Safety, 182.

Quesada-Peñate I., Julcour-Lebigue C., Jáuregui-Haza U. J., Wilhelm A. M., Delmas H.; 2012, Degradation of paracetamol by catalytic wet air oxidation and sequential adsorption, Catalytic wet air oxidation on activated carbons, Journal of Hazardous Materials, 221,222:131-138pp.

Rastkari N., Eslami A., Nasseri S., Piroti E., Asadi A., 2017, Optimizing Parameters on Nanophotocatalytic Degradation of Ibuprofen Using UVC/ZnO Processes by Response Surface Methodology, Pol. J. Environ. Stud. Vol. 26, No. 2: 785-794pp.

Rengaraj S, Yeon K.H., Moon S.H., 2001, Removal of chromium from water and wastewater by ion exchange resins, Journal of Hazardous Materials, 87: Issues 1–3:273–287pp.

Sahunin, C., and Kaewboran, J., 2006, Treatment of Textile Dyeing Wastewater by Photo Oxidation using UV / H 2 O 2 / Fe 2 + Reagents. Science Asia 32, 181–186pp.

Sarkar S., Chakraborty S., Bhattacharjee C.; 2015, Photocatalytic degradation of pharmaceutical wastes by alginate supported TiO_2 nanoparticles in packed bed photo reactor, Ecotoxicology and Envrionmental Safety, 121: 263-270pp.

Semerjian L. and Ayoub G. M., 2003, High-pH–magnesium coagulation–flocculation in wastewater treatment, Advances in Environmental Research 7(2):389–403pp.

Sharma S., Ruparelia J.P. and Manish L.P., 2011, A general review on Advanced Oxidation Processes for wastewater treatment, Institute of Technology, Nirma University, 382 481pp, 08-10pp.

Shemer H., Kunukcu Y.K., Linden K.G., 2006, Degradation of the pharmaceutical Metronidazole via UV, Fenton and photo-Fenton processes Chemosphere, 63 (2):269-276pp.

Sun M.; 2013, The Removal of Pharmaceuticals from Wastewater by Wet-Air Oxidation, Faculty of Natural Sciences and Mathematics, University of Denver.

Suarez D.L., Lebron I.; 1993, Water quality criteria for irrigation with highly saline water, Department of Agriculture, USA, 2: 389-397pp.

Su Kirliliği Kontrolü Yönetmeliği, 2004, Resmi Gazete.

Szabados E., G., Somodi F., Maróti B., Srankó D., Tungler A.; 2017, Wet air oxidation of paracetamol over precious metal/Ti mesh monolith catalyst, Journal of Industrial Engineering Chemistry, 46: 264-372pp.

Teixeira S., Gurke R., Eckert H., Ku¨hn K., Fauler J., Cuniberti G., 2016, Photocatalytic degradation of pharmaceuticals present in conventional treated wastewater by nanoparticle suspensions, Institute for Materials and Institute of Clinical Pharmacology and Faculty of Medicine Carl Gustav Carus, Germany.

Tokumura M., Sugawara A., Raknuzzaman M., Al-Mamun M. H., Masunaga S.; 2016, Comprehensive study on effects of water matrices on removal of pharmaceuticals by three different kinds of advanced oxidation processes, Chemosphere, 159: 317-325pp.

Turbay E. Y., 2013, Efficient Operation of photo-Fenton Process for the Treatment of Emerging Contaminants in Water Solutions, Faculty of Process Engineering, Barcelona.

Wang S.; 2008, Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, Dyes and Pigments, 76: 714-720pp.

Yuan X., Guan R., Wu Z., Jiang L., Li Y., Chen X., Zeng G., 2018, Effective treatment of oily scum via catalytic wet persulfate oxidation process activated by Fe^{2+}, Journal of Environmental Management, 217: 411-415pp.

Yujie H., Nora B. Sutton, Rijnaarts H. H.H., Langenhoff A.A.M., 2016, Degradation of pharmaceuticals in wastewater using immobilized TiO2 photocatalysis under simulated solar irradiation, 182: 132,141pp.

Zazo J. A., Fraile A. F., Rey A., Bahamonde A., Casas J. A., Rodriguez J. J., 2009, Optimizing calcination temperature of Fe/activated carbon catalysts for CWPO, Catalysis Today, 143:341–346pp.

Zeng X., Liu J., and Zhao J., 2018, Catalytic Wet Oxidation of Pharmaceutical Sludge by Molecular Sieve Loaded Cu/Ce, Catalytic Wet Air Oxidation Processes, Catalyts, vol. 8, China.

Zhan W., Wang X., Li D., Ren Y., Liu D. and Kang J.; 2013, Catalytic wet air oxidation of high concentration pharmaceutical wastewater, Water Sciences and Technology, 67.10: 2281-2285pp.

Zhang F., Wang X., Liu H., Liu C., Wan Y., Long Y., Cai Z., 2019, Recent Advances and Applications of Semiconductor Photocatalytic Technology, Applied Sciences

Zhou M. and He J., 2006, Degradation of azo dye by three clean advanced oxidation processes: Wet oxidation, electrochemical oxidation and wet electrochemical oxidation- A comparative study, Department of Environmental Science, 457-625pp.

ACKNOWLEDGEMENT

I would like to thank my supervisor, Assoc. Prof. Dr. Gülin ERSÖZ, who gave me the chance to work on this important subject. Her encouragement, guidance and support from the beginning to the final level enabled me to develop an understanding of the subject.

I offer my regards and blessing to Prof. Dr. Süheyda ATALAY and Research Assistant Burcu PALAS, who supported me in any respect during the completion of the project.

Finally, I want to thank my family for their support and patience during this study.

09 / 12 / 2019

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SUMMARY INFORMATION

I am graduated from Chemical Engineering Department (English) in Ege University at 08/2014. I am going to finish master degree on december, 2019 (Subject is Pharmaceutical Waste water treatment in advanced oxidation processes) in chemical engineering department, Ege University. I had been working as quality controller in Elif Cosmetics/ İDİL. My job description included the controlling of the products (detergent, soap, body splash, wet wipe etc ...) and production processes of them. In additionally, microbiological analysis were going on by me as a scope of quality. Between 08/2015 -01/2019 I had been working in Abdi Ibrahim pharmaceuticals as a research and development analyst in R&D. I had taking roles in Analytic Development Department for different projects to carried out the processes which includes method validations, method transfers and developments, some stability analysis of the projects. The assay, impurity, residual solvents and dissolution analysis were performed in HPLC, UPLC and GC instruments. Since 01/2019 I have taking roles in R&D Department, as an Analytical Development Specialist in Neutec Pharma. My roles as a specialist can be sorted as, controlling and following the projects, preparing documents such as certificates or analytical methods for the dossiers, orienting colleagues who are in my responsibility and checking their analysis

EDUCATION

Master Degree Ege **University – İzmir**
Chemical Engineering– 09/2014 – 12/2019

University **Ege University – İzmir**
Chemical Engineering– 09/2009 – 07/2014

High School **Kırklareli Anatolian High School – Kırklareli**
Physical Science – 09/2005 – 06/2009

WORK EXPERIENCE

01/2019 – Currently Job
Analytical Development Specialist -Chemical Engineer – Neutec Pharma A.Ş
Esenler/İSTANBUL
Department : Research and Development
Position : Full time

Controlling and following the projects, preparation of dossiers for Ministry of Health and performing analytical method development.

018/2015 – 01/2019

Analytical Development Analyst -Chemical Engineer – Abdi İbrahim A.Ş
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Department : Research and Development
Position : Full time

The drugs' processes methods improving and development are done in R&D department for API's and finished product according to the project type. Also the method validations of drugs are performed with some chemical tests for impurities, assays, dissolutions and also for raw materials. Performing the in-vitro dissolution profiles for finished products before bioequivalence studies are also practiced in laboratory. Preparing and publishing the methods related to drug products and conducting method validations for products or drug ingredients, literature and patent search for new drug candidates for company's pipeline.

02/2015 – 07/2015

Chemical Engineer – Elif/İdil Cosmetics
Bornova/İZMİR
Department : Quality Control – R&D
Position : Full time

I had completed my business internship as 20 working days. During my training, I had analysed and reported that some medicines that are produced which are according to production process and controlling steps.

04/2013 – 12/2014

Translator - Kaya Tercüme
Alsancak/İZMİR
Position : Part time

I work as a translator periodical for user manuel and warnings of chemical materials and some detergents from Turkish to English and English to Turkish.

TRAININGS

07/2012 – 08/2012

Engineer Cadet– Deva Holding A.Ş. Çerkezköy/ Tekirdağ
Department : Quality Control
Position : Full time

06/2013 – 07/2013

Engineer Cadet– Tüpraş A.Ş. Aliağa/ İzmir
Department : Process and manufacturing
Position : Full time

COMPUTER SKILLS

Microsoft Office: Excellent
Matlab, AutoCAD, Polymath, Aspen Plus: Very well
Python: Beginner

LANGUAGE SKILLS

English	Reading:	Upper Intermediate
	Writing:	Upper Intermediate
	Speaking:	Upper Intermediate

SOCIAL ACTIVITIES

Reading, tennis, cinema, theatre.

COURSES AND CERTIFICATES

Ege Bilişim Zirvesi
ISO 14001: Çevre Yönetim Sistemleri
ISO 22000: Gıda Güvenliği Yönetim Sistemleri
ISO 9001:2008: Kalite Yönetim Sistemleri
ISO 19011: İç Denetçi
OHSAS 18001: İş Sağlığı ve Güvenliği

ACADEMICAL PROJECTS

- Chemical Engineering Design Project: Diethyl Ether Production

  • Diploma Project: Degradation of Benzoic acid with photo-catalysis method with using FeTiO2/Activated Carbon catalyst and ConceptualDesign Projects

DEVICES

CSTR and Batch reactors, GC, Distillation Columns, UV-visible absorption spectrometers, Vaporizers Coolers, Mixers, HPLC, UPLC, Dissolution testers, UV-visible spectrophotometers, Empower, Distek, ChemStation, Sotax, Open Lab.

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